Effect of Mineralogical Phase and Chemical Composition of Fly Ash on Electromagnetic Wave-Absorbing Properties

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In order to explore the electromagnetic radiation protection function of fly ash as building materials, Scanning Electron Microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Mössbauer were used to analyze the chemical composition and mineralogical phase of two types of fly ash. Electromagnetic parameters of the samples were analyzed and discussed in detail at the frequency range of 1~18 GHz. The results showed that fly ash had electromagnetic wave absorbing property due to porous carbon grain and iron oxide, and that dielectric loss was more than magnetic loss for fly ash and electromagnetic property of type III was more than of type I. There were several absorbing-wave interference peaks at the frequency of 1~18 GHz, at thickness of 10~20 mm epoxy-based fly ash. The cement-based fly ash showed electromagnetic wave-absorbing properties at 10~18 GHz and the biggest absorption reached 14.5 dB at 16 GHz at the thickness of 20 mm, so the fly ash should be expected to be a building material for electromagnetic protection. [doi:10.2320/matertrans.M2017378]

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1. Introduction

Fly ash is the main waste residue produced in thermal power station. Every year, millions tons of fly ash are generated all over the world and have caused great pollution. Annual interest use rate is only 40%. The major compositions of fly ash are SiO₂, Al₂O₃ and Fe₂O₃, and their amount take the around 85% of fly ash. The representative component content of carbon is over 5% for 61% plants, and statistical results of 40 large-scale thermal power plants in China are listed in Table 1.¹⁾

Fly ash has the pozzolonic reactivity so that it can be used widely as a supplementary cementing material in concrete. Further possible utilization requires a detailed knowledge of their morphology, chemical and mineralogical composition. The chemical composition and structure of fly ash particles can influence the electromagnetic properties.²⁻⁵⁾

The chemical composition of unburned carbon is basically identical: 73~91% carbon, 5~19% ash (Fe₂O₃ in ash reaches 28%~30%), 2.5~11.5% volatile substances, and 0.7~1.9% water, which consists of porous spherical particles and some crumbled particles; and most of them are hollow, porous structure, or layer structure by SEM.⁶⁾ The experimental results showed that the unburned carbon in fly ash exhibited the frequency characteristics of microwave attenuation because of bipolar, multi-reflections.^{7,8)} The main mineralogical phases of fly ash are quartz, mullite, magnetite (Fe₃O₄), hematite (Fe₂O₃), other oxides and glassy compound such as silica glass, and the minor mineralogical phase are magnetite. In China, the average content of Fe₂O₃ in fly ash from 40 large-scale thermal power plants is 50~100 g/Kg.⁹⁾

2. Materials and Experimental Methods

In order to compare the effect of particle size on properties, type III and type I fly ash were chosen. Type III fly ash was grey-black, supplied by the Nanjing Second Thermal Power

Table 1 Mineralogical component of fly ash in China.

/mass %						
Mullite	H-glassy pellet	L-glassy pellet	C	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
11.3~29.2	0~21.1	42.2~70.1	1.0~23.5	33.9~59.7	16.5~35.1	1.5~19.7

*H: high-iron; L: low-iron.

Fig. 1 SEM image of fly ash from Nanjing second power plant. (a) Irregular porous particles. (b) Layer char of unburned carbon particles.

Station and at least 32.8% passed through 45 µm mesh. Type I fly ash was light grey-black, supplied by the Nanjing Huaneng Thermal Power Station and at least 92.8% passed through 45 µm mesh. P.O 42.5 cement was produced by China Cement Company.

Morphology of fly ash from Nanjing second power plant by Scanning Electron Microscope at 15 kV (SEM) (JEOL, JSM-5900, Japan) were shown in Fig. 1, which suggested that there were plenty of macrospore in the unburned carbon and other particles.

Fly ash was packed as densely as possible into the sample holder (depth was 0.5 mm) for XRD (Japan Rigaku Corporation, D/Max-rB) and scans were taken from 5 to 80° 2θ at a scanning rate of 10°2θ/min with a step of size of 0.02°2θ.

X-ray photoelectron spectroscopy (XPS) is regarded as electron spectroscopy for chemical analysis (ESCA). XPS survey spectra are used to verify alpha-hematite phase. The stoichiometry of them is precisely controlled by *in situ* XPS

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analysis. XPS of fly ash were tested on XR5 Gun-500 μm (Al $K\alpha$, 15 kV–150 W) in Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China. The C1s spectra were used as standards for the calibration of non-conductive samples. The spectrometer was operated at a pressure of 2×10^{-7} Pa and the resolution of survey spectra was 1 eV.

