

Contents lists available at ScienceDirect

## **Cement & Concrete Composites**

journal homepage: www.elsevier.com/locate/cemconcomp



# Microwave absorbing properties of double-layer cementitious composites containing Mn–Zn ferrite

Xiuzhi Zhang a,b,\*, Wei Sun a,b

#### ARTICLE INFO

Article history:
Received 30 June 2009
Received in revised form 12 July 2010
Accepted 15 July 2010
Available online 17 July 2010

Keywords:
Layered cementitious composites
Impedance matching
Microwave absorption
Reflectivity
Ferrite

#### ABSTRACT

Double-layer cementitious composites filled with Mn–Zn ferrite as microwave absorbers were designed based on the impedance matching theory and electromagnetic wave propagation laws. The results showed that the addition of silica fume can improve the impedance matching between the cementitious composites and free space. Comparing with the single-layer structure, the reflectivity of the double-layer cementitious plates can decrease by 6–8 dB and decrease by 15 dB maximum with 30 wt.% ferrite; in addition, the reflectivity of electromagnetic wave is lower than 10 dB in the frequency range of 11.4–18 GHz. These composites can be potentially used as electromagnetic interference (EMI) materials for buildings.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

The need of preventing electromagnetic interference (EMI) has been increasing with the development and application of electronic science and communication technology [1]. EMI prevention is particularly needed for underground vaults containing transformers and other electronics that are related to electric power and telecommunication [2]. Electronic radiation has been a threat to the public health and has brought out information leakage. Thus, the capacity of a building to prevent the electromagnetic radiation or electromagnetic interference is very important.

There are mainly two methods to prevent and attenuate EMI radiation and leakage, which are shielding and absorption, and the materials that are used to prevent EMI can accordingly be divided into EMI shielding materials and wave absorbing materials. EMI shielding is essentially to form an effective enclosed area with highly conductive materials, in which the external electromagnetic radiation cannot penetrate and internal radiation cannot be easily leaked out. Normally applied EMI shielding cannot eliminate or weaken EMI radiation, and the reflected wave may also interact with the incident wave, which causes disturbance to other units or devices. The EMI radiation can be attenuated to the furthest extent [3] by using electromagnetic wave absorbing materials and transferring the electromagnetic energy to other forms.

Cementitious composites are one of the most common building materials used in engineering construction. Cement-based composites are complex systems that include hydration products, unhydrated cement particles and aggregates of different sizes. Generally, as a whole system cement-based material is slightly conducting, but its EMI shielding effectiveness and wave absorbing property are very low, so admixtures are needed to improve the ability to resist the electromagnetic wave interference. There have been many studies on the reflection loss of cement matrix composites by introducing fillings, such as expanded Polystyrene (EPS) and carbon fibers [4,5].

Ferrite is one of the most commonly used materials as a kind of electromagnetic wave absorber. Many studies have been carried out in Japan in Radio frequency (RF) area to investigate the electromagnetic absorption properties of buildings employing ferrite [6,7]. However, the application has been restricted by the narrow band characteristics of single-absorbers. It is known from many research studies that the microwave absorber with double-layer structure has wider absorption bandwidth and lower reflection loss (RL) than the single-layer absorber in GHz frequency [8].

For the purpose of preparing a low-reflecting absorber in the desired wide frequency range, two fundamental conditions must be satisfied [9,10]: the first is that the incident wave can enter the absorber to the greatest extent (impedance matching characteristic), and the second is that the electromagnetic wave entering into the materials can be almost entirely attenuated and absorbed within the finite thickness of the material (attenuation characteristic). The impedance matching is the principle that the electromagnetic

<sup>&</sup>lt;sup>a</sup> School of Materials Science and Engineering, Southeast University, Nanjing 211189, China

<sup>&</sup>lt;sup>b</sup> Jiangsu Key Laboratory of Construction Materials, Nanjing 211189, China

