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The electromagnetic wave absorbing properties of cement-based composites using natural magnetite powders as absorber

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Abstract
In order to develop a low-cost electromagnetic interference shielding and especially absorbing cement materials. In the present study, the utilization of natural magnetite in cement matrix for this purpose was investigated. The dielectric, magnetic and electromagnetic wave absorbing properties of magnetite/cement composites were characterized in the frequency range of 2.6–3.95 GHz (S band). The results show that dielectric and magnetic losses of the composites were increased, and the performance of the composites in electromagnetic absorbing is greatly improved greatly by adding natural magnetite powders as low-cost absorbers. For magnetite/composites, two matching thickness in range of 1–30 mm were clearly observed. The composites with 15% magnetite show the best absorbing property. Its strongest absorbing peak with a reflection loss of −28 dB at 3.7 GHz, and its absorbing bandwidth (−10 dB) reaches 0.8 GHz.

1. Introduction

In the past several decades, more and more attention were focused on electromagnetic wave absorbing cement-based composites with broad application in the fields of military stealth technology of large fixed targets and electromagnetic interference (EMI) shielding for the health of human beings and normal work of the electronic devices [1]. Cement-based composites with electromagnetic wave absorbing/reflecting function were usually prepared by introducing electromagnetic wave absorbers, such as conductive or magnetic powders into cement [2, 3]. The most frequently used electromagnetic absorbers with large dielectric losses or magnetic losses in cement include carbon materials (carbon filament [3], carbon fiber [4], carbon nanotubes [5, 6], carbon black [7], graphite [8], graphene oxide [9]), metal fiber [10] and ferrites [11]. Recently, He et al prepared the electromagnetic wave absorbing functional aggregate by dispersing TiO₂ powder into clay and then calcining, and then used it in concrete. There experimental results showed that the TiO₂ containing functional aggregate obviously improved the microwave absorption of concrete, and the concrete prepared with functional aggregate showed excellent compressive strength [12].

Although most of aforementioned absorbers are effective and compatible with cement, they are expensive. Some researchers pay attention to developing low-cost absorbers for electromagnetic wave absorbing cements. Khushnood et al used carbonized agricultural residue as cost effective electromagnetic wave absorber in cement composite, and found a significant increase in permittivity, both real and imaginary parts, in 0.2–10 GHz frequency range with direct relation to the added content [13]. Fly ash usually as by-product from coal fired power stations is one of supplementary cement materials for the advantages of economy and durability. Chuang reported that using of fly ash as an admixture results in enhancement of the EMI shielding effectiveness from 4 to 8 dB at 1 GHz, and found that the effectiveness of fly ash for shielding is attributed to the Fe₂O₃ component in the fly ash [14]. Huang et al studied the wave absorbing properties of cement materials blended with high-iron fly ash, and obtained the minimum reflectivity of −11 dB in the range of 9.5–18 GHz [15]. Li et al used low-quality fly ash as cement replacement and found that the electromagnetic absorbing performance of cement composites was enhanced by fly ash due to its complex components and porous structure [16]. Steel slags containing several ferrous...
phases by large proportion may exhibit obvious dielectric losses or magnetic losses and can be used as electromagnetic wave absorbers. Bantsis et al investigated the utilization of metallurgical slags and scrap tire wastes in cement paste, and found that cement paste specimens prepared by the addition of slags exhibit better shielding efficiency [17]. Dai et al investigated the effects of curing time, proportion of steel slag, sample thickness on radar-absorbing properties in the frequency of 1–18 GHz, the sites of absorption peak of the composites do not change at different curing time and proportion of steel slag, but change to lower frequency with the increase of thickness [18].

Natural magnetite can be found concentrated in Russia, Canada, China, Chile, Sweden, Australia, US, Norway, Brazil, and Mexico. Magnetite (Fe₃O₄) is an abundant mineral with an inverse spinel structure in which the oxygen is organized in a cubic close packing with iron atoms placed in tetrahedral and octahedral positions. This special structure makes magnetite have ferromagnetic and semi-conductive properties. Although the synthetic magnetite have been frequently used as electromagnetic absorbers in polymer-matrix composites and it show good absorbing ability [19], the reports on using natural magnetite as absorbers are rare. In the present study, the natural magnetite powders as absorbers were introduced to cement in order to fabricate low cost electromagnetic absorbing cement-based composites. The effects of content of magnetite powders on electromagnetic absorbing properties in the frequency of 2.6–3.9 and 8.2–12.4 GHz were investigated.

