

## Research Article

# Effect of MXene (Nano-Ti<sub>3</sub>C<sub>2</sub>) on Early-Age Hydration of Cement Paste

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As a new two-dimensional material, MXene (nano-Ti<sub>3</sub>C<sub>2</sub>) has been widely applied in many fields, especially for reinforced composite materials. In this paper, mechanical testing, X-ray diffraction (XRD), hydration heat, scanning electron microscope (SEM), and EDS analysis were used to analyze the impact of MXene on cement hydration properties. The obtained results revealed that (a) MXene could greatly improve the early compressive strength of cement paste with 0.04 wt% concentration, (b) the phase type of early-age hydration products has not been changed after the addition of MXene, (c) hydration exothermic rate within 72 h has small difference at different amount of MXene, and (d) morphologies of hydration products were varied with the dosage of MXene, a lot of tufted ettringites appeared in 3 d hydration products when the content of MXene was 0.04 wt%, which will have a positive effect on improving the early mechanical properties of cement paste. MXene has inhibited the Portland cement hydration process; the main role of MXene in the cement hydration process is to promote the messy ettringite becoming regular distribution at a node and form network connection structure in the crystals growth process, making the mechanics performance of cement paste significantly improved.

## 1. Introduction

As we know, nanomaterials yield with small size effects, surface and interface effects, quantum tunneling effects, and quantum size effects. These effects lead to nanomaterials having physical and chemical properties of a special kind [1]. In recent years, with the development of preparation technology of nanomaterials [2], a large-scale preparation of nanomaterials has become possible. Nowadays, cement-based materials are the most common and widely used materials of the world in civil engineering; most of the hydration products have nanostructure [3]. Study has shown that more than 70% hydration products of cement-based material are C-S-H ( $x\text{CaO}\cdot\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ) gel with nanostructure, which plays an important role on the strength of hardened paste [4]. In the hardened cement paste, nanoscale chemical bonding exists among C-S-H gel, and the main contribution of strength is nanometer size effect [5]. Therefore, these of

advanced nanomaterials to modify cement-based materials regulates cement paste microstructure, which not only increases physical and mechanical properties of cement-based materials, but also broadens its range of applications. In short, the nanomodification is an important research field. So, the nanomaterials can be employed to improve the performance of cement-based materials (physical and mechanical properties, durability, etc.). In recent years, some nanomaterials, such as nanosilica, nanoalumina, titanium dioxide, calcium carbonate, iron oxide nanoparticles, nano-clay, carbon nanotubes, and graphene oxide, have been used to modify cement-based materials [6–12], these nanomaterials can improve the mechanical properties, durability and reduce the porosity of cement-based materials.

As a new two-dimensional (2D) crystalline nanomaterial, MXene has a graphite-like structure [13]. According to the theoretical calculation, MXene has good stability and better mechanical properties than the multigraphene and other

TABLE 1: Chemical composition of P·I 42.5 standard cement.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O <sub>eq</sub>	f-CaO	Loss
21.18%	4.73%	3.41%	62.49%	2.53%	2.83%	0.56%	0.72%	1.76%

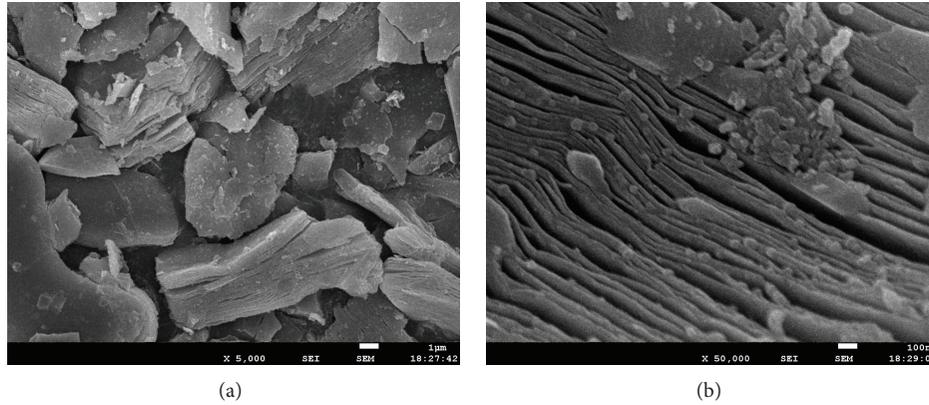


FIGURE 1: SEM image of MXene.

