



## Effects of carbamide on sulfoaluminate cement paste for growing plants



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### HIGHLIGHTS

- Carbamide delays the hydration of CSA cement and prevents the formation of Aft.
- Carbamide increases the fluidity and extends the setting time of CSA cement pastes.
- CSA cement hardened pastes with carbamide can release nitrogen nutrients.

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### ABSTRACT

To better understand the effects of carbamide on the properties of sulfoaluminate cement as potential matrix for eco-concrete suitable for growing plants, the fluidity, hydration heat evolution, setting time, compressive strength development, hydration products, pore characteristics and releasing characteristics of nitrogen nutrients of sulfoaluminate cement with carbamide were investigated. It was found that carbamide can reduce the water demand of sulfoaluminate cement. The fluidity increased from 80 to 149 mm with carbamide content increasing from 0.2 to 4.0 wt.%. Carbamide had noticeable retarding effect on the hydration of sulfoaluminate cement, especially on C<sub>3</sub>S phase. The cumulated hydration heat of sulfoaluminate cement pastes without and with 4.0 wt.% carbamide was 329.5 J/g and 296.3 J/g, respectively. Carbamide retarded initial setting time of sulfoaluminate cement enabling it being able to meet the setting time requirement of GB20472-2006 (Chinese national standard for Sulfoaluminate cement). The early compressive strength of sulfoaluminate cement was low due to the retarding effect caused by carbamide and the production of NH<sub>3</sub> increased the total porosity, but carbamide had limited effects on late age compressive strength of sulfoaluminate cement. Hardened sulfoaluminate cement pastes with carbamide can release nitrogen nutrients which is essential for growing plants. The amount of nitrogen nutrients released from sulfoaluminate cement paste with 2.0 wt.% carbamide cured for 56 days was 0.92 mg/cm<sup>3</sup>, and the cumulative release rate was 75.0%. The presence of carbamide enables hardened cement paste being able to release nitrogen nutrients, suggesting that carbamide can mix with sulfoaluminate cement to produce eco-concrete and release nitrogen nutrients for growing plants.

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### 1. Introduction

With the rapid development of human society and infrastructure, environmental pollution and degradation are further threatening the survival of human society. For the purpose of soil fixation and slope protection to prevent soil erosion and desertification, planting concrete was developed as an environmentally friendly material. It is a new type of porous concrete with porous structure that is suitable for growing plants in it. In recent years,

because of its multiple environmental benefits, such as controlling storm water runoff, restoring groundwater supplies and reducing water and soil pollution, planting concrete has received wide-spread attentions and interests from academia and industry [1–6].

When porous concrete used as planting concrete, enough pores in porous concrete are required to provide the space for plant roots. Good porous concrete with void ratio of 15–25% and strength of 22–39 MPa were produced using cement paste with fluidity of 150–230 mm, accordance with JIS R 5201 and top surface vibration of 10 s with vibrating energy of 90 kN/m<sup>2</sup> during casting [7]. Porous concrete was prepared with recycled aggregates from waste crushed concrete. It was found that the total void ratio of

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the porous concrete with recycled aggregates was up to 22–28%, much higher than that of porous concrete with normal aggregates, but the compressive strength decreased significantly [8]. Pore structure and total porosity played significant roles in the functional and structural performance of porous concrete. The compressive energy absorbed by the porous concrete specimens was found to increase linearly with compressive strength and can be related to the porosity and critical pore sizes in the material [9]. The Katz-Thompson equation was used for analyzing pore structure features, and a correction factor for the Katz-Thompson constant was found to be linearly related to the granulometry-based pore sizes [10]. Image analysis methods and three-dimensional pore distribution density were used to analyze the pore structure of porous concrete. It has been revealed that compressive strength of porous concrete was related to pore size, its distribution and spacing [11,12]. Meanwhile, the computed tomography (CT) images and low-order probability functions were used to investigate and quantify the spatial distribution of voids inside porous concrete specimens [13]. Fundamental information including the influence of w/c, cement paste compositions, coarse aggregate characteristics, void ratio and strength of porous concrete have been studied. However, the alkalinity of porous concrete is too high to be used as the matrix for planting concrete and the optimum method to solve this problem (i.e. high alkali of porous concrete) has not been established. Porous concrete prepared with low alkali sulfoaluminate cement replacing ordinary Portland cement has been investigated [14], and the relationship among coating thickness of cement paste and pore structure features, alkalinity and mechanical property of porous concrete has also been studied. At last it was found that the alkalinity of porous concrete with low alkali sulfoaluminate cement was suitable for growing plants [15]. Besides, another difficulty in popularizing planting concrete is that there is lack of nutrients in porous concrete, which usually causes plants withering and even dying away in large areas. So, this paper moves forward the research by adding nutrients, such as carbamide, to porous concrete during its preparation process. However, carbamide has an evidently adverse effect on Portland cement hydration. Carbonic acid, produced from carbamide dissolution, reacts with calcium hydroxide, which affects hydration of Portland cement. Heat of hydration was reduced, shrinkage strain and carbonation resistance were greatly improved [16]. Carbamide crystals formed in capillaries and pores restrict the thermal-humidity deformations of concrete. When pressure caused by carbamide crystals exceeds the critical value, concrete capillaries crack and the destruction of surface layers starts [17]. So it is reasonable to believe that carbamide has beneficial effects on sulfoaluminate cement, but to the best of the authors' knowledge there is no literature investigated this.

