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The influence of silanes on hydration and strength development of cementitious systems

Xiang-Ming Kong [a,*], Hui Liu [a,b], Zhen-Bao Lu [b], Dong-Min Wang [b]

[a] Key Laboratory of Civil Engineering Safety and Durability of China Education Ministry, Department of Civil Engineering, Tsinghua University, Beijing 100084, China
[b] Department of Chemical Engineering, China University of Mining & Technology, Beijing 100083, China

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ABSTRACT

The influences of three types of silane (tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTES), N-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS)) on flowability, strength development and hydration kinetics of cement pastes and mortars are systematically investigated. Results show that: 1) three silanes exhibit a dispersing effect on cement pastes indicated by the increased flowability of fresh cement pastes, among which AEAPTMS shows the strongest dispersing power; 2) AEAPTMS and APTES retard cement hydration by extending the induction period and reducing the hydration degree at certain ages determined by isothermal calorimetry, measurements of non-evaporable water amount and portlandite content in hydration products at ages before 90 days; 3) AEAPTMS and APTES show positive effect on the toughness of mortars after 7 day curing; and 4) three silanes act differently on strength growth at various ages, which should be a result that is counterbalanced by their influences on hydration kinetics, pore structure, composition and morphology of hydration products.

1. Introduction

Using organo-siloxane in cementitious materials has attracted increasing attentions in recent years, due to the fact that hydrolysis of alkoxyl groups (–OCH_3 or –OC_2H_5) to hydroxyl groups (–OH) and a subsequent condensation with hydroxyl groups on the substrates to form siloxane covalent bonding progressively take place in acidic or alkaline conditions [1,2]. This makes the organofunctional silane be used in very wide applications, e.g. as coupling agents in inorganic filler modified polymer composites [3,4], as steel fiber or polymer fiber modifier in fiber reinforced mortars for improvement of fiber dispersion and enhancement of the interfacial bonding [5,6], as silica fume coating for better workability and lower shrinkage in cementitious mixtures [7,8] and as water repellent agent in mortar or concrete to reduce water penetration [9–11].

Earlier attempts in cementitious system have been made to use silane in surface protection [9,11]. Zhu et al. [12] found that, using silane as water repellent agent, the durability of recycled aggregate concrete was improved. Moreover, the silane-based hydrophobic admixture had a positive effect on protection of galvanized reinforcing steel in concrete from corrosion [13]. Even in the presence of cracks in concrete cover, the water repellency and chloride resistance were enhanced [11,13,14]. The positive benefits of incorporating organosilanes in cementitious system from the view of workability and strength were reported in literatures [15,16]. Xu [7] introduced silanes in cement by coating silica fume particles or as an admixture to improve properties of silica fume cement. It was shown that the workability, tensile strength and compressive strength were enhanced. Similar results have been found in fiber reinforced mortar and mortars with silane-treated sand [5,6,17]. It was found that the pullout energy was remarkably enhanced when fiber was treated by silane [18]. Recently, a new class of organosilane-modified polycarboxylate superplasticizer was developed and attracted increasing attentions [19,20]. It has been confirmed that the silylated functions strongly interact with silicate phases and enhance the sorption of polycarboxylate molecules on the surface of cement particles. In a recent work, Švegl et al. [21] reported that aminosilanes (N-2-aminoethyl-3-aminopropyltrimethoxy silane and aminopropyltrimethoxy silane) improved the workability of cement paste and reduced the water demand. Flexural strength and compressive strength of cement mortars were markedly increased by the addition of aminosilanes after 28 days of curing. In addition, setting time measurement indicated strong retarding effect of aminosilanes on cement hydration.

On the other hand, detailed working mechanism of silanes in cementitious materials has been rarely reported. It has been shown that the addition of various silanes in cementitious materials may be beneficial for some properties, such like workability, mechanical strength and impermeability. However, how silanes influence those properties and why different silanes work differently remain unanswered. At present, only limited information is available on cement hydration in the presence of silanes. The aim of this paper is to lay the groundwork for better understanding the working mechanisms of silanes in cementitious materials. The influences of three types of silane (tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTES),

* Corresponding author. Tel.: +86 10 62783703; fax: +86 10 62797422.
E-mail address: kxm@mail.tsinghua.edu.cn (X.-M. Kong).

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N-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS)) on flowability, strength development of mortars and hydration kinetics of cement are systematically investigated in this paper. Techniques including isothermal calorimetry, inductively coupled plasma optical emission spectrometry (ICP-OES), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) were employed to monitor the cement hydration process and to characterize the microstructure of hardened cement pastes at varied curing ages.

2. Experimental

2.1. Materials

Ordinary Portland cement classified by P.O. 42.5 and compliant with the Chinese standard GB175-2007 was used to prepare the cement pastes and mortars. The chemical and mineral compositions of thecement are presented in Table 1, which were obtained according to the European standard EN 196-2:2005 and the Chinese standard GB/T176-2008 "Chemical Analysis of Cement". The fineness of cement is 2.3% and the density is 3.10 $g \cdot cm^{-3}$. ISO 679 sand was used as the fine aggregate to prepare cement mortars for the flowability as well as the mechanical strength tests. Three types of silane (analytical grade) listed in Table 2 were chosen in this study. Their molecular structures are shown in Fig. 1. Deionized water was used for all experiments.

