Research Article

Effect of Delaminated MXene (Ti_3C_2) on the Performance of Cement Paste

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Delaminated MXene was incorporated into cement to improve the properties of cement composites, and its effects on the hydration process, microstructures, and mechanical properties were investigated, respectively. The investigation results showed that delaminated MXene was well-dispersed in the cement matrix and significantly reinforced the compressive strength of cement, especially when the addition is 0.01 wt%. Meanwhile, the total hydration heat of cement hydration and the quantity of hydration products were increased with the addition of delaminated MXene. In addition, the formation of HD C-S-H gel was promoted, and the microstructure of hydrated cement became more compact.

1. Introduction

Cement-based materials have been widely used in the world, since its first appearance in 1824, for the sake of its excellent properties and low price. However, due to its low flexural strength and complex service environment, performance needs to be further improved. In recent years, nanomaterials have been widely applied in various fields due to their unique properties: small size effect, quantum size effect, surface and interface effect, macroscopic quantum tunneling effect, and dielectric confinement effect [1–3]. With the improvement of nanotechnology and the decrease of the price, the application of nanomaterials in cement-based materials has been realized. Recently, the application of nanomaterials in cement has gradually attracted a great deal of attention. Researchers found that adding the appropriate dosage of nanomaterials can significantly improve the performance of cement-based materials. Barbhuiya et al. [4] found that the microstructure of cement-based material was becoming more compact with the addition of Al_2O_3 . The shift in water-associated band in cement-based material has lower frequency mostly with 4% nano- Al_2O_3 addition. Meng et al.'s [5] experimental results show that when cement was substituted by nano- TiO_2 , the strength of cement mortar at early age increased a lot. But the fluidity and strength

decrease significantly in later ages. The main reason for the early strength increase may be the change and decrease of the nuclear function index, not the increase of hydration products. Lee et al. [6] used nano- SiO_2 and CNTs to improve the early mechanical properties of cement-based materials. At the same time, the addition of SiO_2 could react with hydration product $\text{Ca}(\text{OH})_2$ to generate more C-S-H. Wang et al. [7] present an experimental investigation on the effect of nano- SiO_2 on the compressive strength, shrinkage, and early cracking sensitivity of lightweight aggregate concrete (LWAC). It can be found that adding 3% SiO_2 significantly increased the compressive strength while having no effect on the long-term shrinkage of lightweight aggregate concrete. With the increase of SiO_2 dosage from 1% to 3%, the total cracking area was decreased, and the interfacial transition zone (ITZ) between lightweight aggregate and paste was enhanced.

As a kind of nanomaterials, two-dimensional nanomaterials are thin films or multilayered films or layered compounds with nanoscale thickness. Typical 2D nanomaterials include graphene oxide (GO), LDHs, and layered silicate. Shang et al. [8] found that GO addition significantly reduced the fluidity of cement paste. Li et al. [9] found that with the addition of GO, the dormant period of cement hydration was shortened and greatly accelerated the hydration rate of

C₃A, which increased the electrical resistivity of cement paste due to the nucleation effect of GO. Li et al. [10] proved that addition of LiAl-LDHs can significantly improve the compressive strength at early age and shorten the setting time. Recently, a new 2D material, known as MXene, has attracted a great deal of attention. Taloub et al. [11] found that the mechanical properties of PIPD fiber could be improved by MXene. The previous research results of our research team showed that MXene can improve the early age hydration of cement [12]. The results showed that adding 0.04% MXene can significantly improve early strength of cement-based material. The main role of MXene in the cement hydration process was to promote the messy ettringite becoming regular distribution at a node and form a network connection structure in the crystal growth process. These MXene have a multilayered structure, and a multilayered structure will not be able to give full play to the improvement of mechanical properties. Delaminated MXene, as a family of transition metal carbide/nitride two-dimensional crystal materials with a graphite-like structure, is expected to play a better role. Delaminated MXene has a less layered structure and higher specific area. It has important application value in energy storage electronics and lubrication [13–15]. On the one hand, it could fill in the gaps in the cement particles more effectively. On the other hand, the delaminated MXene with high surface energy plays the role of crystal nucleus, which may promote the cement hydration and improve the compactness of cement paste, while there was little research of delaminated MXene on the cement-based materials. Here, we demonstrated the potential application of delaminated MXene in cement.