<sup>\*</sup> Corresponding author at: School of Materials Science and Engineering, Southeast University, Nanjing 211189, China. Tel./fax: +86 25 52090667. E-mail address: zhangxz74@126.com (X. Zhang).

wave is absorbed in the materials. There are several methods to improve impedance matching between material and free space. One of them is to use low dielectric constant materials to adjust the characteristic impedance of the absorber. Silica fume [11] is a kind of fine non-crystalline silica produced in electric arc furnaces as a by-product during the production of metallic silicon or ferrosilicon alloys, the SiO<sub>2</sub> content of which ranges from 85% to 98%. Silica fume can be used as reactive mineral admixture of concrete; it can react with the calcium hydroxide produced during the cement hydration reaction. Silica fume has three main effects: pozzolanic reaction, micro-filling effect, and morphologic effect, which contributes to excellent mechanical properties and durability of concrete. In addition, silica matrix composites are widely applied as wave-transmitting materials because of its excellent electrical properties and high temperature performance [12]. However, the effect of silica fume on absorbing property has not been reported.

In this paper, silica fume was used to improve the impedance matching for cementitious composites. Two types of microwave absorbers were used: single-layer microwave absorber composed of Mn–Zn ferrite, and double-layer microwave absorber composed of mortar with silica fume mortar as the surface layer and Mn–Zn ferrite mortar as the loss layer. The microwave absorption properties of these composites were investigated and compared.

## 2. Experimental programs

#### 2.1. Raw materials

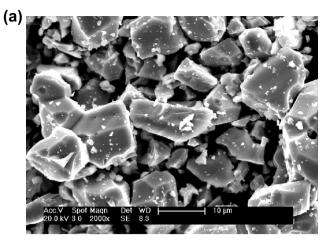
In this study, P II 52.5 Portland cement with compressive strength 75.6 MPa at 28 days was used as matrix, and the nature river sand with maximum size of 2.5 mm was used as fine aggregate, silica fume (Elkem Materials, Shanghai, Microsilica 951-U), as another cementitious material, was added and used for the purpose to improve the impedance matching in this study. The chemical composition and physical properties of these cementitious materials are listed in Table 1.

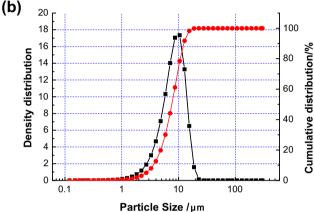
Spinel ferrite (FP), produced by Nanjing-Jinning-Sanhuan FDK Co. Ltd., (China), has density of 5.8 g/cm<sup>3</sup>. Fig. 1 shows its morphology image and particle size distribution. The complex permittivity and complex permeability of ferrite olefin as matrix, measured by coaxial transmission/reflection method, are shown in Fig. 2.

In the mixture, the ratio of water to binder was 0.3:1 and the ratio of sand to binder was 1.5:1. 0.5 wt.% polycarboxylate-based superplasticizer powder was used in the cement. Ferrite was added in the proportion to the weight of the cement.

### 2.2. Sample preparation

The cement, water, silica fume and ferrite (if applicable) were mixed by a rotary mortar mixer. Then the mixture was poured into oiled molds with a size of  $180 \times 180 \text{ mm}^2$  and thickness of 10, 20 and 30 mm according to need. The molds were vibrated for 1 min and the mixture inside was smoothed. Finally the specimens were demolded after 1 day and put into cure for 28 days at  $20 \pm 2$  °C and >90% relative humidity (RH). The composition design of each specimen is shown in Table 2. For double-layer cement-based plates, the second layer was poured onto the first layer surface when





**Fig. 1.** Morphology and particle size distribution of ferrite (a) morphology and (b) particle size distribution of ferrite.

the first-layer cementitious composites reached initial setting status.

#### 2.3. Test method

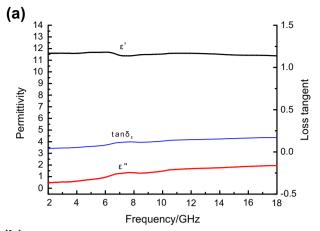
The electromagnetic parameters were measured by transmission/reflection method. The toroidal shape specimens of  $\phi$  7 mm  $\times$   $\phi$ 3 mm  $\times$  4 mm size were measured using S-parameter values at frequency from 2 to 18 GHz.

