Research Article

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Study of the mechanical-electrical-magnetic properties and the microstructure of three-layered cement-based absorbing boards

https://doi.org/10.1515/rams-2020-0014
Received Jan 21, 2020; accepted Feb 12, 2020

Abstract: In this paper, a three-layered cement-based wave-absorbing board is designed and prepared by mixing wave-absorbing fillers such as nano-Si$_3$N$_4$, multi-layer nano graphene platelets (NGPs), nano-Ni, carbon fiber (CF) and carbon black (CB) into cement slurry. The effect of the amount of wave-absorbing fillers on the mechanical properties, resistivity and wave-absorbing reflectivity of cement slurry is studies. The microstructure of NGPs, nano-Si$_3$N$_4$ and the wave-absorbing board are characterized by TEM and SEM. Research shows that low content of NGPs and other wave-absorbing fillers can significantly reduce the resistivity of cement slurry and improve its mechanical strength, and dense massive crystals are precipitated in the cement hydration products. The reflectivity test reveals that in the frequency range of 2~18 GHz, the minimum reflectivity of the three-layered cement-based wave absorbing board reaches $-18.8$ dB, and the maximum bandwidth less than $-10$ dB reaches 15.3 GHz. This study can serve as reference for the preparation of new three-layered cement-based wave absorbing boards.

Keywords: multilayer nano graphene platelets, three-layered wave absorbing board, compressive strength, resistivity, absorbing reflectivity

1 Introduction

Currently electromagnetic waves have become the fourth major source of pollution next to water, atmosphere and noise pollutions, and the harm of electromagnetic pollution is pervasive [1, 2]. In order to reduce the hazardous impact of electromagnetic radiation on the environment, studies have been made by scholars at home and abroad, focusing on the absorption and shielding of electromagnetic waves. Shielding is realized mainly by preventing the penetration of electromagnetic waves by taking advantage of the high conductivity of the material, which forms a closed conductive path. But this method cannot weaken or eliminate electromagnetic waves fundamentally, and electromagnetic waves reflected by the surface of the material will also generate secondary clutter pollution. The use of wave-absorbing fillers in design can convert the energy of electromagnetic waves into heat or other forms of energy to the maximum extent and thus fundamentally avoids the hazards caused by electromagnetic radiation [3, 4].

Due to their easy accessibility and good environmental adaptability, the traditional cement-based composites are widely used in infrastructure such as buildings, roads, bridges, tunnels and ports. The use of fillers in cement-based materials is to improve their rheological property, strength, durability, conductivity and absorbing properties. Nanomaterials have become a new type of absorbing filler with potential applications thanks to their surface size effect, quantum Hall effect, macroscopic quantum tunneling effect and dielectric confinement effect and good electrical conductivity [5–8].

In recent years, some scholars have conducted research on the application of nano graphene platelets (NGPs) and their derivatives in cement-based materials, and achieved fruitful results [9]. The study by Rodrigo et al. [10] shows that cement mortar specimens doped with 0.021% NGPs can increase the compressive strength by 63.6%, 94.1% and 95.7% at 3d, 7d and 28d, respectively, compared with ordinary mortar samples. Sun et al. [11] investigated the electrical response of cement-based com-
composites with NGPs under different loading amplitudes and rates. The results reveal that the composites doped with NGPs are sensitive to the piezoresistive effect and have stable repeatability under different loading conditions. Research by Huang [12] indicates that the doping of NGPs improves the breaking strength of cement-based composites, which is 82% higher than that of ordinary ones, and the electrical conductivity of composites is significantly enhanced. Chen et al. [13] prepared rGO/CF composite by coating the surface of carbon fiber (CF) with reduced graphene oxide (rGO) by electrophoretic deposition. They found that in the X wave band (8.2~12.5 GHz), the absorbing property of the cement-based material mixed with 0.4 wt% rGO/CF is 31% higher than that of the cement-based absorbing boards. The results show that the conductivity of composites is determined by the distribution and contact of graphene in cement matrix. When the doping content of graphene exceeds the percolation threshold, the curing period and water content have little effect on the electrical conductivity of the composite.

