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Influence of triethanolamine on reactivity of hydrated matrix in sodium silicate self-healing system and the mechanism

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HIGHLIGHTS

- TEA was incorporated to increase the reactivity of hydrated cement.
- The self-healing efficiency of sodium silicate system was improved by the complex between TEA and Ca^{2+}.
- TEA enhanced the micromechanical properties of self-healing product.

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ABSTRACT

A suitable binding agent proposed in literatures or patents is sodium silicate, which achieves self-healing by formation of calcium silicate hydrate (C-S-H) in cracks. We systematically investigated the influences of triethanolamine (TEA) on the stimulated C-S-H, sodium silicate/hydrated cement and real self-healing system. Results suggest that TEA addition induces the C-S-H to arrange in order and forms sponge-like structure. In sodium silicate/hydrated cement sample, the morphology of C-S-H is simultaneously affected by the heterogeneous nucleation and restriction effect of hydrated cement particles, and the reticulate structure is observed. It is believed that the formation of TEA-Ca^{2+} facilitated the dissolution of solid Ca from hydration products, hence increases the chemical reactivity of hydrated cement matrix and the actual binding ability is improved due to the increment of high density C-S-H. Finally, the improved performance of self-healed area was demonstrated by optical microscope, SEM and Raman analysis, meanwhile the promotion in micromechanical properties of C-S-H was studied by AFM.

1. Introduction

As the mainstay of infrastructures, cementitious materials have been of great importance for centuries. Researches on the new clinker formulations, improved mechanical properties and high durability may not fully satisfy the requirement in engineering [1]. One of the principle consideration in this field is the cracking due to external loading and or their intrinsic fragile property [2], which exacerbates the ingress of aggressive agents into the materials and reduces the stability and functionality of infrastructure [3,4]. However, this kind of deterioration is inevitable even since the very beginning of the service life, the inspection and restoration process is often labor and capital intensive [1], especially for large scale infrastructures such as highways and tunnels are still in continuous service and in such cases repair work becomes very difficult [3]. Under such circumstance, bio-inspired self-healing abilities is potentially promising to improve the serviceability of concrete structures because they enable recovery of the structural integrity of matrix materials without any manual intervention and thus improve the performance of compromised structures [5,6]. Previous researches have highlighted self-healing potential for the restoration of performance and properties of cement-based materials. Considerable research efforts have been devoted to innovative strategies such as expansive agents, shape memory material and bacterial during the past few decades [7–10].

Besides to sense cracks, a proper healing agent is necessary to ensures the system to work efficiently [2,11,12]. The self-healing process mainly depends on the pozzolanic effect [13], and many material such as fly ash [14], and even some waste polymer [15] have been used. A suitable healing agent proposed in literatures or patents is sodium silicate. Rattner [16] once used the microcapsules incorporating sodium silicate in concrete to achieve self-healing. In his research, concrete was firstly loaded to the point of almost breaking, after curing for about 1 week, the sample proceeded to recover 26% of its original strength. The longer repair

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period and lower efficiency are considered as problematic disadvantages for its wider utilization.

Triethanolamine (TEA) has been universally used as grinding aids and setting time regulator for cement hydrations in the past decades [17,18]. The chelation mechanism of amino alcohols such as TEA with metal ions is based on complexation reaction, wherein amino alcohols act as an electron pair donor. It is noticed that the chelating effects of TEA with metal ions are supposed to either accelerate or retard cement hydration toward initial setting time depending on the dosage used [18]. However, the chelation effects of TEA on the cement rehydration process are still missing. Researches on the reaction between TEA and hydration products are supposed to provide the essential information for its utilization in self-healing.

In our research, a thorough investigation with regard to the effect of TEA on C-S-H, hydrated cement and self-healed system was conducted by means of X-ray diffraction (XRD), optical microscope, scanning electron microscopy (SEM), BET, Raman spectra, nanoindentation and atomic force microscope (AFM). The saturated and oversaturated $Ca(OH)_2$ solutions were employed to elucidate the working mechanism of TEA from a chemical point of view. The TEA addition largely improves the healing efficiency and provides a creative insight on the formation of the C-S-H in sodium silicate self-healing system.

2. Materials and methods

2.1. Materials

Class G high sulfur-resistant oil well cement (OWC, HSR) was obtained from Jiahua Special Cement Co., Ltd., China. X ray fluorescence spectrometer (XRF, S4 Pioneer, Bruker AXS) was employed to determine the mineralogical compositions, which is given in Table 1. Sodium silicate (AR) and Triethanolamine (TEA, AR) were provided by Jiangtian Chemical Co., Ltd., (Tianjin China).

2.2. Preparation of C-S-H

The preparation of C-S-H is mainly according to Chen [19]. First a 0.1 mol/L sodium silicate solution and a saturated $Ca(OH)_2$ solution were prepared. Next, the prepared sodium silicate solution was added to the saturated $Ca(OH)_2$ by drop with continual stirring for 5 min. After setting to equilibrium at room temperature under sealed conditions, the suspensions were separated via centrifugation at 8000 rpm, then the precipitation was freeze dried for 24 h. To evaluate the effect of TEA on C-S-H, 0.4 ml TEA was added to the system.