series of excellent properties [14–16]. Therefore, many researchers believe that MXene has very broad application prospects in the energy storage, lubrication and composite reinforcement, and other fields. As for most binding materials in 21st century, two-dimensional material (MXene) in cement application research has not been reported yet. Lv et al. reported the impact of graphite oxide (abbreviated as GO, a layered structure like MXene) on the microstructure of hydration products of cement-based composites [17–22]. They confirmed that GO played a template role in the process of cement composite hydration and put forward the regulation mechanism of GO in cement-based composite microstructure. In this work, we studied the effects of MXene on early-age hydration of Portland cement paste. The hydration process and products were investigated by mechanical testing, XRD, hydration heat, and SEM. The amount of MXene was optimized, and the influence mechanism for MXene on early-age hydration of Portland cement paste was obtained.

## 2. Materials and Methods

**2.1. Preparation of Sample.** P·I 42.5 standard cement of concrete admixtures detection (Qufu United Cement Company, China), component analysis is shown in Table 1. MXene was prepared according to the previous report [23]; scanning electron micrograph was shown in Figure 1. Mixing water was tap water.

In this experiment, the amounts of MXene were 0%, 0.04%, and 0.08%. MXene was ultrasonically dispersed in water for 5 minutes to prepare dispersion liquid, using the dispersion containing MXene when molding paste. The water-binder ratio (abbreviated as w/b) is 0.35 like Senff et al. use in their paper [24–26]. And, in our work, if the water-binder ratio is as high as 0.4, the paste will be too runny and difficult to be casted; however if the water-binder ratio is as low as 0.3,

it will be difficult to cast because of thickness of paste. The cement was then added and the mixture was stirred at low speed for 1 min and then at high speed for 1 min in cement paste mixer. The resulting cement paste was immediately poured into a 10 mm × 10 mm × 10 mm mold. Then the samples were cured at 20 ± 1°C and 95% relative humidity. After 24 h, the specimens were removed from the mold and cured at the same condition until the compressive strength was tested at the age of 1 day, 3 days, and 7 days. After compressive strength test, samples are packed in small bottle with anhydrous ethanol for microscopic tests. Microstructural properties of hydrated cubes were evaluated.

**2.2. Characterization of Sample.** The compressive strength of the cement paste was measured based on GB/T17671-1999 (the national standard of China) by using a WDW-20 hydraulic test machine (Jinan Ruijin Experimental Instrument Co., China). For each mixture at each age, six 10 mm × 10 mm × 10 mm cubic samples were tested for assessing the compressive strength of cement paste. The loading rate of the test was 0.2 mm/min.

XRD was used to analyze the hydration products phase of cement pastes. Few samples dried at 70°C for 2 h were crushed and grounded to powder. X-ray diffractometer (XRD, D8ADVANCE, Bruker, Germany) tests were conducted with a powder diffraction method, with Cu Ka, voltage 40 Kv, and current 40 mA. Scan range was 5°–70°, 0.02°/step, 0.4 s/step.

The hydration exothermic rate of each paste was measured by TAM Air calorimeter (TA Instruments Co., USA) to assess the effect of MXene on the hydration of cement paste. Samples were prepared at a w/b ratio of 0.5, with mixtures (cement was evenly mixed with MXene of 0%, 0.04%, and 0.08% amount in advance) and mixing water at a temperature of 20°C. With dry cement (content MXene, total of 5 g) loaded in the 20 mL disposable glass ampoule and water (2 g) loaded in the syringe(s), the admix ampoule was first equilibrated

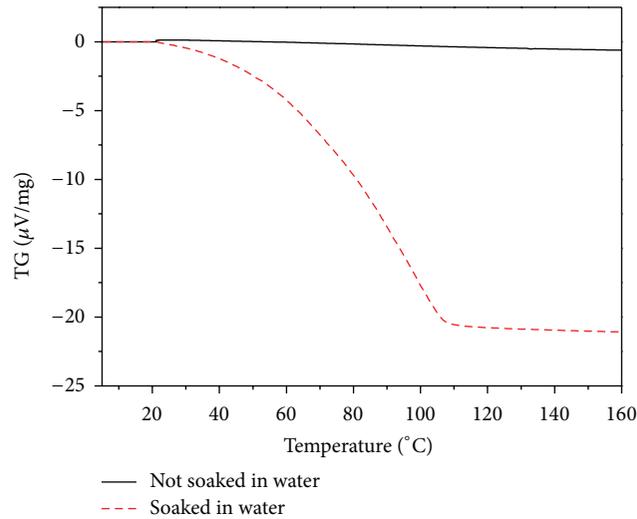


FIGURE 2: TG transformation of MXene soaked and nonsoaked in water.