Nano-Ni is an excellent magnetic medium absorbing filler. Its absorption mechanism for electromagnetic energy depends on three effects, i.e. the electron scattering caused by thermal vibration of lattice electric field, the electron scattering resulting from impurity and lattice defects and the interaction between electrons. Due to the strong activity of nano-Ni, the movement of electrons increases under electromagnetic wave radiation, which accelerates magnetization and converts electromagnetic wave energy into heat energy. Meanwhile, with large magnetic permeability, it has strong electromagnetic interaction with high-frequency electromagnetic waves, hence its highly efficient absorption performance. As mentioned above, studies have been reported on the mixing of NGPs into cement-based materials to improve the pore structure of cement slurry, promote the hydration process, and enhance the mechanical properties. However, few reports are available on doping nano-Si$_3$N$_4$, NGPs, nano-Ni, CF and CB into cement slurry to prepare three-layered cement-based absorbing boards. In this paper, three-layered cement-based absorbing boards are used to study the effect of nano-Si$_3$N$_4$, NGPs, nano-Ni, CF and CB on the mechanical strength, microstructure, electrical resistivity and absorption properties of cement slurry, laying some theoretical foundations for the development of new types of cement-based absorbing boards.

2 Experiment

2.1 Experimental materials

The materials in the experiment include ordinary Portland cement (P•II Grade 42.5), produced by Jiangsu Conch Cement Factory and its quality meets the requirements of “General Purpose Portland Cement” (GB175-2007). NGPs, nano-Si$_3$N$_4$, nano-Ni and CF are supplied by Beijing Zhongke Leiming Technology Co., Ltd. The indicators of NGPs are as follows: purity is greater than 99.5 wt%, thickness is 0.4~20 nm, diameter is 5~10 μm, number of layers is 1~5 layers, density is 0.23 g/cm$^3$, volume resistivity is 4×10$^{-6}$ Ω·cm. The indicators of nano-Ni are as follows: purity is greater than 99.9 wt%, average particle diameter is 50 nm, specific surface area is 23.2 m$^2$/g, bulk density is 0.22 g/cm$^3$, crystal form is near-spherical, and the color is black. The indicators of nano-Si$_3$N$_4$ are: purity is greater than 99.9 wt%, average particle diameter is 500 nm, specific surface area is 10.3 m$^2$/g, bulk density is 0.116 g/cm$^3$, crystal shape is face-centered cubic, and the color is grayish white. CF performance indicators are: diameter is less than 8μm, carbon content is greater than 95%, tensile strength is larger than 3500 MPa, tensile modulus is larger than 210 GPa, elongation is less than 2.1%, density is 1.74~1.79×10$^3$ kg/m$^3$, resistivity is 1.0~1.6 Ω·cm. The silica fume is produced by Shanghai Lidian Silicon Fume Material Co., Ltd., and the performance indicators are as follows: total alkalinity is less than 1.5%, SiO$_2$ content is larger than 85%, specific surface area is 15m$^2$/g, activity index is greater than 105%, water content is less than 3.0% and water absorption rate is less than 125%. The water reducer, produced by Shanghai Sanrui Polymer Material Technology Co., Ltd., is a polycarboxylic acid, with the water reducing rate being around 45%. The dispersing agent, a white flocculent powder, is Carboxymethy cellulose supplied by Hebei Xingtai Cellulose Co., Ltd.

2.2 Mix proportion design

According to the “transmission line” theory of electromagnetic wave propagation, some of the electromagnetic wave energy incident on the surface of the material is reflected due to the mismatch between the interface impedance of the material and the spatial wave impedance. Some energy is absorbed by the wave absorbing filler inside the material and converted into other forms of energy, and some is transmitted. It is difficult for a layer of structural material mixed with a single type of wave absorbing filler to real-
Table 1: Mix proportion and thickness of board.

| NO   | NGPs (%) | Nano-Ni (%) | CF (%) | CB (%) | Nano-Si$_3$N$_4$ (%) | Silica fume (%) | Water reducer (%) | Ds (%) | W/C (%) | Tb (mm) |
|------|----------|-------------|--------|--------|---------------------|----------------|-------------------|--------|---------|--------|
| E0   |          |             |        |        |                     |                |                   |        |         |        |
| Up   |          |             |        |        |                     |                |                   |        |         |        |
| GPE1 | Middle   | 0.025       | 0.75   |        |                     | 10             | 0.32              | 0.31   | 30      |        |
| Down |          | 0.5         | 4      |        |                     | 10             | 0.33              | 0.32   | 11      |        |
| GPE2 | Middle   | 0.025       | 0.75   |        |                     | 10             | 0.33              | 0.32   | 11      |        |
| Down |          | 1.0         | 4      |        |                     | 10             | 0.36              | 0.38   | 0.80    | 11     |
| GPE3 | Middle   | 0.05        | 0.75   |        |                     | 10             | 0.35              | 0.33   | 11      |        |
| Down |          | 0.5         | 4      |        |                     | 10             | 0.35              | 0.35   | 0.74    | 11     |

Note: Up, Middle, Down and All represent the matching layer, absorbing layer, absorbing & reflecting layer and the whole of the three-layer cement-based wave absorbing board. Ds denotes dispersant, and Tb denotes thickness of board.