The electromagnetic wave absorption properties of the cementitious composite materials were tested by NRL [13] as shown in Fig. 3. The test frequency ranges from 8 to 18 GHz. The vector network analyzer (VNA) was calibrated before the test to minimize the horn-to-horn coupling and ensure high measurement accuracy. Then the sample was put on the reflecting plate, and the horns are placed at a glancing angle relative to the sample surface, creating a single two-way transmission path to prevent multiple reflections between the horns and the sample.

Cementitious composites are compounded of aggregate, hydrated product (C-S-H, calcium hydroxide, ettringite, etc.), unhy-

**Table 1** Chemical compositions and physical properties of raw materials.

Raw materials	Chemical		Specific surface (m <sup>2</sup> /kg)							
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Loss	
Cement Silica fume	21.50 95.48	5.12 0.27	3.42 0.83	65.3 0.54	1.05 0.97	2.03 0.80	0.66 -	0.2	0.46 1.11	380 22,000



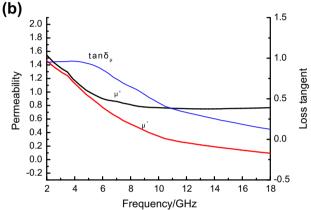


Fig. 2. Electromagnetic parameters of the Mn–Zn ferrite (a) permittivity and (b) permeability.

**Table 2**Thickness and composition of each sample.

No.	Thickness	s (mm)	Compositio	Composition (wt.%)		
	Surface layer	Loss layer	Filling material	Surface layer	Loss layer	
SPC SSF SFP10 SFP30 SFP50 D1 D2	10 5	30 30 30 30 30 30 20 25	nothing SF FP FP FP SF/FP SF/FP	SI FI FI	100 F 15 P 10 P 30 P 50 FP 30 FP 30	

*Note*: S stands for the single-layer absorber, PC stands for the plain cement mortar, SF stands for the silica fume, FP10 stands for 10% ferrite content, C stands for cement and D stands for double-layer absorber.

drated cement particles, pore, and free water [14]. Due to high permittivity, water inside the material has a great effect on its dielectric property, leading to different electromagnetic absorbing performance of the material. In order to reduce the influence of the free water in the composite material, the samples were dried at 60 °C prior to the test until the weight did not change with time.

## 3. Results and discussion

#### 3.1. Microwave theory

Fig. 4 shows that a transverse electromagnetic (TEM) wave at an incidence vertical to the absorber surface is vertically reflected back from a double-layer microwave absorber composed of surface and loss layers.

The return loss coefficient of a metal-terminated wave absorber system is given by Eq. (1) and (2): [15]

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \tag{1}$$

$$Z_{in}=Z_2\frac{Z_1\tanh(\gamma_1d_1)+Z_2\tanh(\gamma_2d_2)}{Z_2+Z_1\tanh(\gamma_1d_1)Z_2\tanh(\gamma_2d_2)} \eqno(2)$$

where  $Z_{in}$  is the input impedance measured from the surface to the absorber to the termination,  $Z_1$ ,  $\gamma_1$ , and  $d_1$  are characteristic impedance, propagation constant and the thickness of the microwave absorber loss layer, respectively.  $Z_2$ ,  $\gamma_2$ , and  $d_2$  are characteristic impedance, propagation constant and thickness of the microwave absorber surface layer, and  $Z_0$  is characteristic impedance of vacuum,  $Z_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} = 377~\Omega$ . The characteristic impedance and propagation constant are expressed by the complex relative permeability  $\mu_r = \frac{\dot{\mu}}{\mu_0} = \mu' - j\mu''$  and the permittivity  $\varepsilon_r = \frac{\dot{\varepsilon}}{\varepsilon_0} = \varepsilon' - j\varepsilon''$ 