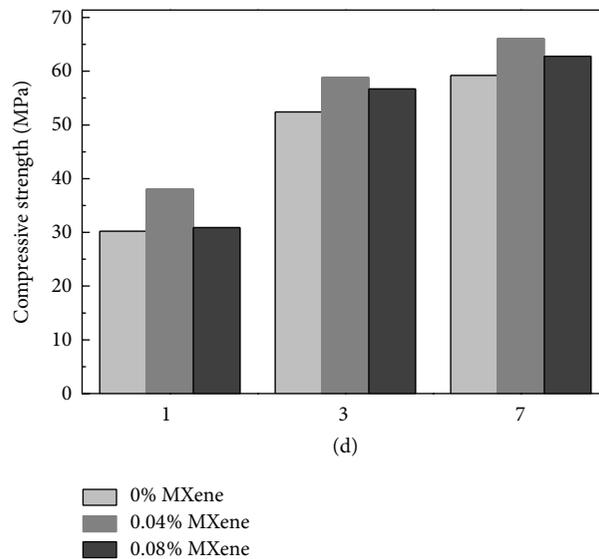


FIGURE 3: Compressive strength with 0%, 0.04%, and 0.08% amount of MXene at 1 d, 3 d, and 7 d.

in the TAM Air calorimeter with the materials separated for 30 minutes. Pushing the syringe(s) with stirring the cement paste, the reaction can then be initiated by manually injecting the water from the syringe(s) into the glass ampoule. Then, the hydration exothermic rate within 72 h was tested.

Scanning electron microscope (SEM, JSM-6390LVH, JEOL, Japan) was used to analyze the morphology of cement paste. Small fractured samples at every hydration age were soaked in anhydrous ethanol to stop hydration and dried at 60°C for 4 h. Then the sample was coated with 20 nm of gold to make it conductive.

Differential thermal analysis (TG-DTA, HCT-3, Beijing Hengju Scientific Instrument Company, China) was used to test the absorption capacity of MXene. 0.5 g MXene was added into 10 mL water and stirred symmetrically for 1 h, and then the redundant water was drained with filter paper. In this test, the heating rate is 5°C/min.

### 3. Results and Discussion

**3.1. TG-DTA.** TG-DTA analysis was used to test the absorption capacity of MXene with its layer structure. TG transformation of MXene soaked or nonsoaked in water was showed in Figure 2. Before 100°C, the TG curve of MXene which has been soaked in water changed, while the dry MXene was almost unchanged, which suggested that the interlayer of MXene could absorb water.

**3.2. Compressive Strength.** Modification effect of MXene on cement can be expressed through its influence on the macroscopic mechanical properties. Effects of 0%, 0.04%, and 0.08% content of MXene on the compressive strength of cement paste are shown in Figure 3. The compressive strength of MXene-added paste was enhanced at early ages. In addition, the higher the MXene amount, the worse