2. Experimental procedure

The starting materials are commercial cement (Poland cement, type 42.5 R), deionized water, and natural magnetite (Fe₃O₄) used as absorber. Cement, water, and magnetite powders were mixed for 10 min by a mortar mixer. The volume ratio of water to the total cement was 0.34. Then the mixture was poured into oiled molds with the sizes of 72.14 × 34.04 × 3.0 mm³, a vibration table and a float were used to compress and smooth the specimens. The samples were remolded after 1 d and cured in air at room temperature for 28 d.

The chemical composition used magnetite was characterized by energy loss spectroscopy (EDS). Phase composition of the magnetite was characterized by using x-ray powder diffraction (XRD) recorded at 20 from 10° to 70° at a scanning rate of 1° min⁻¹ using an Ultima x-ray diffractometer (Rigaku, Japan) with Cu Kα radiation. The microstructures of cement-based composites were characterized by scanning electron microscope (SEM).

The real and imaginary parts of the complex permittivity (ε′, ε″) and permeability (μ′, μ″) of the cement-based composites were calculated based on scattering parameters measured by a Vector-network Analyzer (Agilent E8362b: 10 MHz–20 GHz) using the method of rectangular wave guide method in the frequency of 2.6–3.95 GHz at room temperature, which was based on the measurements of the reflection and transmission module and in the mode TE₁₀. The calculation algorithm is usually called the Nicholson–Ross–Weir (NRW) algorithm [20].

According to the transmission theory, for a single-layer absorber composite, the reflection loss (R) can be calculated from the equations shown below based on metal back-panel model.

\[
R_L(\text{dB}) = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|
\]

\[
Z_{in} = Z_0 \sqrt{\frac{\mu_c}{\varepsilon_r}} \tanh \left( f \frac{2\pi d}{c} \sqrt{\frac{\mu_c}{\varepsilon_r}} \right)
\]

Where Z₀ is the normalized input impedance at free space and material interface, εₚ = ε' - jε'' is the complex permittivity, and μₚ = μ' - jμ'' is the complex permeability of absorbers, f is the frequency of the microwave in free space, d is the thickness of the absorber, and c is the velocity of light in free space [20]. The impedance matching condition is given by Zₚ = 1 to represent the perfect absorbing properties. The impedance matching condition is determined by the combinations of six parameters, ε', ε'', μ', μ'', f and d, the reflection loss curve versus frequency can be calculated at a specified thickness from εₚ and μₚ.

3. Results and discussion

3.1. Chemical composition and microstructure characterization

Table 1 shows the EDS results of magnetite used in our work. It demonstrates that the main elements are oxygen and iron, and aluminum impurity is rare. The XRD pattern of magnetite is shown as figure 1. There are characteristic peaks at 2θ = 18.52, 30.34, 35.621, 37.26, 43.20, 53.66, 57.22 and 62.93 which can be assigned to (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of cubic spinel structure (Fe₃O₄), respectively [19]. Maybe, the alumina content is too little; no impurity phases can be detected. The SEM micrographs of cement-based materials are showed in figures 2(a) and (b). Figure 2(a) exhibits that the magnetite powders were dispersed uniformly in cement matrix. Figure 2(b) shows that the interface zone between cement matrix and magnetite is porous.
3.2. Dielectric and magnetic properties

Figures 3(a) and (b) show the variations of $\varepsilon'$ and $\varepsilon''$ of complex permittivity of cement-based composites with increasing content of magnetite. It can be shown that the $\varepsilon'$ for pure cement is nearly constant at 4.8 and the $\varepsilon''$ is almost zero, and the values of both $\varepsilon'$ and $\varepsilon''$ increase continuously as the content of magnetite increases from 0 to 20 wt%. It is worthy pointing that the $\varepsilon'$ increases faster than the $\varepsilon''$, and the $\varepsilon''$ increase obviously if the content of magnetite is more than 10 wt%. The $\varepsilon'$ is mainly associated with the amount of polarization occurring in the material and the $\varepsilon''$ is a measure of dissipated electric energy.