Ordinary cement-based materials have a high dielectric constant and impedance. In order to match their surface with the wave impedance in space, a matching layer needs to be designed so that electromagnetic waves incident on the surface of cement-based materials can smoothly enter their interior. The layer should have a low impedance. The matching layer needs to be doped with cavity and light wave-transmitting material, which can regulate the impedance effectively and achieve the goal of gradual impedance change [15]. According to the previous research results of the research group on conductive cement-based materials, electricity and magnetism have a certain correlation. Combined with the previous research results, the comprehensive mix ratio of the three-layer wave-absorbing material was determined. Nano-Si$_3$N$_4$ is a ceramic-based nano material prepared by a special process, with small particle size, large specific surface area, and uniform distribution. It has high surface activity, high purity, low bulk density, 95% ultraviolet reflectance, high mechanical strength, good chemical corrosion resistance, and high strength especially at high temperature. It is likely to form dense dispersed phase in composite materials, thus improving their comprehensive performance greatly. Its magnetic loss tangent value is $3 \times 10^{-3}$, and has good wave permeability. Considering the problem of dispersion, the amount of nano-functional materials in cement-based materials should not exceed 5%, and the amount selected in this test is 2%. The middle layer is designed as an absorbing layer, and magnetic media fillers (NGPs and nano-Ni) with good absorption performance are mixed, so that electromagnetic waves can be absorbed to the maximum extent without excessive reflection or transmission. The bottom layer is designed as an absorbing & reflecting layer, and carbon-based materials (CF and CB) with excellent conductivity are mixed. A closed conductive network formed by conductive fillers is used to prevent electromagnetic waves from passing through, so that some energy of the electromagnetic waves is converted into electric heat energy and the rest is reflected to the absorbing layer for continuous absorption. With this design idea in mind, according to the research team’s previous studies, a new type of three-layer cement-based absorbing board is prepared by mixing resistive, dielectric and magnetic media absorbing fillers. In order to ensure similar fluidity of the slurry while formed, the mixing ratio and board thickness in this design are shown in Table 1 (the mass of cement is taken as 1), and the designed sample size is $300 \times 300 \times 30$ mm$^3$.  

2.3 Test Method

2.3.1 Slurry preparation

Add 60°C of water into a beaker, slowly add dispersant into the water as required, and stir to ensure that the dispersant is fully dissolved in the water. Then, add the required CF into the beaker and stir evenly to fully disperse CF for later use. Weigh the required materials, and put cement, silica fume and CB into a stirring pot. After they are stirred, add the evenly dispersed CF. Finally, a certain amount of water and water reducer are added into the mixture, which is stirred at low speed for 2.5 min, and after a pause of 20 s, is stirred at high speed for 2.5 min to obtain the slurry required for absorbing & reflecting layer molding.

Weigh the required cement, silica fume and nano-Ni, and put them into a stirring pot. After they are stirred evenly, add the required NGPs dispersion liquid into it (NGPs is a dispersed aqueous solution provided by the manufacturer. Before use, the aqueous solution is dispersed ultrasonically for 20 minutes, other absorbers have better dispersibility, same as general gelling materials). Finally, water and water reducer are added into the mixture, which is stirred at low speed for 2.5 min, and after a pause of 20 s, is stirred at high speed for 2.5 min to obtain the slurry required for the absorbing layer molding.

Weigh the required cement, silica fume and nano-Si$_3$N$_4$, and put them into a stirring pot. After they are stirred evenly, water and water reducer are added into the mixture, which is stirred at low speed for 2 min, and after a pause of 20 s, is stirred at high speed for 2 min to obtain the slurry required for the matching layer molding.