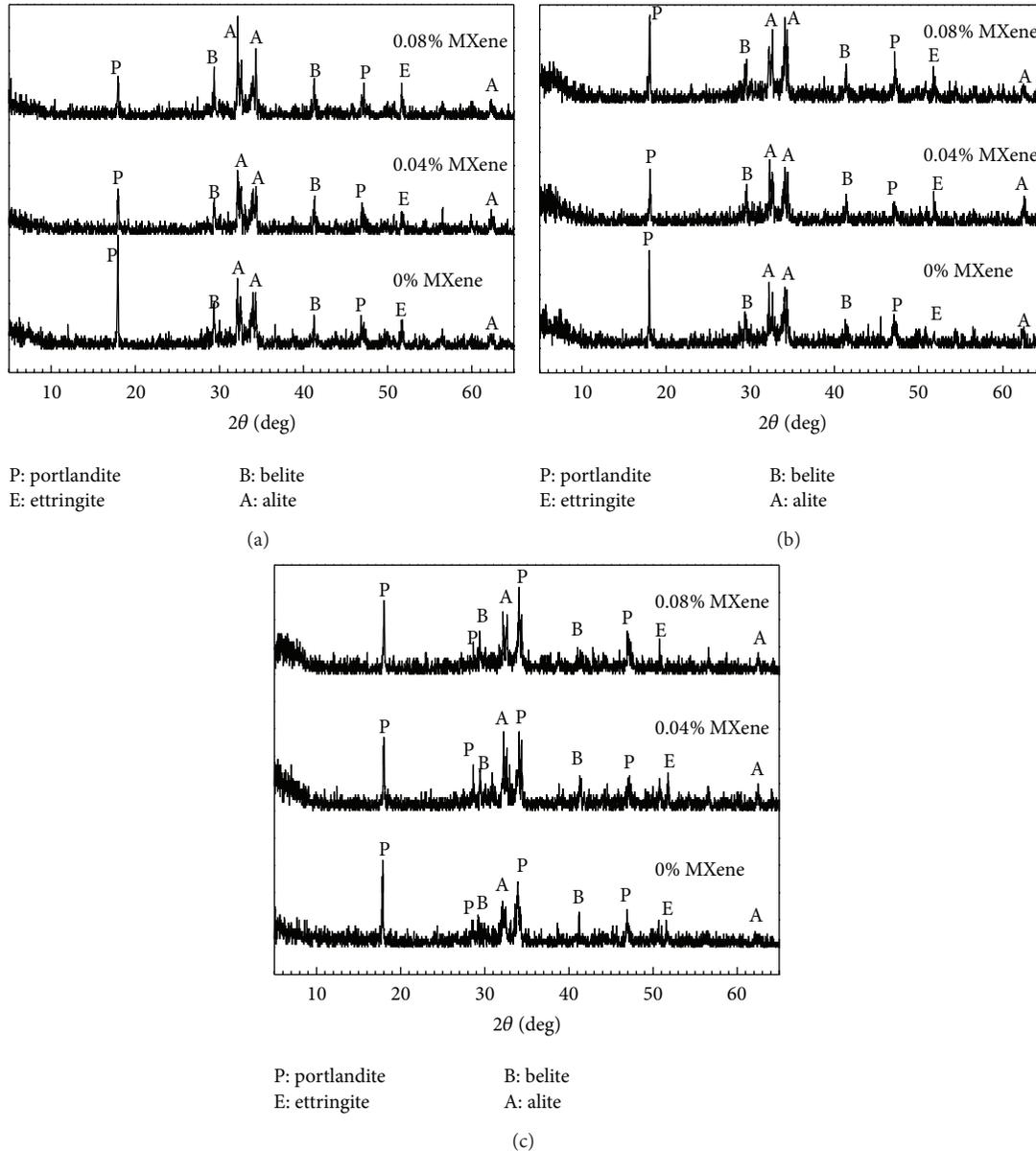


FIGURE 4: XRD analysis of cement paste with 0%, 0.04%, and 0.08% amount of MXene at day 1, day 3, and day 7 ((a), (b), and (c)  $2\theta = 5-70^\circ$ ).

the enhancement: the compressive strength of 0.04% amount increased by 26.2%, 12.4%, and 11.7% at 1 d, 3 d, and 7 d, respectively, while the compressive strength of 0.08% amount only increased by 2.3%, 8.2%, and 6.1%, respectively. To explore the reasons for the strength gain characteristics of the cement paste, the early-age hydration characteristics of Portland cement paste were further evaluated.