^{57}Fe Mössbauer spectroscopy has several manifest advantages, such as 100% selectivity for iron, without interference from other elements of monocrystals, polycrystalline and amorphous materials, and also of “*in situ*” studies. It can be used for determining the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in hematite because Fe-bearing mineralogical phase play an important role in absorbing-wave materials. The mineralogical phase of fly ash were measured by a Mössbauer spectrometer instrument type VIS-1170-MO and ^{57}Co (Pd) source with 25 mCi activity, in constant acceleration, at room temperature (293 K), at equal velocity scale. The spectra were calibrated using a α -Fe foil and the experimental data were analyzed by MossWinn3.0.

Electromagnetic parameters of round ring sample (thickness was 2.0 mm and outer/inner diameter was 7.0/3.0 mm) were tested at the frequency of 1–18 GHz in Nanjing University by the waveguide method of round coaxial and fly ash was used in the proportions by weight relative to oxygen resin, namely, 60:40.

Reflectivity were evaluated by the arch method using an HP8722ET vector network analyzer and standard horn antennas in an anechoic chamber according to GJB2038-94.¹⁰⁾ The sizes of samples were 180 mm $\times$ 180 mm at the thickness of 10 mm, 20 mm. The absorbing-wave properties of fly ash were tested by weight proportion as: fly ash:epoxy:polymerizer = 1.5:1:1. The addition of Type III fly ash was nearly 10% because of low activity in hydrated

cement and the weight proportion of hydrated cement with fly ash were listed in Table 2.

3. Results and Discussion

3.1 Chemical components

Chemical compositions of fly ash and cement samples analyzed by XRF (Rigaku 3063) were shown in Table 3; especially the content of carbon was analyzed by Carbon/sulphur Detector (JTY-CS206) in Nanjing University.

3.2 X-ray diffraction analysis

The results of XRD analysis were shown in Fig. 2. All sharp peaks can be identified to either quartz (SiO_2) or mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The broad diffraction peak indicated the presence of amorphous (glassy) phase in fly ash sample. These data show that despite the complex composition, the fly ash always contains separable glass, quartz-mullite, and Fe spinel (Fe_2O_3 , Fe_3O_4). The fly ash is enriched in magnetite-hematite which has potential applications such as absorbing electromagnetic wave.

3.3 X-ray photoelectron spectroscopy analysis

Figure 3 revealed that O, Si, Ca, Al, Fe can be identified on the samples. The amount ratio of several main peaks were shown in Table 4 which were consistent with the results in Table 3.

Table 2 Weight proportion of samples.

	Cement	Sand	Water	Fly ash (content)
Hydrated cement	1	0	0.29	0.15 (13%)
Mortar	1	3	0.5	0.45 (10%)

Table 3 Chemical component of materials.

	/mass %							
	SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	LOI	C
Nanjing second power plant	46.22	28.24	3.63	0.74	-	2.81	13.0	5.12
Huaneng power plant	54.7	28.98	4.48	0.56	0.58	5.24	2.24	1.11
Cement	22.60	5.03	63.11	1.46	2.24	4.38	1.18	-

Fig. 2 X-ray diffraction pattern of the fly ash. (1) Nanjing second power plant. (2) Huaneng power plant.

Fig. 3 XPS survey spectra of fly ash surface. (1) Nanjing second power plant. (2) Huaneng power plant.

Table 4 Quantitative analysis of several main peaks.

	Nanjing second power plant			Huaneng power plant		
	Peak BE /eV	FWHM /eV	At. %	Peak BE /eV	FWHM /eV	At. %
C1s	282.56	2.13	46.33	282.76	1.08	35.64
O1s	531.70	2.83	52.65	531.66	2.64	62.99
Fe2p	711.84	5.09	1.02	711.59	4.91	1.38

Fig. 4 XPS spectra of carbon element on fly ash surface. (1) Nanjing second power plant. (2) Huaneng power plant.

Fig. 5 XPS spectra of iron element on fly ash surface. (1) Nanjing second power plant. (2) Huaneng power plant.

The surface properties of the carbons were analyzed by using XPS as shown in Fig. 4. As seen the binding energies were centered at 282.5 eV and 284.4 eV which can be attributed to carbide and carbon respectively and indicated a notable disassociation in the spectra.¹¹⁾

Figure 5 indicated the presence of Fe and Fe components in the Fe 2p spectra. The binding energy (BE) and chemical state were listed in Table 5. As seen the binding energies are centered at 705.9, 709.1 and 711.8 eV, which can be attributed to Fe (II)-S, Fe (III)-O and Fe (II)-S, respectively.¹²⁾

The surface properties of the oxygen element were analyzed by using XPS as shown in Fig. 6. As seen the binding energies are centered at 531.7 eV which can be attributed to an O^{2-} species.