The small $\varepsilon'$ and $\varepsilon''$ of pure cement indicates that both the polarization ability and dissipating ability of electric energy are very small. The permittivity of natural magnetite is much higher than that of pure cement [19]. In accordance with classical effective permittivity theory, the permittivity of composites has positive relations with the permittivity of its components and their volume fraction [21]. So, the magnetite with high permittivity can increase the permittivity of cement-based composites.

### Table 1. Chemical compositions of magnetite powders used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass wt.%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>73.27</td>
<td>44.23</td>
</tr>
<tr>
<td>O</td>
<td>26.08</td>
<td>54.96</td>
</tr>
<tr>
<td>Al</td>
<td>0.65</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Figure 1. XRD pattern of magnetite with 10 wt% magnetite.

Figure 2. SEM micrographs of cement-based composites (a) low magnification; (b) high magnification.
The space charge polarization is another reason for that the $\varepsilon'$ and $\varepsilon''$ increases with increasing content of magnetite. The contribution of the space charge polarization appears due to the heterogeneity of the material. Both the $\varepsilon'$ and $\varepsilon''$ of magnetite are higher than that of pure cement. The presence of semi-conducting magnetite in the insulating cement matrix results in the formation of more interfaces and a heterogeneous system due to some space charge accumulating at the interface.

The values of $\mu'$ and $\mu''$ of complex permeability in the frequency range of 2.6–3.9 GHz of all cement-based composites are shown in figures 4(a) and (b), respectively. The $\mu'$ and $\mu''$ of pure cement are almost unity and zero, respectively, since the cement is non-magnetic. The effects of incorporating the magnetite into the cement matrix are to raise $\mu'$ above unity and $\mu''$ above zero throughout the whole frequency range. In addition, the $\mu''$ increases faster than the $\mu'$ as increase of content of magnetite.

3.3. Electromagnetic wave absorbing properties

Figure 5(a) shows the influence of sample thickness (1–30 mm) on the reflection losses of composites with different content of magnetite. It can be observed that the sample thickness has a notable influence on the reflection loss of magnetite/cement composites, and there are two obvious matching thicknesses varying with content of magnetite. One matching thickness (4–8 mm) is called thin matching thickness, and the other one (12–24 mm) is called thick matching thickness. Both thick and thin matching thicknesses are moved to a thinner side as increasing of magnetite content. Figures 5(b) and (c) show the reflection losses at thin and thick matching thickness in frequency of 2.6–3.95 GHz, respectively. It can be seen that, at thin matching thickness, the composites with 15% magnetite show best absorbing property. Its strongest absorbing peak with a reflection loss of $-28$ dB at 3.7 GHz, and its absorbing bandwidth ($<-10$ dB) reaches 0.8 GHz. At thick matching thickness, the composites with 10% and 15% magnetite show strong absorbing performance at high frequency part. Interestingly, the composites with 20% at both thin and thick matching thickness exhibit worse absorbing performance.
Materials with good electromagnetic absorbing ability should meet the two conditions: First, the characteristic impedance of materials should be as close to the impedance of free space as possible; second, the incident electromagnetic wave can enter absorbing materials, in which the electromagnetic wave is attenuated rapidly. The first condition required that the complex permittivity of the materials is close to its permeability, and the second condition required that the materials have high dielectric loss or/and magnetic loss. In present investigation, the ferromagnetic magnetite can increase both the dielectric and magnetic losses of cement-based composites. But, both real and imaginary parts of permeability of magnetite/cement composites are much lower compared with that of permittivity, especially for cement-based composites with high content of magnetite. So, it is believed that the impedance matching characteristic of cement-based becomes worse as increasing of magnetite content. Therefore, the cement-based composites with 20% magnetite do not show the best absorbing performance.

4. Conclusions

Cement-based composites with different natural magnetite contents were fabricated, and their dielectric, magnetic and electromagnetic absorbing properties were studied in the frequency of 2.6–3.95 GHz (S band). The results show that the dielectric and magnetic losses of the composites were increased, and the electromagnetic absorbing performance of the composites is greatly improved by adding natural magnetite powders as low-cost absorbers. For magnetite/composites, two matching thickness in range of 1–30 mm were clearly observed. The composites with 15% magnetite show the best absorbing property. Its strongest absorbing peak with a reflection loss of $-28 \text{ dB}$ at 3.7 GHz, and its absorbing bandwidth ($<-10 \text{ dB}$) reaches 0.8 GHz when the matching thickness is 5 mm.

Acknowledgments

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