In this study, the effects of delaminated MXene on the properties of cement-based materials were studied. The delaminated MXene composites demonstrated significant improvement in mechanical properties, and the optimum dosage of delaminated MXene was obtained. Hydration and microstructural analysis were performed, and they provided in-depth understanding on the mechanism of mechanical reinforcement.

2. Materials and Methods

2.1. Preparation of the Sample. Chemical composition (by weight) of P-I 42.5 Portland cement (provided by the Qufu United Cement Company, China) was shown in Table 1. For the preparation of ternary layered ceramic material Ti₃AlC₂ (MAX phase), Ti powder, Al powder, and C powder were mixed together and were sintered for 2 h in a tubular furnace in Argon atmosphere at 1400°C. And then, Ti₃AlC₂ was etched with NaF and HCl mixed solution to get MXene Ti₃C₂. Finally, the delaminated MXene was obtained according to the reference [16]. The thickness of delaminated MXene is 2–10 nm; the length and width of delaminated MXene are 1–20 μm; the specific surface area is 47.8 m²/g; and the molar ratio of Ti to C is about 3:2. The microstructure of delaminated MXene was shown in Figure 1. In this experiment, the dosage of delaminated MXene was set to 0.00 wt%, 0.01 wt%, 0.03 wt%, 0.05 wt%, and 0.07 wt%, respectively (abbreviated as CM1, CM2, CM3, CM4, and

CM5). Delaminated MXene was ultrasonically rinsed with deionized water for 10 min. The pastes were prepared with the same water to the binder ratio of 0.35 [17]. The cement was added to the water and stirred at low speed for 2 min; then, the mixture was stopped for 15 s and then mixed at high speed for 2 min in a cement paste mixer. The paste was put into the 10 mm × 10 mm × 10 mm molds for vibration [12]. The samples were cured in moist air at 20 ± 1°C with more than 90% relative humidity for 1 d, followed by demolding. After that, the samples were cured in saturated lime solution till the age required.

2.2. Characterization of the Sample

2.2.1. Compressive Strength. The compressive strength of cement-based materials with and without delaminated MXene at 1, 3, 7, and 28 curing ages was tested based on GB/T7897-2008 by using a WDW-20 hydraulic test machine (Jinan Ruijin Experimental Instrument Co., China). The results were presented using the average of three samples, which can provide an indication of the effect of delaminated MXene on the mechanical properties of pastes.

2.2.2. XRD Test. Powder XRD patterns were collected for the hardened pastes at 28-days using an X-ray diffractometer with an incident beam of Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) for a 2θ scanning range of 5°–80°. Samples were dried at 40°C for 24 h. After drying treatment, the samples were crushed and grounded to powder for the XRD test. The XRD-Rietveld method was adopted for the quantitative phase analysis of hydrated cement pastes.

2.2.3. Hydration Heat. The heat of hydration of cement pastes with and without delaminated MXene was determined by the TAM Air calorimeter (TA Instruments Co., USA). The water to cement ratio (w/c) was 0.35. The effect of delaminated MXene on the early hydration process of cement was observed by measuring the hydration process at 20°C for 72 hours.

2.2.4. SEM. The scanning electron microscope (FESEM, Merlin Compact, Carl Zeiss NTS, Acceleration voltage = 15 kV) was used to analyze the morphology of the cement-based material. Small fractured samples at each hydration age were soaked in anhydrous ethanol to stop hydration and dried at 40°C for 24 h. The fractured surfaces were then coated and placed under vacuum prior to imaging.