Fig. 6 XPS spectra of oxygen element on cement surface.

3.4 Mössbauer analysis

Figure 7 showed that the Mössbauer spectra of the fly ash contained superimposed single peak, doublets and sextets. Spectra 1, 2 contained doublets peaks and Spectra 3, 4 contained sextet's peaks. It was suggested that there were four kinds of iron form in fly ash at least, and Mössbauer parameters were shown as in Table 6.

Table 6 showed that fly ash contained maghemite (α - Fe_2O_3), magnetite (Fe_3O_4) and Fe^{3+} -mullite where the Fe -mullite and maghemite were present as major phase. Haematite (α - Fe_2O_3), magnetite (Fe_3O_4) have internal magnetic field, which can contribute to the magnetic behavior.^{13,14} According to Mössbauer theory, $Fe^{2+} 3d^6$ has one more outer electron than $3d^5$ of Fe^{3+} , so the δ of Fe^{2+} is more than δ of Fe^{3+} , which is 1.14 mm/s and 0.44 mm/s respectively. Based on the theory, the state of iron is easy to be identified.

3.5 Electromagnetic parameters testing

Electromagnetic parameters tested at the frequency range of 1–18 GHz were shown in Fig. 8.

Table 5 Qualitative and quantitative XPS results of state of iron on fly ash surface.

	Nanjing second power plant			Huaneng power plant		
Binding energies /eV	705.9	709.1	711.8	708.2	710.8	712.3
Chemical state	Fe(II)-S	Fe(II)-O	FeOOH Fe(II)-S	Fe(II)-S	Fe(III)-O Fe(II)	Fe(II)-S

Fig. 7 Mössbauer spectra of fly ash. (1) Nanjing second power plant. (2) Huaneng power plant.

Table 6 Mössbauer parameters of fly ash.

	Area (%)	IS(δ) (mm/s)	QS(Δ) (mm/s)	Hhf (Koe)	Γ (mm/s)	Assignment
Nanjing second power plant	43.8 %	0.28(8)	1.1(8)	-	0.54(0)	Fe^{3+} -mullite
	19.7 %	1.1(1)	1.9(0)	-	0.49(2)	Pyrite (FeS_2)
	15.3 %	0.26(2)	-0.0(6)	505.(7)	0.51(3)	Haematite (α - Fe_2O_3)
	21.3 %	0.36(7)	0.0(1)	464.(5)	0.53(4)	Magnetite (Fe_3O_4)
Huaneng power plant	34.3 %	0.22(3)	1.12(2)	-	0.54(0)	Fe^{3+} -mullite
	19.8 %	0.74(1)	1.37(0)	-	0.49(2)	Pyrite (FeS_2)
	28.0 %	0.37(4)	-0.19(5)	510.(5)	0.51(3)	Haematite (α - Fe_2O_3)
	17.9 %	0.55(8)	-0.34(0)	442.(3)	0.53(4)	Magnetite (Fe_3O_4)

Fig. 8 The electromagnetic parameters of fly ash at frequency of 1~18 GHz. (1) Nanjing second power plant. (2) Huaneng power plant.

Table 7 Electromagnetic parameters of Nanjing second power plant fly ash.

Frequency/GHz	ϵ'	ϵ''	$\tan\delta_e$	μ'	μ''	$\tan\delta_m$
1	5.22	0.24	0.046	1.11	0.015	0.014
2	5.10	0.29	0.057	1.09	-0.002	-0.002
3	5.03	0.30	0.060	1.09	-0.01	-0.009
4	5.00	0.28	0.056	1.09	-0.004	-0.004
5	5.01	0.25	0.050	1.07	0.008	0.008
6	5.04	0.25	0.050	1.04	0.01	0.010
7	5.07	0.27	0.053	1.02	0	0
8	5.06	0.28	0.055	1.02	-0.01	-0.010
9	5.06	0.29	0.057	1.02	-0.01	-0.010
10	5.00	0.27	0.054	1.02	-0.01	-0.010
11	4.97	0.28	0.056	1.03	-0.002	-0.002
12	4.90	0.23	0.047	1.04	0.01	0.010
13	4.90	0.18	0.037	1.04	0.04	0.038
14	4.96	0.27	0.054	1.00	0.02	0.020
15	4.87	0.32	0.066	1.04	0.01	0.010
16	4.94	0.39	0.079	1.05	0.03	0.029
17	4.87	0.77	0.159	1.02	0.02	0.019
18	4.47	0.73	0.165	1.03	0.002	0.002

