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Cement-based composites endowed with novel functions through controlling interface microstructure from $Fe_3O_4@SiO_2$ nanoparticles

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ABSTRACT

In this paper, $Fe_3O_4@SiO_2$ nanoparticles (NPs) were introduced in the surface layer of cement-based materials derived by magnetic field to create a wave adsorbing layer. The cement-based materials treated with $Fe_3O_4@SiO_2$ NPs revealed superior microwave-absorption property comparing with the samples treated with pure Fe_3O_4 NPs. Because of a SiO_2 coating on Fe_3O_4 NPs, water absorption rates of cement mortars treated with $Fe_3O_4@SiO_2$ NPs have reduced by 45.3%. In addition, the SiO_2 coating on Fe_3O_4 NPs bonded wave absorbing materials on the surface of cement-based composites by forming a mass of SiO_2 and calcium silicate hydrate (C-S-H) gels. The $Fe_3O_4@SiO_2$ NPs can be considered as an ideal wave absorption surface-treatment agent for cement-based composites.

1. Introduction

Extensive electronic devices have been applied as essential tools in our daily lives, such as mobile phones, computers and other electronic products. However, the influences of the electromagnetic interference (EMI) and the microwave pollution have been increasingly investigated in recent years [1,2] because the EMI shielding building can protect human health [3–7] and also protect military stealth.

Cement is currently the most widely used building material in engineering constructions, however, the electrical conductivity and EMI shielding properties are not as good as we expected with exposure to extreme cases if there were no additional treatment. It is a simple and practical method to increase EMI shielding effectiveness of the cement based materials by introducing EMI shielding fillers [8,9]. The most widely used fillers are carbon, metal powders, and ferrites [10–12]. Ferrite is a common electromagnetic wave absorber owing to its excellent absorption performance. Some researchers have studied the electromagnetic absorption properties of cement-based materials employing ferrite [13]. Zhang and sun have designed double-layer cementitious composites using Mn–Zn ferrite as microwave absorbers [14].

Fe_3O_4 has high magnetic performance, high saturation magnetization, and low cost, thus it has been widely studied for microwave absorption absorbers [15,16]. However, Fe_3O_4 material has bad thermal stability which may lead to the loss of single domain pole or special nature of magnetic materials, thus the bad property restricts their wide application. Meanwhile, Fe_3O_4 is prone to be oxidized in humid conditions. In order to improve the microwave-absorption and oxidize-resistance properties of Fe_3O_4-based magnetic materials, some methods involving a protective layer route with non-magnetic substances including SiO_2, TiO_2, Al_2O_3 have been developed [17]. Among these materials, SiO_2 acts as an ideal material to tailor the surface properties, while basically maintaining the morphology and physical property of the core nanomaterials [18]. Furthermore, researchers have reported that nano-SiO_2 can effectively increase the durability [19], mechanical properties [20], and hydration process [21] of cement-based material to a great extent. Hou and his co-workers have reported that colloidal nano-SiO_2 and its precursor acted as surface treatment agents to make a dense surface structure of cement-based material for its resistance to the impacts of environment [22]. They also reported the pozzolanic reactivity of nano-SiO_2 on cement-based materials.

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Calcium silicate hydrate (C-S-H) gel was formed through its reaction with calcium hydroxide of cement by nano-SiO_2 introducing into cement-based materials [23]. Such alternatives decreased the pore size and increased the amount of C—S—H gel. Thus, nano-SiO_2 made cement-based materials denser and more durable.

To enhance the EMI shielding performance, microwave absorbers were introduced in cement based materials through different ways, including mixing with cement matrix or spraying/brushing coatings on the surfaces of cement materials. For surface coating spraying, the durability of the coating is the biggest challenge if the coating materials were not effectively treated. Commercial microwave absorbers containing EMI shielding additives to guarantee the perdurability, but sometimes a detrimental effect over wave absorptive performance is consequently caused. Meanwhile, the dispersion of microwave absorption absorbers, especially nanomaterials, is considered as an important parameter whatever introduction way (mixing, spraying, brushing, etc.) Therefore, improving the durability, wave absorptive performance and dispersion for surface treatment with microwave absorption absorbers is a huge challenge. In this work, Fe_3O_4@SiO_2 nanoparticles (NPs) were studied to act as microwave absorber and surface treatment agent on cement-based materials to improve wave absorption properties and to reduce water absorption rate. Fe_3O_4@SiO_2 NPs were introduced into the cement-based materials by magnetic field owing to the excellent magnetic property of Fe_3O_4. A SiO_2 coating on Fe_3O_4 NPs could not only bond wave absorbing materials on the surface of cement-based composites, but also make the surface dense decreasing water absorption rates. The magnetic property, and dispersion of Fe_3O_4@SiO_2 NPs were studied, which were advantaged to permeate into cement-based materials in magnetic field. The test for wave-absorbing property and water absorption rate of treated cement-based composites were carried out to investigate the performance and bonding effect.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonia ($NH_3 \cdot H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and tetraethyl orthosilicate (TEOS) was purchased from China National Pharmaceutical Group Corporation (Sinopharm). Deionized water, which was supplied by a Millipore system (18.2 MΩ cm $^{-1}$), was used in the whole preparation process. Type I ordinary Portland cement (OPC) was used following the Chinese standard-GB 175-2007. The physiochemical properties of the cement are listed in Table 1.