2.3. Paste experiment

The Class G high sulfur-resistant oil well cement pastes (W/C = 0.44) were hydrated at 60 °C for 7 days. The hydrated paste was ground and sieved through 70 mesh, and the obtained powder was then mixed with the healing agent and cured at 60 °C. In summary, the following samples were prepared.

Water reference (WR): ground cement paste + water
Sodium silicate reference(SR): ground cement + sodium silicate solution (24%)
TEA/Sodium silicate samples (TS): ground cement + sodium silicate solution (24%) + TEA (TEA: cement = 0.002, 0.004, 0.01)

2.4. Preparation of self-healing areas

To evaluate the binding effect, 6 samples hydrated for 7 days at 60 °C were fabricated to ensure accuracy of test results. To ensure similar size of cracks in all samples, the scalpel was used to create approximate 200um wide cracks.

2.5. Characterization

The mineralogical components of the reaction products at given curing periods were studied using X-ray diffraction (XRD, X'Pert Pro, Holland). Scans were carried out from 5 to 70°/2θ, with a step size of 0.0167° and a speed of 0.04988°/s. BET analysis (N_2 adsorption) was employed to investigate the total pore volume and pore size of samples. The samples WR, SR and TS were all was ground and sieved through 70 mesh before XRD and BET analysis. Nanoindentation test (Nanoindenter, G 200, Agilent, USA) was used to characterize the micromechanical properties of hydrated samples (WR, SR and TS). For nanoindentation test, a small cube of size approximately 5 mm × 5 mm × 5 mm was carefully cut out from the middle portion of the specimen, and then was polished by to achieve a smooth surface. The indenter tip in our research is Berkovich indenter.

To explore the extraction efficiency of TEA, the conductivity of saturated $Ca(OH)_2$ aqueous was measured via conductivity meter (DDS-307, Rex Electric Chemical, China) and the pH of oversaturated $Ca(OH)_2$ solution was measured using a pH meter (FE20, Mettler toledo, Shang Hai), which has been also described by Zhang [17].

Digital Microscope (VHX-11, Japan) and SEM were utilized to characterize the morphology of self-healed cracks, and the corresponding components were obtained via Raman spectra (excitation wavelength 532 nm, DXR Microscope, USA). For digital characterization, the sample was observed directly, after that, the samples was coated with platinum for SEM characterization. The self-healed areas of samples without any treatment were characterized by Raman and AFM. AFM (NanoscopeV, Dimension Icon, Bruker, USA) was used to precisely evaluate the topography and elastic modulus of self-healed areas, and accurately determine the micromechanical properties of the newly formed phase in cracks.

3. Results and discussions

3.1. Effects of TEA on C-S-H

3.1.1. XRD measurement

The XRD patterns of simulated C-S-H with and without TEA are presented in Fig. 1, which manifest broad reflections related to the nanosize of the particles. The characteristic reflections attribute to simulated C-S-H are at 7.2°, 29.1°, 31.9°, 49.6°, 55.2° and line up well with published results [20–22]. These peaks are corresponded to the d_{002}, d_{110}, d_{200}, d_{020} and d_{112} reflections [20]. The first reflection in blank C-S-H sample at 7.2° is a sign of 3D ordering. When TEA was added, the hump of 1.2 nm d_{002} at 7.2° disappears, which is ascribed to the rearrangement of simulated C-S-H structure and

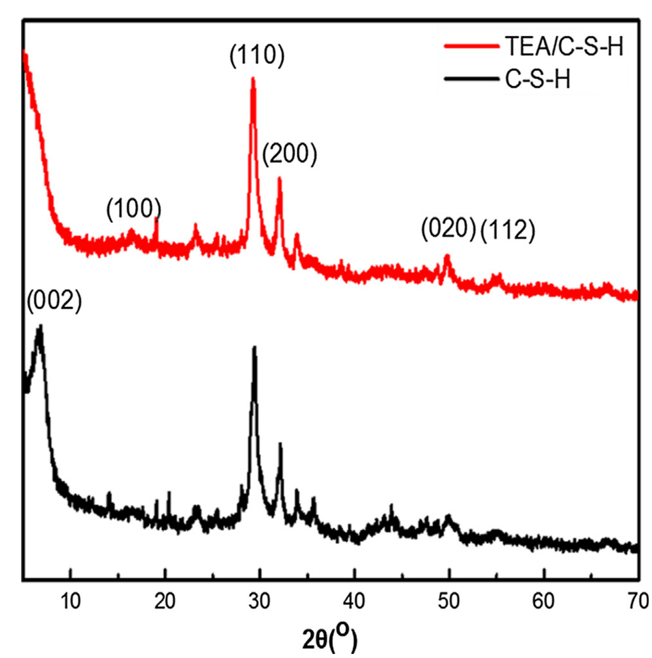

Fig. 1. XRD spectra of stimulated C-S-H with and without TEA.

Table 1
Chemical composition of cement by XRF.

Composite	CaO	SiO_2	Fe_2O_3	SO_3	Al_2O_3	K_2O	MgO	P_2O_5	Loss
Content (%)	71.4	15.2	6.12	2.84	2.09	0.760	0.820	0.540	0.230