2.2.5. Nanoindentation. The nanoindentation was performed in an Hysitron TI-950 instrument. Specimens were cut and embedded in polyacrylamide. The semiautomatic polisher was used to polish the samples. Then, the dried surfaces were grinded in a sequence of SiC papers (grit #500, #1000, and #4000) and polished in a cloth sequentially with 9 μm and 3 μm diamond sprays. Finally, the specimen surfaces were cleaned by washing in alcohol and ultrasonic bathing. The operating conditions of the instrument were as following: the standard Berkovich diamond indenter was used. The distance between the indentation lattices was 10 μm, and the large sample data was obtained to represent the properties

TABLE 1: Chemical composition of cement (wt%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	f-CaO	Loss
% (by weight)	21.88	4.49	3.45	64.65	2.36	2.44	0.51	0.90	1.31

FIGURE 1: SEM image of delaminated MXene.

of the whole material by using the test lattice of 15×15 , using the 5-2-5 (s) loading mode. The effect of delaminated MXene on the hydration of cement can be judged through observing the amount of LD C-S-H and HD C-S-H in the sample.

2.2.6. Differential Thermal Analysis Test. Differential thermal analysis (DTA) was carried out under Ar atmosphere using the HCT-3 instrument at $10^\circ\text{C}/\text{min}$ up to 900°C .

3. Results and Discussion

3.1. Compressive Strength. Compressive strength values of reference cement and cement containing delaminated MXene at different ages were given in Figure 2. Each reported compressive strength value was derived from the average of three duplicate specimens. As the curing age extended, the compressive strength increased correspondingly because of the ongoing hydration reaction of the cement. It was also found that by adding delaminated MXene, the compressive strength of cement was increased. When 0.01 wt% delaminated MXene was added, the compressive strength was increased by 20.2%, 45.2%, 32.6%, and 27.8% compared with the control sample at 1, 3, 7, and 28 days, respectively. While when the dosage of delaminated MXene content increased from 0.01 wt% to 0.07 wt%, the compressive strength was adversely decreased. The compressive strength value of the cement with 0.07 wt% delaminated MXene increased by 2.4%, 10.7%, 12.4%, and 8.0% compared with the reference sample at 1, 3, 7, and 28 days, respectively. It was indicated that a lower dosage of delaminated MXene was more effective for the compressive strength. In order to explore the strength gain characteristics of the cement paste with delaminated MXene, more hydration characteristics of cement paste were further evaluated.

3.2. X-Ray Diffraction. The influence of delaminated MXene on the cement hydration products after hydration for 1 day was studied by XRD when the dosages of delaminated

FIGURE 2: The compressive strength of paste with different contents of delaminated MXene.

MXene were 0 wt%, 0.01 wt%, 0.03 wt%, 0.05 wt%, and 0.07 wt%, and the results are shown in Figure 3. Figure 3 shows the diffraction peaks of Aft, $\text{Ca}(\text{OH})_2$, and C-S-H that are the hydrated as well as unhydrated C_3S and C_2S of cement pastes. It can be seen from Figure 3 that the addition of delaminated MXene has no effect on the type of cement hydration products. The intensities of $\text{Ca}(\text{OH})_2$ peaks increased slightly after admixing delaminated MXene in the cement paste. The result showed that there were about 40.3%, 30.4%, 13.2%, and 6.3% increments of the magnitude of the intensity of $\text{Ca}(\text{OH})_2$ when the dosages of delaminated MXene are 0.01 wt%, 0.03 wt%, 0.05 wt%, and 0.07 wt%, respectively. When the content of delaminated MXene was 0.01 wt%, the peak of $\text{Ca}(\text{OH})_2$ was the highest. The result indicated that the addition of delaminated MXene can promote the hydration process and thus improve the assembly of $\text{Ca}(\text{OH})$ obtained during hydration. This was consistent

FIGURE 3: X-ray diffraction pattern of cement hydration products with different contents of delaminated MXene.

FIGURE 4: TG-DTA curves of cement paste with different contents of delaminated MXene at 1 d curing age.

with the results of Ma et al. [18] and Zhang et al. [19] researches; some kinds of nanomaterials promoted hydration of cement but had no effect on hydration products. In these cases, the main roles of nanomaterials in cement-based materials were filling and nucleation.