$$Z = \sqrt{\frac{\mu_0}{\epsilon_0}} \sqrt{\frac{\mu_r}{\epsilon_r}} = \sqrt{\frac{\mu_0}{\epsilon_0}} \sqrt{\frac{\mu_r' - j\mu_r''}{\epsilon_r' - j\epsilon_r''}} \tag{3}$$

$$\gamma = \frac{j\omega\sqrt{\mu_0\varepsilon_0}\sqrt{\mu_r\varepsilon_r}}{v} = \frac{j\omega\sqrt{(\mu_r' - j\mu'')(\varepsilon_r' - j\varepsilon'')}}{v} \tag{4}$$

where v is the speed of the microwave,  $\omega$  is the angular frequency of the incident plane wave, j is the imaginary unit, and  $\epsilon_0$  and  $\mu_0$  are the permeability and permittivity of the air, respectively.

If the microwave absorber is single-layer, Eq. (2) becomes Eq. (5):

$$Z_{in} = Z_1 \tanh(\gamma_1 d_1) \tag{5}$$

since the reflection loss is a function of  $Z_{in}$ , it can be expressed as follows:

Reflection loss  $(RL)[dB] = 20 \log |\Gamma|$ 

$$=20 log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \tag{6}$$

The principle of the metal-backed microwave absorber is to make use of the reflection reduction by impedance matching. If there is no reflection, the normalized input impedance with respect to the impedance of the free space should be  $Z_{in} = Z_0$ . The impedance matching condition depends on the values of the absorber electromagnetic parameters.

## 3.2. Absorption properties of single-layer cementitious plates

Cement matrix is slightly conductive and has weak microwave absorption capability [16]. The attenuation of electromagnetic wave by cement paste, just as by fly ash [17], can be mostly attributed to the dielectric and magnetic loss of the metal oxide components and some minerals in the cement.

Fig. 5 shows the reflectivity of PC (sample 1). The minimum reflectivity of PC is higher than -8 dB, and the absorption ability decrease with the frequency. It can be seen that the reflectivity of samples with the ferrite content increasing. In addition, the cement cure surface is visually smoother with higher ferrite content. As a microwave absorbent, ferrite with high permittivity and permeability (Fig. 2) can attenuate the electromagnetic energy by dielectric loss, magnetic loss and hysteresis loop loss [18]. However, the increase of ferrite content changes the impedance matching between cement material and free space, which makes the incident wave more difficult to transmit into the material and to get attenuated by the wave absorber. So adding ferrite can decrease the microwave reflection loss of the cementitious composite material, and higher ferrite ratio indicates lower reflection loss.

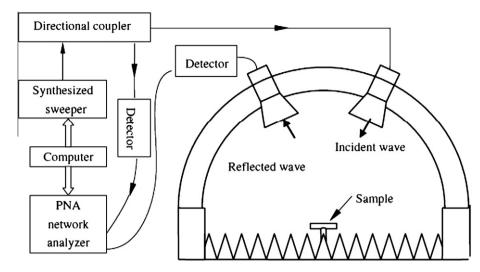


Fig. 3. Sketch of the NRL reflectivity measurement system.

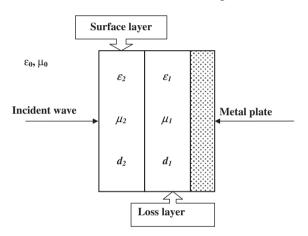


Fig. 4. Structure of the proposed double-layer microwave absorber.

This is further verified by the fluctuation in the reflection loss curve of sample 5 (Fig. 5). When the ferrite content is 30%, the reflectivity curve becomes smooth, and the maximum reflectivity is below other samples. So the optimum ferrite content is 30 wt.%.