2.2. Paste experiments

Measurements of workability, hydration degree, and microstructural characterization were carried out on cement pastes. As APTES and AEAPTMS are water soluble, while TEOS is water insoluble, prior to being mixed with cement, the silanes were dissolved or dispersed into water to acquire water solution or uniform emulsion by high-speed stirring. In the preparation of cement pastes, cement was gradually added into a 2.5 L stirring mixer pre-charged with the silane solution (or emulsion) over a time span of 2 min at 62 rpm. After a 10 s interval, mixing was resumed for another 2 min at 125 rpm. The whole mixing process took about 5 min in total.

Dosages of silanes in cement pastes were determined as follows. The dosage of APTES was set as 1.0% by weight of cement (bwoc) and the other two, AEAPTMS and TEOS, were respectively added into cement paste with the same mole amount as APTES. In order to determine the hydration degree and microstructure of hardened specimens, the mixtures were then casted in steel molds for curing. The samples were demolded after being cured in a standard curing room (20 ± 2 °C, relative humidity > 95%) for 24 h. Afterwards, they were wet cured in a water bath at 20 °C until testing. At the selected ages, the samples were firstly fractured into pieces with a maximum particle size of 1 cm, then soaked in acetone and stored for at least 24 h to cease further cement hydration. Thereafter, they were dried in an oven at 65 °C for 24 h.

Measurements of non-evaporable water (NEW) content, XRD, TGA and isothermal calorimetry were used to quantitatively or qualitatively characterize cement hydration degree. The morphology of the hydration products was observed by SEM. Pore structure of hardened cement pastes (hcps) was characterized by MIP.

Table 2
Characteristics of the silanes used.

Silane	Molecular weight, (g/mol)	Water miscibility	Stability in pore solution
TEOS	209	Insoluble	Not stable
APTES	221.37	Totally soluble	Stable for 24 h
AEAPTMS	222.36	Totally soluble	Stable for 24 h

2.2.1. Flowability of the fresh cement pastes

The mini-cone tests were conducted according to Chinese standard GB/T 2419-2005 (2005) to evaluate the flowability of the fresh cement pastes (fcps) prepared at a fixed water-to-cement ratio (w/c) of 0.35 with addition of various silanes. After mixing of the fcps, the mixing bowl was immediately covered with a wet cloth to avoid water evaporation and then was stored for 0, 25, 55 and 115 min. At a predetermined interval, a portion of the fcps was extracted and then remixed at a speed of 125 rpm for 30 s to ensure homogeneity. After that, the flowability of the fcp was measured by mini-cone test which was represented by the spread flow. A cone with an upper diameter of 36 mm, a lower diameter of 60 mm, and a height of 60 mm was used in the test. The spread diameter was recorded as the average of two perpendicularly crossing diameters. Since the whole mixing process took about 5 min, counting from the time point of water to cement contact, each fcp was actually tested at 5, 30, 60, and 120 min after the contact of cement with water, respectively. The flowability tested at 5 min was defined as the initial flowability.

The effect of methanol and ethanol which are the hydrolysis products of silanes on the flowability of fcps was also investigated. The amounts of methanol and ethanol added as admixture were equal to the amounts that were produced by complete hydrolysis of the silanes.

2.2.2. Sorption of silane on cement grains and the ionic concentrations in aqueous phase of hydrating cement pastes by ICP-OES analysis

The elemental concentrations including sodium, potassium, calcium, aluminum, silicon and sulfur ([Na], [K], [Ca], [Al], [Si], [S]) in aqueous phase of a hydrating fresh cement paste were measured by ICP-OES analysis. In order to obtain sufficient pore solution from the hydrating cement pastes, the water-to-cement ratio was set as 0.5. The cement pastes were prepared by mixing the cement with water solution/emulsion of silanes. The pastes were slowly agitated in sealed polyethylene flasks by a head-over laboratory agitator to keep them homogenous for periods of 5 min, 30 min, 1 h, 2 h, 4 h, and 8 h. The well mixed fresh cement paste was centrifuged to separate the aqueous phase from the paste mixture at 3000 rpm for 10 min. The obtained supernatant liquid was then filtrated with a membrane filter with a pore diameter of 0.22 μm, and the filtrate was subjected to chemical analysis by inductively coupled plasma optical emission spectrometry (ICP-OES), using an IRIS Intrepid II XSP. Evolution of the various ion concentrations in aqueous phase of fcps was then obtained.

Upon addition of silane into a cement paste, many chemical and physical processes are involved once silane gets contact to water and to cement phase. Hydrolysis of silane leads to transformation of $-OCH_3$ group to –OH group and the subsequent condensation of –OH groups causes either gelation or formation of SiO_2 sol, and/or sorption of silane on –OH containing surface. Usually, the hydrolysis

Table 1
Composition of cement.

Chemical composition (mass %)								Mineral composition (mass %)			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2Oeq	f-CaO	C_3S	C_2S	C_3A	C_4AF
22.10	4.04	3.38	61.91	2.66	2.87	0.56	0.79	57.34	18.9	6.47	11.25

Note: The composition was obtained according to EN 196-2:2005 and Chinese Standard GB/T176-2008 "Chemical Analysis of Cement".