3.3. DTA-TG Analysis. In order to detect possible changes in the formation of hydration products, cement formulations were analyzed on cement paste with different contents of delaminated MXene at 1 d curing age, while DTA-TG curves of 1 day hydrated blends are presented in Figure 4. It can be seen that DTA-TG mainly includes three endothermic peaks around 100°C, 460°C, and 680°C. Compared with the DTA-TG atlas, it can be seen that the endothermic peak around

100°C is due to the evaporation of the free water and the dehydration of C-S-H and AFt; the second one located at 460°C is attributed to Ca(OH)_2 ; and the third one at 680°C is caused by the decomposition of CaCO_3 which is due to the carbonization of CH in the process of preparing the samples. So, the following equation [20] can be used to calculate Ca(OH)_2 content:

$$M = \left(\frac{m_1}{18} + \frac{m_2}{44} \right) \times 74. \quad (1)$$

In the formula, M is the mass percentage of Ca(OH)_2 in the sample, m_1 is the weight loss caused by the dehydration of Ca(OH)_2 , m_2 is the weight loss caused by the dehydration of CaCO_3 , and 18, 44, and 74 mean the molecular weights of H_2O , CO_2 , and Ca(OH)_2 , respectively.

It can be seen that when 0.00 wt%, 0.01 wt%, and 0.07 wt% delaminated MXene were added, the weight loss rates of Ca(OH)_2 are 1.35%, 1.49%, and 1.36%, and the weight loss rates of CaCO_3 are 1.73%, 1.19%, and 1.62%, respectively. Thus, the total production of Ca(OH)_2 is 7.96%, 8.13%, and 8.04%. It was indicated that the addition of an appropriate amount of delaminated MXene promotes the generation of Ca(OH)_2 .

3.4. Hydration Heat. The influences of delaminated MXene on the hydration of cement at the early age within 72 h were investigated by the heat calorimetry technique, and the results are shown in Figures 5(a) and 5(b). As shown in Figure 5(a), the addition of delaminated MXene changed the rate of heat release. It was clearly demonstrated that the

FIGURE 5: (a) Hydration heat flow of cement-based materials with different dosages of delaminated MXene. (b) Total hydration heat with different dosages of delaminated MXene.

more the delaminated MXene, the later the hydration exothermic heat appears before 10 h. At 20~40 h, it can be found that when the dosage of delaminated MXene increases, the cement hydration rate increases gradually. It was inferred that delaminated MXene inhibited the early hydration process, however accelerated the later hydration process. This is similar to the result of Yin et al. [12]. This may be related to the unique layered structure of MXene. The water was absorbed by gaps between layers of MXene, leading to a reduction of water that can be involved in the hydration process at the first few hours. After about 10-13 h, the hydration exothermic heat with MXene was faster than the control sample, which may be partly attributed to the release of water absorbed in the MXene layer, causing a continuous hydration process. Through Figure 5(b), it can be found that the addition of delaminated MXene increased the total heat release rate of cement hydration within 72 h, meaning that the hydration of cement was accelerated by delaminated MXene. The total hydration heat reaches the highest when 0.01 wt% delaminated MXene is added.

3.5. Morphology. SEM was carried out to study the influence of delaminated MXene on the microstructure of cement. The morphology of different cement paste samples CM1 (Figures 6(a) and 6(b)), CM2 (Figures 6(c) and 6(d)), and CM5 (Figures 6(e) and 6(f)) at 1 d and 7 d was shown in Figure 6. As can be seen, the main hydration products of cement hydration are C-S-H gel, ettringite, and $\text{Ca}(\text{OH})_2$; the influence of the microstructure of cement-based materials is also different due to the different dosages of delaminated MXene. From Figure 6(a), it can be seen that without delaminated MXene, the hydration products are less, and the microstructure of cement is looser. It also can be found that there is significant increase of the hydration products, and the microstructure of hydrated samples is denser with the 0.01 wt% delaminated MXene from Figures 6(b) and 6(c). It was indicated that addition of delaminated MXene

promotes the formation of hydration products. The microstructure of CM2 and CM5 was more compact than the CM1 at 1 d. On the one hand, it was considered that the nucleation effect of nanomaterials accelerated the early stage of hydration of cement. On the other hand, it was inferred that delaminated MXene filled the pores in the cement-based materials, which causes the structure to become more compact. However, with the dosage increase of delaminated MXene, CM5 presents looser microstructure than that of CM2. The reason maybe that delaminated MXene could accelerate the hydration rate of cement, and more hydration products are produced in a short period of time. But too much hydration products formed in short time will be overlapped together disorderly, which makes the CM5 structure loose. This was consistent with the test results for compressive strength in Section 3.1.