In this study, carbamide as the fertilizer component was mixed with sulfoaluminate cement and nitrogen release characteristic was studied. Effects of carbamide on fluidity, setting time, hydration heat, compressive strength, hydration products and pore structure of sulfoaluminate cement were studied. In addition, the release of nitrogen nutrients from sulfoaluminate cement with carbamide was also characterized. The findings of this study lay the foundation for preparation and application of planting concrete which is able to slowly release fertilizer for growing plants during its service life.

## 2. Experimental

### 2.1. Raw materials

The chemical components of sulfoaluminate cement which meets the requirements of GB20472-2006 [18] are showed in Table 1. Quantitative X-ray diffraction (QXRD) analysis results of sulfoaluminate cement are presented in Fig. 1 while its main phases from QXRD analysis are quantified in Table 2. Carbamide (with

99.0% purity) purchased from Sinopharm Chemical Reagent Co., Ltd, China was adopted as nutritional component and mixed with sulfoaluminate cement in this research.

### 2.2. Experimental process

In this research, there were nine sulfoaluminate cement mixtures tested with carbamide content from 0.2 to 4.0 wt.%. The mixture without carbamide was designed as the reference mixture. All of the mixtures had a water/cement ratio (w/c) of 0.27. Samples were cast in 20 mm × 20 mm × 20 mm moulds, vibrated to remove air bubbles, and cured at 20 ± 2 °C and 95% relative humidity (RH). The samples were removed from the moulds after 24 h and then cured in a water tank at 20 ± 2 °C for 3, 7, 14, 28 and 56 days when relevant tests were conducted.

### 2.3. Measurement methods

#### 2.3.1. Fluidity

The fluidity of the sulfoaluminate cement pastes was determined using the concrete admixture homogeneous experimental method specified in GB/T 8077-2000 [19]. The samples were prepared with the w/c of 0.45. Water was mixed with carbamide at first and then with sulfoaluminate cement. The fluidity was determined by measuring the diameters of the cement pastes using a cone (60 mm height, 36 mm top diameter, 60 mm bottom diameter). The maximum diameter of the spread sample and its perpendicular diameter were measured. The average of these two values was defined as the fluidity.

#### 2.3.2. Setting time

The initial and final setting time of the sulfoaluminate cement pastes was determined by the Vicat apparatus accordance with the Chinese national standard GB/T 1346-2011 [20]. The initial setting time was recorded as the time when the needle created a hole of 37–38 mm in depth, while the final setting time was recorded as the time when the needle failed to create an indentation of 0.5–1 mm in depth.

#### 2.3.3. Thermal analysis

An isothermal heat-conduction calorimetry (TAM air C80, Thermometric, Sweden) was used to measure the hydration heat evolution of sulfoaluminate cement. The w/c of the sulfoaluminate cement pastes was 0.5 and the test was conducted at the temperature of 30.0 ± 0.1 °C.

In addition, thermogravimetric analysis (TGA) was carried out in argon atmosphere using a Mettler-Toledo TGA/DSC/1600HT instrument at the heating rate of 25 °C/min up to 900 °C. The amount of ettringite in the hydrated sulfoaluminate pastes was determined as described later, assuming that the weight loss of the hydrating sulfoaluminate cement paste between 100 °C and 150 °C corresponds to 20 molecules of crystal water per molecule of ettringite [21].

#### 2.3.4. X-ray diffraction (XRD)

XRD data were collected on a D8 ADVANCE X-ray diffractometer with strictly monochromatic Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) produced by Bruker in Germany. Hydration products were measured in the range of 5° to 65° (2 $\theta$ ) with a scan speed of 2°/min, an accelerating voltage of 40 kV and a current of 40 mA.

#### 2.3.5. Compressive strength

The compressive strength of the sulfoaluminate cement samples with the sizes of 20 mm × 20 mm × 20 mm were measured after cured for 1, 3 and 28 days. Six samples were tested for each mixture at each designated age under compression and the average value was taken as the representative compressive strength of the mixture.

#### 2.3.6. Pore structure and porosity

The porosity and pore size distribution of hardened cement pastes were determined by mercury intrusion porosimetry (MIP Micromeritics, AutoProe 9500 IV). At the ages of 1 and 28 days, the hardened cement pastes were crushed and immersed into ethanol solution to stop hydration. Before MIP testing, the samples were dried at 50 °C for 48 h until a constant mass was reached.

#### 2.3.7. Release of nitrogen nutrients

Sulfoaluminate cement pastes with different contents of carbamide were cured at 20 ± 2 °C and 95% RH for 24 h and then removed from the moulds. Three samples all with the sizes of 20 mm × 20 mm × 20 mm were soaked in 200 ml water and then sealed. After 1, 3, 7, 14, 28 and 56 days all water was poured out and adjusted to a constant volume of 250 ml to measure the amount of nitrogen nutrients released. It is worth noting here that after water was poured out, additional 200 ml water was added again for next test [22]. A UV-5200 PC type spectrophotometer was used for the test and the HJ 636-2012 [23] water quality-measurement of total nitrogen was referred.

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