**3.3. X-Ray Diffraction.** Cement hydration is a very complex, heterogeneous multiphase chemical reaction process and is the result of setting and hardening of cement hydration. Its hardened cement paste is a heterogeneous multiphase system, the solid phase by a variety of hydration products and residual clinker posed and gaps exist in the water and air, belonging to the solid-liquid-gas three-phase porous

body. The phase spectrum of cement hydration products is really complex, adding a reference standard to meet further increases the chance overlapping spectral lines, leading to quantitative analysis difficulty by using X-ray diffraction system for quantitative analysis of multiphase controversial [27, 28]. Therefore, X-ray diffraction is only used for qualitative analysis in this research. Many other researchers also use X-ray diffraction only to determine the change of hydration products before and after the addition of nanomaterials in cement-based materials [29]. Figures 4(a), 4(b), and 4(c) illustrate the XRD analysis of cement paste with 0%, 0.04%, and 0.08% concentration of MXene at day 1, day 3, and day 7, respectively. Ettringite ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_4\cdot n\text{H}_2\text{O}$ , abbreviated as Aft), portlandite ( $\text{Ca}(\text{OH})_2$ , abbreviated as CH), alite ( $3\text{CaO}\cdot\text{SiO}_2$ , abbreviated as  $\text{C}_3\text{S}$ ), and belite ( $2\text{CaO}\cdot\text{SiO}_2$ ,

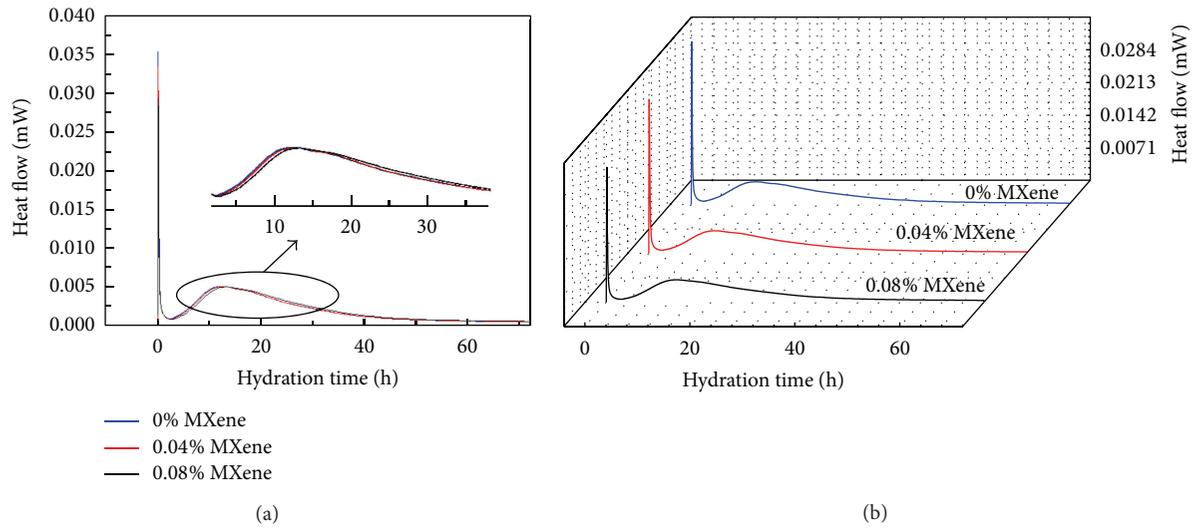


FIGURE 5: The cement paste hydration exothermic rate with 0%, 0.04%, and 0.08% concentration of MXene within 72 h.