From Fig. 8(1), we knew that the real part of complex permittivity ϵ' of electric loss was near 5, and the imaginary part of complex permittivity ϵ'' had one notable peak at the frequency of 18 GHz; μ' of magnetic loss was more than 1, and μ'' nearly equals 0. From Fig. 8(2), we knew that ϵ' of electric loss was near 4, and ϵ'' had two notable peaks at the frequency of 11–12 GHz and 18 GHz and μ' of magnetic loss was more than 1, and μ'' nearly equals 0. Consequently, electric loss of fly ash of Nanjing second power plant was more than of Huaneng power plant which were consistent with the result in Table 3 that content of Fe_2O_3 was only about the half of carbon.

Electric loss tangent and magnetic loss tangent are taken as $\tan\delta$ which are calculated by eq. (1). The total electromagnetic loss is the sum of $\tan\delta_e$ and $\tan\delta_m$.

$$\tan\delta_e = \epsilon''/\epsilon' \quad \tan\delta_m = \mu''/\mu' \quad (1)$$

The calculated results of two samples were shown in Table 7 and Table 8 respectively.

As shown in Table 7, electric loss tangent $\tan\delta_e$ reached maximum at the frequency of 17–18 GHz but magnetic loss tangent $\tan\delta_m$ reached maximum at 13 GHz, and $\tan\delta_e$ were 2~5 times more than $\tan\delta_m$, which have indicated that fly ash was electric attenuation absorbent more than magnetic

Table 8 Electromagnetic parameters of Huaneng power plant fly ash.

Frequency /GHz	ϵ'	ϵ''	$\tan\delta_e$	μ'	μ''	$\tan\delta_m$
1	4.30	0.11	0.026	1.10	0	0
2	4.24	0.15	0.035	1.09	-0.009	-0.009
3	4.18	0.17	0.041	1.10	-0.014	0.013
4	4.15	0.15	0.036	1.11	-0.002	0.002
5	4.17	0.11	0.026	1.10	0.013	0.012
6	4.20	0.11	0.026	1.08	0.02	0.019
7	4.23	0.14	0.033	1.06	0.012	0.011
8	4.25	0.16	0.038	1.07	0.007	0.007
9	4.28	0.19	0.044	1.07	0.011	0.010
10	4.31	0.27	0.063	1.08	0.036	0.033
11	4.25	0.41	0.097	1.05	0.067	0.064
12	4.05	0.34	0.084	0.99	0.061	0.062
13	4.05	0.25	0.062	0.98	0.022	0.022
14	4.07	0.23	0.057	0.99	0.003	0.003
15	4.06	0.24	0.059	1.00	-0.008	0.008
16	4.07	0.19	0.047	1.00	-0.007	0.007
17	4.16	0.20	0.048	0.99	-0.010	0.010
18	4.16	0.32	0.077	0.99	-0.034	0.034

attenuation absorbent which were consistent with the content of Fe_2O_3 and carbon in Table 3.

As shown in Table 8, electric loss tangent $\tan\delta_e$ of Huaneng power plant fly ash reached maximum at the frequency of 18 GHz but the value was only half of Nanjing second power plant fly ash. Magnetic loss tangent $\tan\delta_m$ of Huaneng power plant fly ash was as same as of Nanjing second power plant fly ash, which was consistent with the content of Fe_2O_3 and carbon in Table 3. Because carbon powder and FeO are electric attenuation absorbents, which have higher electric loss tangent and the electromagnetic energy is mainly attenuated as a resistor.¹⁵⁾

In conclusion, it was clear that electric loss was more than magnetic loss for fly ash and the electromagnetic wave-absorbing property of type III was slightly more than of type I except 11–12 GHz.

According to the electromagnetic theory, the reflection coefficient for coated single-layer electromagnetic microwave absorbing materials is the function of real and imaginary part of complex permittivity and complex permeability, frequency (f) and thickness (d), which can be denoted as eq. (2).¹⁶⁾

$$R = 20 \lg \left| \frac{\sqrt{\frac{\mu_r}{\epsilon_r}} \tanh[j(2\pi fd/c)\sqrt{\mu_r\epsilon_r}] - 1}{\sqrt{\frac{\mu_r}{\epsilon_r}} \tanh[j(2\pi fd/c)\sqrt{\mu_r\epsilon_r}] + 1} \right| \quad (2)$$

Fig. 9 Reflectivity of epoxy-based fly ash of Nanjing second power plant. (1) Calculated reflectivity. (2) Experimental reflectivity.