2.3.2 Molding

The mold used is a three-layer laminated one, and the molding method is layer casting. The size of the mechanical property sample mold is 40×40×160 mm$^3$, and the size of the resistivity sample mold is 25×25×25 mm$^3$. A 16 mm ×30 mm copper mesh is embedded about 5mm from the ends as an electrode, and the size of the reflectivity sample mold is 180×180×30 mm$^3$. The formed sample is placed in a constant temperature and humidity chamber (the temperature is 20±2°C, and the relative humidity is greater than 90%). After 24 hours, demoulding is continued under this condition, and each group forms three test pieces.

2.3.3 Test method

1) The mechanical property test is performed on a universal testing machine in accordance with relevant requirements in DL/T 5126-2001 Specifications. The compressive strength shall be uniformly loaded at the rate of 2.4 kN/s and the bending strength shall be uniformly loaded at the rate of 20 N/s until failure. The bending strength $R_f$ is calculated according to Eq. (1), and the unit is MPa, accurate to 0.1 MPa.

$$R_f = 1.5F_fL/b^3$$

where $F_f$ denotes the load in the middle of the specimen when broken (N), $L$ is the distance between supporting cylinders (mm), and $B$ is the side length of the section of the test piece (mm).

The compressive strength $R_c$ is calculated according to Eq. (2):

$$R_c = F_cL/A$$

where $F_c$ represents the maximum load at the time of failure (N), and $A$ represents the area of pressed part (mm$^2$).

2) For resistivity ($\rho$), the multimeter is used to measure the resistance ($\Omega$) of the test specimen at 3d, 7d and 28d, respectively. The measured distance between the two electrodes of the specimen is $L$ (cm), the measured cross section is $A$ (cm$^2$). Then, the resistivity can be obtained according to the equation $\rho = RA/L$.

3) The measuring system of the absorbing reflectivity is an arcuate system, which consists of a signal source, a vector network analyzer (HP8722ES Type) and a test antenna. The test is conducted according to the radar absorbing material test standard GJB2038-2011, and the reflectivity is calculated according to Eq. (3):

$$\Gamma = \frac{P_a}{P_m}$$

where $\Gamma$ denotes the reflectivity of flat-board RAM, $P_a$ denotes the reflective power of flat-board RAM temboard (mW), and $P_m$ denotes the reflective power of the same size of good conductor metal board (mV).

3 Results and discussion

3.1 Characterization of NGPs and nano-Si$_3$N$_4$

The transmission electron microscope (TEM) image of NGPs is shown in Figure 1a, and the scanning electron mi-
The scanning electron microscope (SEM) image of nano-Si$_3$N$_4$ is shown in Figure 1b.

**Figure 1:** TEM image of NGPs and SEM image of nano-Si$_3$N$_4$

From Figure 1a, it can be clearly seen that NGPs have a unique planar fold structure with a high aspect ratio. It is shaped like a transparent film, and its edge is rolled to form folds, which makes it possible to adsorb heterogeneous particles for modification. In addition, its folded structure increases the contact area with the matrix interface, resulting in higher adhesion and pullout resistance, thus enhancing the mechanical properties of the composite material. As can be seen, NGPs have a diameter of about 5 to 10 $\mu$m and a thickness of about 0.5 to 20 nm. From Figure 1b, it can be seen that nano-Si$_3$N$_4$ is an irregular face-centered block crystal with different sizes and shapes and the average particle size is approximately 0.5 $\mu$m.

### 3.2 Analysis of mechanical properties

Figure 2 shows measured values of the compressive strength of the matching layer, absorbing layer, absorbing & reflecting layer and the whole at 7d and 28d of the three-layered cement-based wave absorbing material doped with nano-Si$_3$N$_4$ and NGPs.

**Figure 2:** Compressive strength of GPE1 ~ GPE3

From Figure 2, it can be seen that the compressive strength of the absorbing layer doped with NGPs and nano-Ni increases obviously with the NGPs content. The compressive strength of GPE3 absorbing layer at 7d and 28d is 73.6 MPa and 95.8 MPa, respectively, an increase of 15.4% and 15.8% compared with GPE1 absorbing layer. Compared with E0 (reference block), the compressive strength at 7d and 28 increases by 32.3% and 33.5%, respectively. The test results are consistent with the research findings of Mohamed Saafi et al. [16]. The increase in compressive strength of the absorbing layer is attributed to the unique fold structure of NGPs, which plays a temboardeffect in the cement hydration process. It makes the cement hydration crystals densify and thicken, produces toughening and reinforcing effects, and thus improves the pore structure of cement slurry.