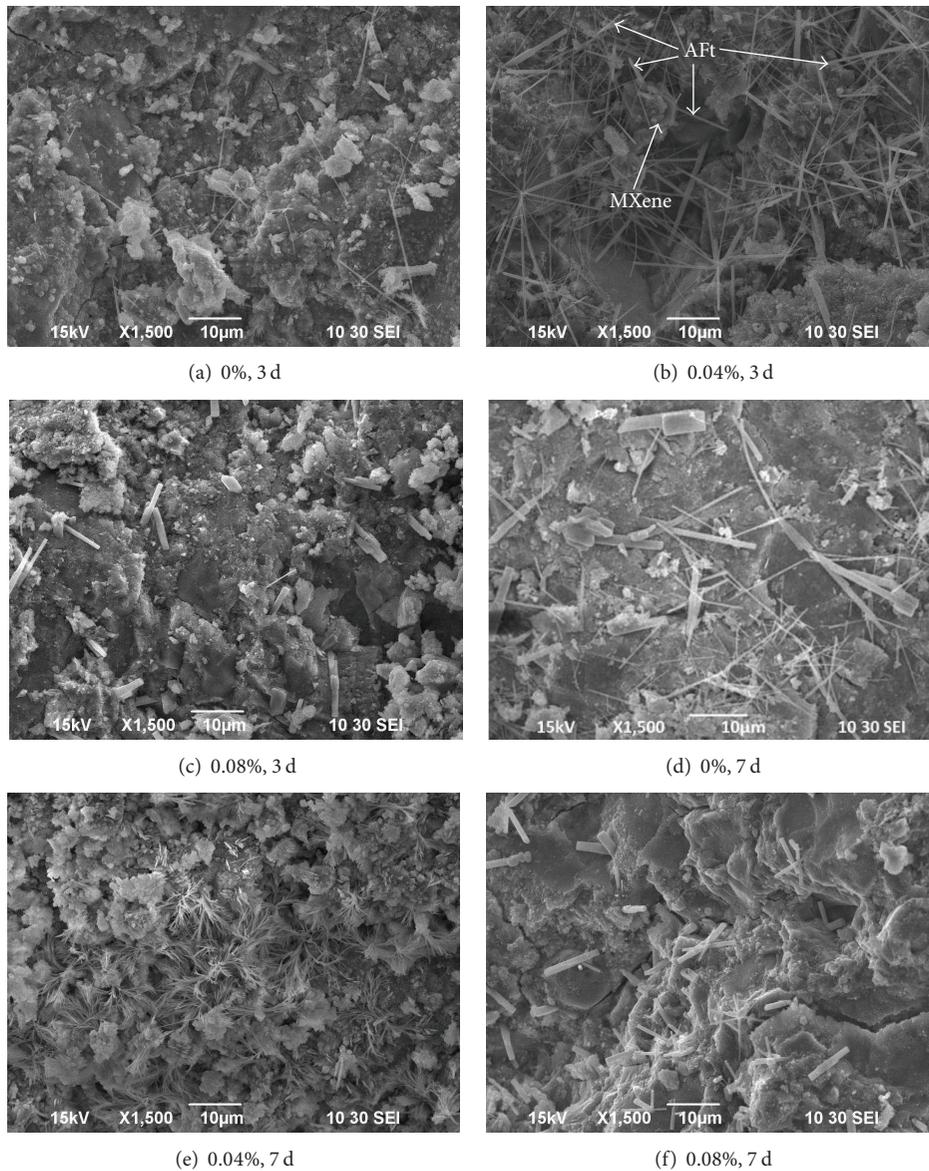


FIGURE 6: SEM micrographs of cement hydration products at day 3 and day 7 with 0%, 0.04%, and 0.08% amount of MXene.