3.6. Nanoindentation. Different materials have different modulus of elasticity; nanoindentation can be used to detect the modulus of elasticity of different positions in cement-based materials and as a judgment to correspond the substances in cement-based materials. According to Constantinides and Ulm [21] and Velez et al. [22] research, it can be divided into four sections of 0~13 GPa, 13~26 GPa, 26~39 GPa, and >39 GPa according to the elastic modulus, which corresponds to micropore, LD C-S-H, HD C-S-H, and $\text{Ca}(\text{OH})_2$, respectively. The micromechanical properties of composites of Portland cement were listed in Table 2. The part of 50 GPa~100 GPa can be regarded as the mixture of unhydrated cement clinker and hydration product. The elastic modulus of cement clinker was generally greater than 100 GPa. In order to investigate the effect of MXene on the hydration products and microstructure of cement-based materials, the elastic modulus of cement-based materials with 0.00 wt%, 0.01 wt%, and 0.07 wt% was studied by nanoindentation. The modulus mapping was clearly distinguished in Figure 7; the gray part of the picture was unhydrated

FIGURE 6: SEM images of samples CM1 (a, b), CM2 (c, d), and CM5 (e, f) hydrated for 1 d and 7 d.

TABLE 2: Micromechanical properties of composites of Portland cement [22].

	C_3S	C_2S	C_3A	C_4AF	Alite	Belite
E (GPa)	135	130	145	125	125	127
H (GPa)	8.7	8	10.8	9.5	9.2	8.8

cement clinker; the outside of cement clinker was covered by materials with different elastic moduli; and the value of elastic modulus decreases in turn. It was seen from Figures 7(a)–7(c) that when 0.01 wt% of delaminated MXene was added, the gray part (unhydrated cement clinker) in the diagram was the least. As can be seen from Table 3, the proportions of HD C-S-H in the three specimens are 50.4%, 56.9%, and

54.6%, respectively. The experimental results demonstrated that the addition of MXene not only promoted the formation of cement hydration products but also promoted the formation of HD C-S-H gel in cement hydration products. The CM2 sample with 0.01 wt% MXene dosage exhibited most formation of hydrated product HD C-S-H gel, which is consistent with the mechanical property.

4. Conclusions

The effect of delaminated MXene on the properties of cement was investigated in this research. Based on the results of compressive strength testing, SEM, XRD, hydration heat, and nanoindentation, the following conclusions were drawn:

FIGURE 7: (a) Contour map of indentation on modulus in GPa (CM1). (b) Contour map of indentation on modulus in GPa (CM2). (c) Contour map of indentation on modulus in GPa (CM5).

TABLE 3: Interval range of hydration products with different amounts of MXene (%).

	Micropore	LD C-S-H	HD C-S-H	Total
CM1	7.8	41.8	50.4	100
CM2	4.6	38.5	56.9	100
CM5	0.9	44.5	54.6	100

C-S-H was promoted with the addition of delaminated MXene

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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- (1) The compressive strength of cement with delaminated MXene was improved. The optimal dosage of delaminated MXene was 0.01 wt%
- (2) The early hydration of cement was inhibited by delaminated MXene. However, the rate of hydration reaction became faster with delaminated MXene after 10–13 h. Meanwhile, the total hydration heat of cement hydration within 72 h was increased with the addition of delaminated MXene
- (3) There was no new hydration phase formed when delaminated MXene was added into cement. The amount of hydration products was increased with the addition of delaminated MXene, which made the structure of hydrated cement pastes more compact. Besides, it was clear that the formation of HD

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