Where, f and d are the frequency of the electromagnetic wave and the thickness of the materials respectively, c is the speed of light, π is the constant, ε_r and μ_r are the permittivity and permeability respectively, j is the imaginary unit.

Based on the electromagnetic parameters in Fig. 8(1), the theoretical reflectivity computed by using formula (2)¹⁷⁾ was shown as in Fig. 9(1), which were similar with experimental value shown as in Fig. 9(2).

3.6 Reflectivity testing

3.6.1 Reflectivity of fly ash

The absorbing wave properties of fly ash (Nanjing second power plant) were shown as in Fig. 9(2). There were several absorbing-wave peaks at the frequency of 1–18 GHz, and the biggest absorption reached 14.5 dB at 16 GHz which were consistent with the electromagnetic parameters in Fig. 8(1); at the same time, absorbing effectiveness increased with the increase of sample thickness. In the high frequency, Fe_2O_3 have higher permeability, which can absorb electromagnetism wave by domain wall resonance and natural resonance.^{18,19)} On the other hand, Type III fly ash contains obvious unburned carbon, when electromagnetic wave penetrates into carbon porous or layer structure, which can cause loss of electromagnetic wave energy by multi-reflections, damping vibration equivalent to a bipolar and conductive network or electron-tunneling conduction.²⁰⁾

According to the electromagnetic wave theory, when the thickness of the specimen is equal to a quarter of wavelength or it's odd times, the reflection waves from the two surfaces of specimen will interference, which can weaken the reflection wave energy. And with the increase of frequency, the interference peak will appear in turn. When the specimen thickness and the wavelength satisfy eq. (3), the interference happens.

$$d = (2n + 1) \frac{\lambda_0}{4\sqrt{\varepsilon_r\mu_r}} \quad (3)$$

where: d is the specimen thickness; λ_0 is the incident electromagnetic wavelength in vacuum; ε and μ are the permittivity and permeability respectively.

Taken the largest peak at the frequency of 16.2 GHz and 18 GHz as the initial condition of 20 mm sample and 10 mm sample respectively, the several calculated interference peak

Table 9 The sites of the calculated interference peaks.

d/mm	20	20	20	20	20	10	10	10
n	0	1	2	3	4	0	1	2
Frequency /GHz	1.8	5.4	9.0	12.6	16.2	3.6	10.8	18

sites were listed in Table 9, which matched very well with the peaks in Fig. 9(2). Thus the several peaks in Fig. 9 are inferred as the interference peaks.

3.6.2 Reflectivity of fly ash based on cement

Reflectivity of cement-based Type III fly ash (Nanjing second power plant) cured for 3 months were tested as shown in Fig. 10.

The absorbing wave properties of mortar (with 10% fly ash) were more than of hydrated cement (with 13% fly ash), which were similar with experimental value shown as in Fig. 9(2). The absorption of mortar in 10~18 GHz frequency range were all over 6 dB. As the main components of the standard sand, SiO_2 has low dielectric constant, which can improve the free space impedance matching performance, thus increase the wave absorption performance.

4. Conclusions

From the results and discussion mentioned above, the following generalized conclusions can be drawn:

- (1) Mineralogical phase and chemical composition electromagnetic properties of two samples are nearly the same. Fly ash exhibits electromagnetic wave absorbing property, due to porous or layer structure, carbon powder and iron oxide. In general electromagnetic wave-absorbing property of type III fly ash is slightly more than of type I fly ash.
- (2) Fly ash contains maghemite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4) and Fe^{3+} -mullite where the Fe-mullite and maghemite are present as major phase. Haematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4) have internal magnetic field, which can contribute to the magnetic behavior. Electric loss tangent $\tan\delta_e$ are 2~5 times than magnetic loss tangent $\tan\delta_m$, which mean that fly ash are electric attenuation absorbent more than magnetic attenuation absorbent.

Fig. 10 Reflectivity of cement-based fly ash. (1) Hydrated cement. (2) Mortar.

- (3) There are several absorbing-wave interference peaks at the frequency of 1–18 GHz, and the biggest absorption reaches 14.5 dB at 16 GHz at the thickness of 20 mm.
- (4) The absorbing wave property of mortar with 10% type III fly ash is more than of hydrated cement with 13% type III fly ash, whose absorption is over 6 dB in 10~18 GHz frequency range.

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