#### 3.3. Absorption properties of the double-layer cementitious plates

In order to prepare a low-reflecting absorber in the desired wide frequency range, two fundamental requirements must be satisfied [9]: the impedance matching characteristic and the attenuation

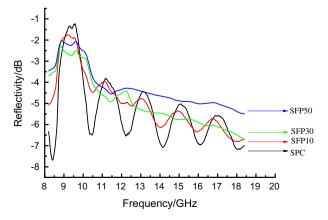


Fig. 5. Effect of dosage of ferrite on the reflectivity of plates.

characteristic. The double-layer absorbing structure can attain these aims. In a double-layer electromagnetic wave absorber, one layer acts as low-impedance resonator and another as impedance transformer. By combining these two layers, broadband operation can be achieved.

## 3.3.1. Effect of silica fume on electromagnetic properties

PC has higher permittivity ( $\varepsilon_r$  = 7.0,  $\mu_r$  = 1.0) comparing with free space, which causes impedance mismatch and inhibits the incident wave transmission into the material, therefore, its microwave absorbing property is low. As a common mineral admixture of concrete, silica fume contains significant amount of reactive SiO<sub>2</sub> and gives low permittivity and permeability ( $\varepsilon_r$  = 2.7,  $\mu_r$  = 1.0). Silica-based composites are used as radar radome of flyer due to its low permittivity and excellent microwave transparency [8]. Therefore, silica fume can be used to adjust the microwave transparency and electromagnetic parameter values of the cementitious composites.

When silica fume was added into cementitious mortar, the reflectivity was lower than the same w/c plain cement mortar (PC) as shown in Fig. 6. The reflectivity decreased about 4 dB from 8 to 18 GHz. The reflectivity curve was observed more planar at higher frequency. Silica fume of very large specific area is randomly distributed in cementitious composites. Comparing with unhydrated cemented particles, silica fume with small size particles can fill into the pores of the material so that the hydrated cementitious composites are more compact. The microwave penetration for silica fume is more difficult than for PC, so the reflectivity loss of interference is decreased but impedance matching of material is improved, and the total reflection loss is increased as shown in Fig. 6. Silica fume is thus chosen to add to the mortar as the surface layer to improve the impedance matching.

## 3.3.2. Absorption properties of double-layer cementitious composites

The double-layered cementitious plates were prepared with impedance matching layer and loss layer. The surface layer is the mortar added with 10 wt.% silica fume, and the loss layer is the mortar added with 30 wt.% ferrite.

As predicted, the double-layered cementitious material has better microwave absorption properties than the samples with single-layer structure. Fig. 7 shows the microwave absorption change with frequency for double-layer samples 6 and 7 of same total thickness. It is observed that the reflectivity of double-layer cementitious absorber shows broadband characteristics from 8 to 18 GHz frequency. The thickness of impedance matching layer is

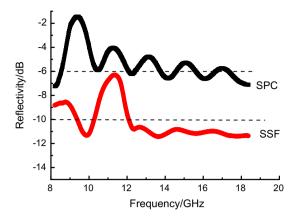


Fig. 6. Effect of silica fume on reflectivity of cementitious plates.

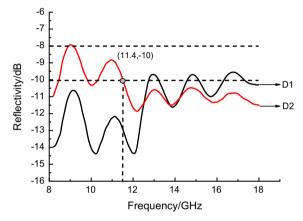


Fig. 7. Reflectivity of the samples with different thicknesses.

different for samples 6 and 7, which contributes to different reflectivity curves. The reflection loss of sample 7 is better than sample 6 at high frequency, and the absorption bandwidth under  $-10~\mathrm{dB}$  is 6.6 GHz ranging from 11.4 to 18 GHz. For sample 6 with 10 mm thick impedance matching layer, the minimum reflectivity reaches  $-15.0~\mathrm{dB}$  at 12 GHz and the bandwidth under  $-10~\mathrm{dB}$  is 4.6 GHz.

## 4. Conclusions

The microwave absorption properties of single-layer and double-layer cementitious absorbers with the ferrite and silica fume were investigated. Based on the above experimental results, the conclusions can be summarized as follows:

(1) The mortar with silica fume can be used as an impedance matching layer to adjust the permittivity of the surface materials of the cement-based absorbing material in order to attain the impedance matching.