2.2. Methods

2.2.1. Synthesis of Fe_3O_4 and Fe_3O_4@SiO_2 microwave absorbers

Fe_3O_4 NPs were synthesized by coprecipitating Fe (II) and Fe (III) chlorides in aqueous solution with the existence of NH_4OH as an equation below [24].

$$Fe^{2+}\,(aq) + 2Fe^{3+}\,(aq) + 8NH_4OH\,(aq) \longrightarrow Fe_3O_4\,(ppt) + 8NH^{4+}\,(aq) + 4H_2O \quad (1)$$

The detail prepared process of iron oxide was as follows: 4.97 g of iron (II) chlorides and 13.5 g of iron (III) chlorides were dissolved in 200 mL of water at 28 °C and stirred for 20 min. The pH value of obtained solution is adjusted to 9 by the addition of 35% ammonia solution. The black precipitates were washed with ethanol several times and collected from the solution by magnetic separation. The precipitates were dried under vacuum at 50 °C for 12 h.

The coating of silica shell was carried out by the Stöber method. The Fe_3O_4NPs (0.1 g) were dispersed into water (100 mL) in an ultrasonic bath at 25 °C. Subsequently, 10 mL of $NH_3 \cdot H_2O$ was added into the obtained solution. Ethanol (100 mL) and TEOS (3 mL) mixture was dropped into the above-obtained solution under the ultrasonic bath of 30 °C for 3 h. After the reaction, the solution was concentrated and stocked for the next step.

2.2.2. Cement-based materials preparation, curing and surface treatment

Mortar samples with water-to-cement ratio of 0.6 and a cement-to sand ratio of 1/3 were prepared in this system. The water/cement ratio was 0.6. Cement and sand were mixed for eight minutes by adding water before molded in 180 mm × 180 mm × 20 mm rectangular molds, and then the samples were covered with plastic sheet. The samples were demolded after 24 h and put into curing for 28 days until test. The curing condition is at 20 ± 2 °C and >90% relative humidity. The sample was obtained for the measurement of wave absorption properties. Rectangular molds (4 cm × 4 cm × 16 cm) were used to obtain the samples for the measurement of water absorption rate. The obtained samples with size of 4 × 4 × 2 cm^3 were cured for 28 days until test.

Fe_3O_4 and Fe_3O_4@SiO_2 NPs were dispersed in water under the same molar concentration. The cement-based materials were then dried at 60 °C for 24 h before being sprayed with Fe_3O_4 and

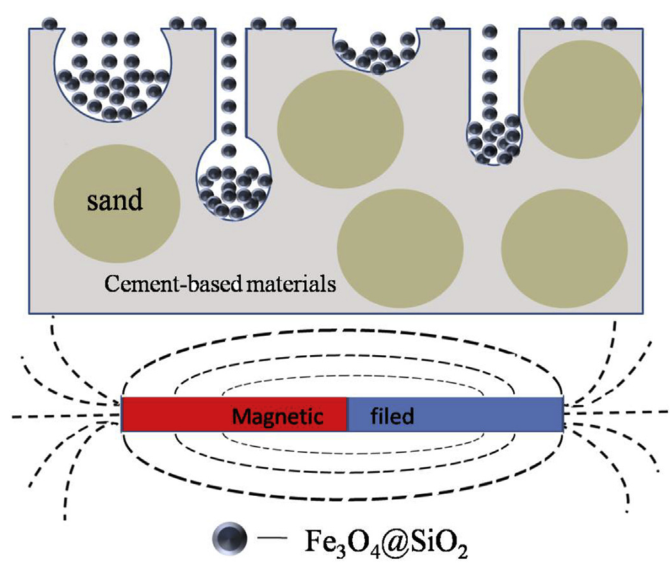

Fig. 1. Schematic illustration of surface treatment process of Fe3O4@SiO2 NPs under magnetic field.

Table 1
Physiochemical properties of cement.

SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	LOI	Total	Density g/cm^3	Fineness m^2/kg	28-day compressive strength, MPa
21./1	4.7	3.5	3.3	62.9	2.8	1.1	99.4	3.1	390	50.1