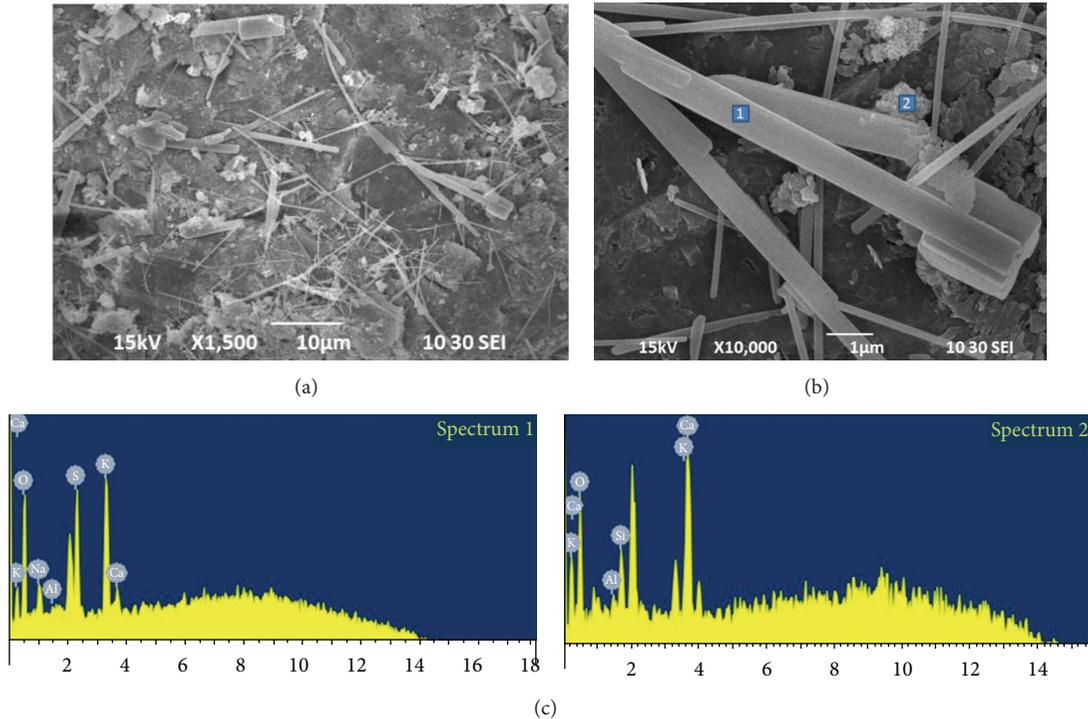


FIGURE 7: EDS analysis of hydration products at day 3 without MXene.

abbreviated as  $C_2S$ ) were found to be the major phases for all the mixes. After incorporating MXene, X-ray diffraction pattern of the hydration products in each age was still a characteristic diffraction peak of these substances, and no new characteristic peak appeared, and no new phase appeared, which showed that MXene did not participate in cement hydration process, may only affect the crystal nucleation growth process, or played other roles.

**3.4. Hydration Heat.** The cement paste hydration exothermic rate with 0%, 0.04%, and 0.08% amount of MXene within 72 hours is shown in Figure 5. Portland cement hydration is an exothermic process. Clinker mineral can be immediately dissolved in water;  $3CaO \cdot Al_2O_3$  (abbreviated as  $C_3A$ ) hydration was firstly produced and then the Aft was rapidly formed in the presence of gypsum. So, the first exothermic peak appeared around the tens of minutes. Subsequently, the hydration rate of  $C_3A$  was decreased with the increase of the number of Aft. The hydration exothermic rate was also slowed correspondingly. In the following ten hours,  $C_3S$  began to hydrate, causing the formation of C-S-H and CH phase. Thus, the second exothermic peak appeared. Before 13.3 h, we found that, with the increase of MXene concentration, the rate of hydration heat was slowed, indicating that MXene has inhibited the Portland cement hydration process. This may be related to the unique structure of MXene; the water was absorbed by gap between layers of MXene as studied before, leading to a reduction in water used for hydration process. After 13.3 h, the hydration exothermic heat with 0.08% concentration of MXene was faster than that of the other two dosages, which may be attributed to the release

of water absorbed in MXene layer, causing a continuous hydration process.

**3.5. Morphology.** To further explore the role of MXene in enhancing the early-age mechanical properties of cement paste, morphology of cement hydration products in different age periods was observed by SEM. Figures 6(a)–6(f) represent the SEM images of 0%, 0.04%, and 0.08% MXene content mixtures cured up to 3 and 7 days. According to the EDS analysis (see Figures 7(a)–7(c)), Ca, Si, O, and S are the main elements, which can yield the conclusion that C-S-H and ettringite were the main hydration products of specimens with 0%, 0.04%, and 0.08% MXene cured for 3 and 7 days. For all the mixtures, the amount and distribution of ettringite were quite different. Fewer ettringites with messy distribution and a lot of tiny needle-like crystals were exhibited in Figure 6(a). Extraordinarily, with 0.04% concentration of MXene at day 3, many regular ettringites with needle-like crystals got together at one node. With the increase of MXene concentration, ettringite with short rod crystal appeared at day 3. Additionally, with the help of EDS analysis (see Figure 8), a fact that C-S-H was grown in the surface of MXene was authenticated, which shows that MXene played nucleation effect in the cement hydration process. At day 7, C-S-H and ettringite were also mainly found in cured specimens with 0%, 0.04%, and 0.08% MXene. However, ettringite has grown from small needle-like crystals to stubby rod-like crystals, which have positive implications for improving the mechanical properties. Agminate ettringites at some nodes formed mesh structures which are shown in Figure 6(e). The results indicated that the main role of MXene in the cement