The compressive strength of GPE2 absorbing & reflecting layer at 7d and 28d is 27.2 MPa and 35.7 MPa, respectively, a decrease of 24.3% and 21% compared with GPE1 absorbing & reflecting layer, which might be related to the failure of uniform dispersion of CF. Compared with E0, it decreases by 45.5% and 43.9%, respectively. The reason may be that CF and CB have high water absorption. In order to ensure proper fluidity of the cement slurry, a large water-binder ratio is adopted in the CF molding process, resulting in the incompact structure of hydration products. Meanwhile, the “ball effect” due to the incorporation of CB in the matrix reduces the interfacial action between the matrices.
It can also be seen that the overall compressive strength of the three-layered wave absorbing materials at 7d and 28d is between the compressive strength of the matching board and the absorbing & reflecting layer at 7d and 28d, respectively. According to the nonlinear theory of composites, the overall strength is often determined by the lower strength part of the composites.

### 3.3 Analysis of conductivity

Figure 3 shows the measured values of the compressive strength and resistivity of the matching layer, the absorbing layer, the absorbing & reflecting layer, and all layers at 3d, 7d, 28d of the three-layered cement-based absorbing material doped with nano-Si$_3$N$_4$, NGPs and other nanofillers.

As can be seen from Figure 3, when absorbing fillers such as NGPs, nano-Ni, CF and CB are doped, the resistivity of the absorbing layer and absorbing & reflecting layer is reduced effectively, which varies within the order of $10^2$ to $10^3$ $\Omega$-cm. Compared with the reference test block (E0), they all show a relatively large decrease, especially at 28d. The resistivity of the test blocks doped with 1% CF+4%CB in the absorbing & reflecting layer is consistent with the research results of Chen et al. [17]. However, the measured value of the resistivity of the absorbing layer is too large, which may be related to the amount of the absorber. When the content of the absorbing filler is low, the particles are randomly distributed in the cement-based absorbing board. Because of the long distance between the particles, it is difficult for the potential they carry to cross the barriers between them, so doping the absorbing material has little effect on the resistivity of the absorbing board. In this study, the absorbing fillers NGPs and nano-Ni have good electrical conductivity. Due to their relatively low amount, it is impossible to form a closed or connected conductive network in the matrix, so their effect on the resistivity of the absorbing layer is small.

CF and CB have excellent conductivity, and they form an inter-connected conductive network when filled in the absorbing & reflecting layer matrix, thus reducing its resistivity dramatically. For the test specimen with the same mix proportion, the resistivity at 28d is significantly higher than that at 7d. The reason might be with the continuing hydration of cement, free water molecules in the cement slurry decreases continuously, so the connection path of the water molecules with nano-absorbent particles decreases and the resistivity increases. Compared with E0, the resistivity of the matching layer at 3d has increased by about 25% and the resistivity at 7d and 28d has increased by about 10%. This may be related to the fact that the nano-Si$_3$N$_4$ doped in the matching layer is an electrical insulator.

It can also be seen from Figure 3 that the overall resistivity of the three-layered absorbing board is closer to the absorbing & reflecting layer, which is approximately 1.25 to 1.4 times that of the absorbing & reflecting layer. The three-layered absorbing board can be abstractly understood as paralleling three resistors of different values at both ends of a power supply. According to Ohm’s law, the overall resistance in a parallel circuit is determined by the resistor with smaller resistance, and it is closer to that smaller resistance.

According to the Schelkunoff equation, the electromagnetic wave absorption performance of a material is related to its conductivity and permeability, which increases with the increase of conductivity and permeability. Since the conductivity is inversely proportional to the resistivity, the electromagnetic wave absorption performance of a material decreases as its resistivity increases [18]. Pierre R et al. [19] showed that materials with a resistivity between 10 to $10^3$ $\Omega$-cm have fairly good electromagnetic wave shielding and absorbing capabilities.

### 3.4 SEM analysis

Figure 4 shows the SEM images of the absorbing layer and the absorbing & reflecting layer of GPE1 to GPE3 doped with different types of absorbing-fillers.