- (2) The microwave reflectivity of the single-layer mortar filled with ferrite is higher than that of the plain mortar due to the mismatching of the impedance.
- (3) The design of double-layer structure has excellent absorption property because of the impedance match of materials. The impedance match layer is made of silica fume mortar and the loss layer is added with 30 wt.% ferrite. The minimum reflectivity of the double-layer plate reaches –15 dB at 12.0 GHz when the impedance matching layer thickness is 10 mm. The absorption bandwidth below –10 dB is 6.6 GHz ranging from 11.4 to 18 GHz when the impedance matching thickness is 5 mm.

#### References

- [1] Chung DDL. Electromagnetic interference shielding effectiveness of carbon materials. Carbon 2001;39(2):279–85.
- [2] Cao JY, Chung DDL. Coke powder as an admixture in cement for electromagnetic interference shielding. Carbon 2003;41(12):2433-6.
- [3] Guang HT, Liu SH, Duan YP, et al. Cement based electromagnetic shielding and absorbing building materials. Cem Concr Compos 2006;28(5):468–74.
- [4] Guang HT, Liu SH, Duan YP, et al. Investigation of the electromagnetic characteristics of cement based composites filled with EPS. Cem Concr Compos 2007;29(1):49–54.
- [5] Wang C, Li KZ, Li HJ, et al. Influence of CVI treatment of carbon fibers on the electromagnetic interference of CFRC composites. Cem Concr Compos 2008:30(6):478–85.
- [6] Yamane T, Numata S, Mizumoto T, Naito Y. Development of wide-band ferrite fin electromagnetic wave absorber panel for building wall. In: Electromagnetic compatibility, 2002. EMC 2002 international symposium, vol. 2; 2002. p. 799– 804.
- [7] Morimoto M, Kanda K, Hada H, et al. Development of electromagnetic absorbing board for wireless communication environment. In: Proceedings of the conference of architectural institute of Japan, D-1; 1998. p. 1069–70.
- [8] Cao MS, Zhu J, Yuan J, et al. Computation design and performance prediction towards a multi-layer microwave absorber. Mater Des 2002;23(6): 557–64
- [9] Zhang BS, Feng Y, Xiong J, et al. Microwave-absorbing properties of deaggregated flake-shaped carbonyl-iron particle composites at 2–18 GHz. Magn IEEE Trans 2006;42(7):1778–81.
- [10] Oikonomoua A, Giannakopouloub T, Litsardakis G. Design, fabrication and characterization of hexagonal ferrite multi-layer microwave absorber. J Magn Magn Mater 2007;316:827–30.
- [11] Toutanji Houssam A, Tahar El-Korchi. The influence of silica fume on the compressive strength of cement paste and mortar. Cem Concr Res 1995;25(7):1591–602.
- [12] Place TM, Bridges DW. Fused quartz reinforced silica composites [A]. In: Proceedings of the tenth symposium on electro-magnetic windows [C], Georgia Institute of Technology; 1970. p. 338-42.
- [13] He S. Performance test of radar absorbing materials. Mater Eng 2000;2:37–40 [in Chinese].
- [14] Mehta PK, Paulo JM Monteiro. Concrete. 3rd ed. America: McGraw-Hill Companies, Inc.; 2006. p. 21–47.
- [15] Feng YB, Qiu T, Shen CY. Absorbing properties and structural design of microwave absorbers based on carbonyl iron and barium ferrite. J Magn Magn Mater 2007;318(1–2):8–13.
- [16] Chung DDL. Materials for electromagnetic interference shielding. J Mater Eng Perform 2000;9(3):350–4.
- [17] Cao JY, Chung DDL. Use of fly ash as an admixture for electromagnetic interference shielding. Cem Concr Res 2004;34(10):1889–92.
- [18] Dionne Gerald F. A review of ferrites for microwave applications. Proc IEEE 1975;63(5):777-89.