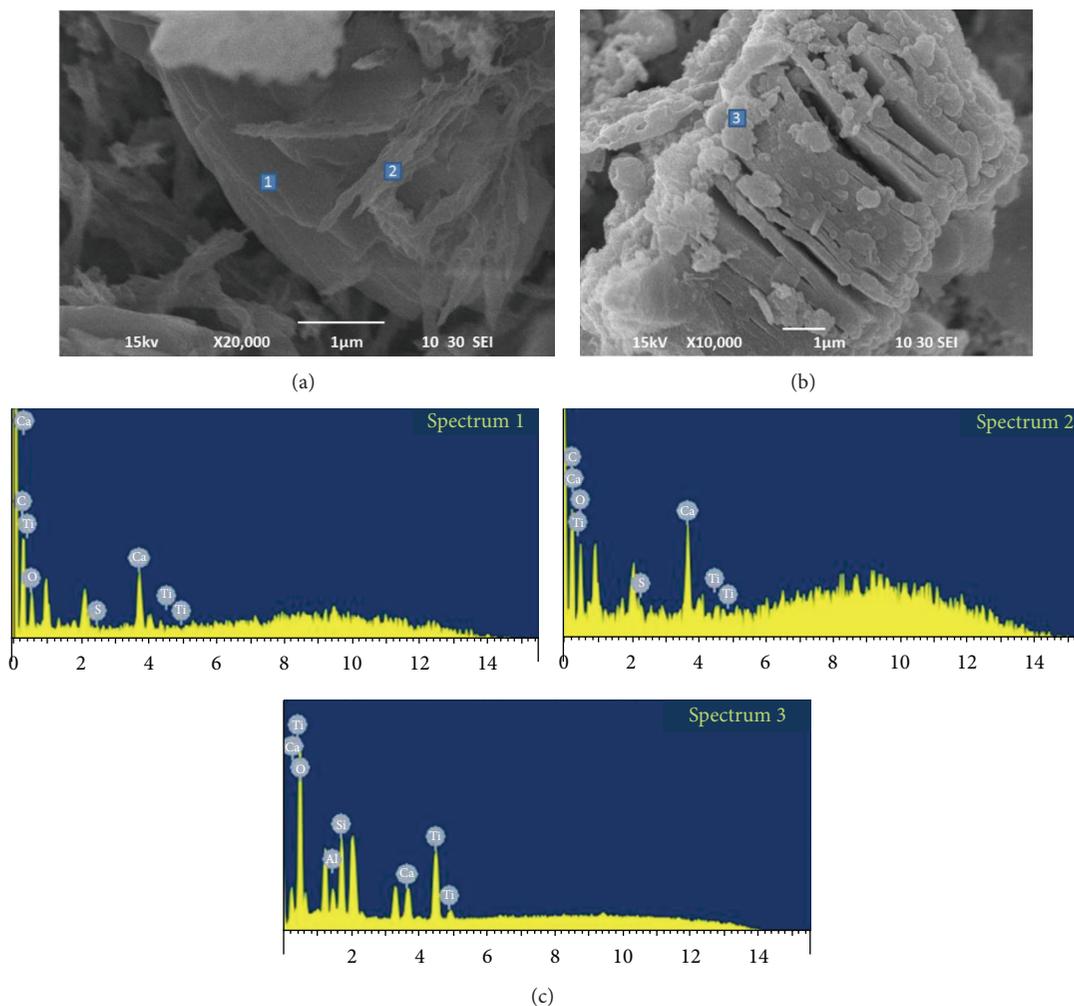


FIGURE 8: EDS analysis of hydration products at day 1 with 0.04% amount of MXene.

hydration process was to promote the transformation of messy ettringite into regular distribution at a node, forming network connection structure in the process of crystal growth and improving the mechanical performance of cement paste significantly.

#### 4. Conclusion

Addition of MXene can significantly improve the early-age compressive strength of cement paste. With 0.04 wt% amount of MXene, the compressive strength was improved 26.2%, 12.4%, and 11.7% at day 1, day 3, and day 7, respectively, while, with 0.08 wt% amount of MXene, the compressive strength was only improved 2.3%, 8.2%, and 6.1% at day 1, day 3, and day 7, respectively. Portland cement hydration process was inhibited with the addition of MXene, and the inhibition was negatively correlated with the content. MXene provides a growth point of C-S-H gel and ettringite in the cement hydration process. Some chaotically distributed Aft turning was densely distributed at the nodes, forming a network structure with 0.04 wt% concentration of MXene, which has positive significance for the mechanical properties

of the cement. MXene is a potential material for improving the properties of cement in engineering.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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