It can be observed from Figure 4 that the main crystalline products of the cement slurry are still Aft, AFm, CH and C-S-H gels after adding the absorbing fillers. At this
time, however, large numbers of flaky and compact block crystals are generated, which exhibit different forms depending on the amount and type of the absorbing filler. In Figure 4(a), plenty of layered block crystals are precipitated and they are dense. In Figure 4(b), large dense block crystals with clear and smooth texture are observed. In Figures 4(c) and (e), it can be seen that CF is uniformly dispersed in a monofilament form in the matrix and no clustering occurs. At this time, the hydration products are loosely intertwined in a rod form and they are not very dense. In Figures 4(d) and (f), it can be seen that CF is uniformly dispersed in the matrix with good bonding, and a conductive network has been formed. However, there are some clusters and it is not dense.

NGPs have an ultra-high specific surface area and are capable of adsorbing large quantities of free water in the matrix. As the hydration reaction continues to develop, the unhydrated cement particles near the surface of NGPs get free water and are hydrated gradually, thereby forming a tightly structured hydrated crystal on the surface of NGPs, which can improve the mechanical properties of the cement slurry significantly. In order to ensure proper fluidity of the cement slurry, the absorbing & reflecting layer is formed with a larger water-to-binder ratio. According to the SEM images, it is apparent that the hydration product is fluffy, which is the main reason for the decrease in compressive strength. As the doping amount of CF increases, this phenomenon gets particularly noticeable, but CF overlaps well.

3.5 Analysis of the wave transmission performance of Nano-Si$_3$N$_4$

In order to reduce the impedance of the matching layer, 2% nano-Si$_3$N$_4$ is added to the cement slurry to improve its wave transmission performance. When the electromagnetic waves are transmitted to the matching layer, some reflection occurs on the layer's surface because they are not completely matched with the impedance of the space waves. In the process of transmission, some electromagnetic waves transmitted to the matching layer will be converted into heat energy and are lost, but most of the waves will pass through the matching layer. Because the matching layer has a high resistivity, it can be considered as an insulating layer with a thickness of $d$. The electromagnetic waves transmitted to the interior are composed of reflection, transmission, and attenuation, which can be expressed as:

$$T + R + A = 1$$

where $T$ is the transmission coefficient, $R$ is the reflection coefficient, and $A$ is the attenuation coefficient.

Assume that the matching layer is uniformly distributed and the reflection coefficient remains unchanged
with the change of frequency. According to Eq. (4), the transmission coefficient has a linear relationship with the attenuation coefficient, and it decreases with the increase of the attenuation coefficient. The matching layer should be filled with wave transmitting materials with good performance.

In order to investigate the wave transmitting ability of the nano-Si$_3$N$_4$, the present study has tested the reflectivity of the cement slurry with 2% nano-Si$_3$N$_4$ at 28d, as shown in Figure 5.

![Figure 5: Absorbing reflectivity of the matching layer doped with 2% nano-Si$_3$N$_4$](image)

As can be seen, in the frequency range of 2–18 GHz, the cement slurry in the matching layer with 2% nano-Si$_3$N$_4$ has a minimum reflectivity of $-2.11$ dB at 2.25 GHz and the effective bandwidth greater than $-1$ dB reaches 8.97 GHz. The reflection loss is low and it is even positive in some frequency bands, which indicates that the electromagnetic waves are completely transmitted at this point. According to the Ref. [20], the reflectivity of ordinary cement-based materials is in the range of $-3$--$-4$ dB, which shows that nano-Si$_3$N$_4$ has good wave transmitting performance and that the design of the matching layer is reasonable.

### 3.6 Analysis of the absorbing reflectivity

Reflectivity is an important indicator to evaluate the absorbing performance of materials. When the reflectivity is smaller than $-5$ dB, the material can be used for electromagnetic wave absorption and shielding in general civil buildings. When the reflectivity is smaller than $-7$ dB, the material can be used for electromagnetic wave absorption and shielding in the important civil buildings and military facilities [21].

The test results of absorbing reflectivity of samples GPE1–GPE3 at 28d are shown in Figure 6.

![Figure 6: The absorbing reflectivity of GPE1–GPE3](image)

It can be seen that in the frequency range of 2–18 GHz, GPE1 has a minimum reflectivity of $-14.8$ dB at 2.22 GHz and the effective bandwidth smaller than $-10$ dB is 4.45 GHz. In contrast, GPE2 has a minimum reflectivity of $-18.8$ dB at 2.39 GHz and the effective bandwidth smaller than $-10$ dB is 15.3 GHz, while GPE3 has a minimum reflectivity of $-16.4$ dB at 2.17 GHz and the effective bandwidth smaller than $-10$ dB is 14.3 GHz. In the frequency range of 2–18 GHz, the reflectivity of the three-layered absorbing board is all below $-7$ dB, which realizes full coverage of the test frequency and achieves the goal of wide-band wave absorption.

Compared with the two-layered absorbing board doped with the same filler, the absorbing performance of the three-layered absorbing board is significantly enhanced. Its minimum reflectivity is reduced by about 28.6% and the effective bandwidth smaller than $-10$ dB is increased considerably. The enhancement mechanism of the absorbing performance of the three-layered absorbing board is due to the fact that the matching layer is added in the structure design, which enables the electromagnetic waves incident on the surface of the material to be introduced without much reflection on the surface. It can be seen from Figure 6 that compared with GPE1, the minimum reflectivity of GPE3 is reduced by about 15% and the effective bandwidth smaller than $-10$ dB is increased by about 3.2 times, which indicates that NGPs have obvious absorbing performance. Compared with GPE1, the minimum re-
reflectivity of GPE2 is reduced by 21.3% and the effective bandwidth smaller than −10 dB is increased by 3.4 times. This trend reveals that CF has obvious absorbing performance. Compared with GPE1, the doping amount of absorbing fillers of GPE2 and GPE3 has both changed, but the minimum reflectivity of GPE2 is slightly lower than that of GPE3, which may result from the doping amount of the NGPs that fails to reach the threshold of absorption and percolation. Plenty of literature shows that the conductive percolation threshold of the CF is about 1 wt% of its doping amount, so the change of the doping amount of NGPs does not have a significant effect on the absorbing performance as the change of doping amount of CF does.

4 Conclusion

Low content of NGPs can significantly improve the compressive strength of cement slurry. Compared with ordinary cement slurry, the compressive strength of cement slurry mixed with 0.05% NGPs at 7d and 28d increases by 32.3% and 33.5%, respectively. The unique planar fold structure of NGPs is the main reason for the improvement of the mechanical properties of the cement slurry. When wave-absorbing fillers such as NGPs and nano-Ni are added, the resistivity of the absorbing layer and the absorbing & reflecting layer can be reduced effectively, and the resistivity of the three-layered cement-based wave-absorbing board changes in the order of $10^2$~$10^3$ Ω·cm. It is closer to the absorbing & reflecting layer in magnitude, approximately 1.25–1.4 times that of the absorbing & reflecting layer.

NGPs have good wave-absorbing performance, and the change of its content has an obvious impact on the wave-absorbing performance. Compared with the absorbing board doped with 0.025% NGPs, the minimum reflectivity of the absorbing board doped with 0.05% NGPs is reduced by about 15%, and the effective bandwidth less than −10 dB is increased by 2.2 times or so. Nano-Si$_3$N$_4$ has good wave transmission performance. In the frequency range of 2–18 GHz, the matching layer of cement slurry doped with 2% Nano-Si$_3$N$_4$ has a minimum reflectivity of −2.11 dB at 2.25 GHz, and an effective bandwidth of 8.97 GHz higher than −1 dB.

The absorption performance of the three-layered absorbing board is obviously better than that of the one-layered and two-layered absorbing board. The design of the matching layer doped with nano-Si$_3$N$_4$ is the main mechanism to improve its absorption performance. The three-layered cement-based wave absorbing board prepared in this study has excellent absorption performance and a wide frequency band, and has potential applications in the electromagnetic wave shielding and absorption of important civil buildings and military facilities.

Acknowledgement: This work was funded by the National Natural Science Foundation of China (No. 51908285).

References

[1] Li, K., C. Wang, H. Li, X. Li, H. Ouyang, and J. Wei. Effect of chemical vapor deposition treatment of carbon fibers on the reflectivity of carbon fiber-reinforced cement-based composites. Composites Science and Technology, Vol. 68, No. 5, 2008, pp. 1105–1114.
[2] Sun, Y. F., T. S. Zhou, P. W. Gao, M. Chen, H. W. Liu, and Y. Xun. Microstructure and microwave absorbing properties of cement based material reinforced with reduced graphene oxide and nanoparticles. Strength of Materials, No. 4, 2019, pp. 115–123.
[3] Li, B., Y. Duan, and S. Liu. The electromagnetic characteristics of fly ash and absorbing properties of cement-based composites using fly ash as cement replacement. Construction & Building Materials, Vol. 27, No. 1, 2012, pp. 184–188.
[4] Guan, H., S. Liu, Y. Duan, and J. Cheng. Cement based electromagnetic shielding and absorbing building materials. Cement and Concrete Composites, Vol. 28, No. 5, 2006, pp. 468–474.
[5] Typek, J., N. Guskos, G. Zolnierkiewicz, D. Sibera, and U. Narkiewicz. Magnetometric study of ZnO/CoO nanocomposites. Reviews on Advanced Materials Science, Vol. 57, No. 1, 2018, pp. 11–25.
[6] Parihar, V., M. Raja, and R. Paulose. A brief review of structural, electrical and electrochemical properties of zinc oxide nanoparticles. Reviews on Advanced Materials Science, Vol. 53, No. 2, 2018, pp. 119–130.
[7] Bobylev, S. V. and A. G. Sheinerman. Effect of crack bridging on the toughening of ceramic/graphene composites. Reviews on Advanced Materials Science, Vol. 57, No. 1, 2018, pp. 54–62.
[8] Glukharev, A. G., and V. G. Konakov. Synthesis and properties of zirconia-graphene composite ceramics: A brief review. Reviews on Advanced Materials Science, Vol. 56, No. 1, 2018, pp. 124–138.
[9] Sun, Y., M. Chen, P. Gao, T. Zhou, H. Liu, and Y. Xun. Microstructure and microwave absorbing properties of reduced graphene oxide/Ni/multi-walled carbon nanotubes/Fe$_3$O$_4$ filled monolayer cement-based absorber. Advances in Mechanical Engineering, Vol. 11, No. 1, 2019, pp. 1–11.
[10] Silva, R. A., G. Paulo de Castro, M. Sergio da Luz, et al. Enhanced properties of cement mortars with multilayer graphene nanoparticles. Construction & Building Materials, Vol. 149, 2017, pp. 378–385.
[11] Sun, S., B. Han, S. Jiang, X. Yu, Y. Wang, H. Li, and J. Ou. Nano graphene platelets-enabled piezoresistive cementitious composites for structural health monitoring. Construction & Building Materials, Vol. 136, 2017, pp. 314–328.
[12] Huang, S. Multifunctional graphene nanoplatelets reinforced cementitious composites. Master thesis. National University of Singapore, Singapore, 2012.
[13] Chen, J., D. Zhao, H. Ge, and J. Wang. Graphene oxide-deposited carbon fiber/cement composites for electromagnetic interference shielding application. *Construction & Building Materials*, Vol. 84, 2015, pp. 66–72.

[14] Jiang, L., S. Bai, J. Ming, S. Jiang, and D. Tao. Electrical conductivity of the graphene/cement composites. *Journal of Harbin Engineering University*, Vol. 39, No. 3, 2018, pp. 601–606.

[15] Zhang, X. and W. Sun. Preparation and microwave absorbing properties of three layered cement-based composites. *Sciverse Science Direct Procedia Engineering*, Vol. 27, 2012, pp. 348–356.

[16] Saafi, M., L. Tang, T. Fung, M. Rahman, and J. Liggat. Enhanced properties of graphene/fly ash geopolymeric composite cement. *Cement and Concrete Research*, Vol. 67, 2015, pp. 292–299.

[17] Chen, M., P. Gao, F. Geng, L. Zhang, and H. Liu. Mechanical and smart properties of carbon fiber and graphite conductive concrete for internal damage monitoring of structure. *Construction & Building Materials*, Vol. 142, 2017, pp. 320–327.

[18] Sun, Y., P. Gao, H. Peng, *et al.* Electromagnetic wave absorbing and mechanical properties of cement-based composite panel with different nanomaterials. *Advanced Composites Letters*, Vol. 26, No. 1, 2017, pp. 6–11.

[19] Pierre, R. and C. Maecel. Composition of reactive powder concretes. *Cement and Concrete Research*, Vol. 25, No. 7, 1995, pp. 1501–1511.

[20] Min, C. *Study on Electrothermal and Sensitive Properties of Multiphase Conductive Cement-based Materials*. Doctoral dissertation. Nanjing University of Aeronautics and Astronautics, China, 2018.

[21] Guo, Z. Q. *Study on Electromagnetic Wave Absorbing Properties of Multi-walled Carbon Nanotube/Cement Composites*. Doctoral dissertation. Dalian University of Technology, China, 2013.