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Combined effect of isobutyltriethoxysilane and silica fume on the performance of natural hydraulic lime-based mortars

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HIGHLIGHTS

- Natural hydraulic lime-based mortars were modified by combined use of silica fume and isobutyltriethoxysilane.
- Density, water absorption and shrinkage of modified mortars decreased.
- Pore structure of modified mortars was refined, mechanical and durability properties were greatly improved.
- Silica fume did better in improving mechanical strength while isobutyltriethoxysilane in cohesion and durability properties.
- Combined use of silica fume and isobutyltriethoxysilane made mortars have the best performance.

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ABSTRACT

Natural hydraulic lime (NHL)-based mortars were prepared by introducing isobutyltriethoxysilane (SO) and silica fume (SF) as partial replacement of NHL by percentage of 20%. Main physical, mechanical and durability properties of mortars were evaluated. Compared with control mortars, apparent density, water absorption and shrinkage of modified mortars decreased, mechanical and durability properties were improved. Generally, SF was more effective than SO in improving main physical and mechanical properties of mortars. The reason was attributed to pozzolanic reaction between SF and $Ca(OH)_2$, which generated more hydrate product and refined pore structure. SF modified mortars showed the highest compressive strength (CS). The combined use of SF and SO showed the largest improvement in mortars' flexural strength (FS) and bond strength (BS), for that SO played a bridge coupling role between components in mortars. Durability properties of mortars were greatly improved by the presence of SO and it was related to water repellency of SO. Mortars prepared with SF and SO had the highest durability.

1. Introduction

The employment and development of hydraulic lime mortars has a long history. Their application could date back to Greek and Roman period [1,2]. As the appearance of Portland cement (PC), application of hydraulic lime mortars shrunk, for that setting rate of PC mortars was faster and mechanical strength of PC mortars was higher [3]. Recently, NHL regained wide application because its strength characteristic can meet the lower strength requirement for some construction structures and it has advantages in the repair of old architectures [4–6]. NHL is produced from fired limestone which contains a certain amount of clay impurities below the sintering temperature. It is divided into three classes: NHL2, NHL3.5 and NHL5, based on the $Ca(OH)_2$ content and on the CS developed after 28 days of curing. The scientific research on NHL mainly included NHL-based grout [7–10] and mortars [11–14] in the past decades. Zhou et al. [15] applied NHL in the restoration of rock painting in Guangxi, China. They concluded that NHL-based mortars had good compatibility with restored stone. Relevant study proved that it did not bring soluble salt when NHL was used to restore stones [5]. Ma et al. [16,17] studied on the reinforcement material for the fresco in the humid environment and they concluded that, hydraulicity of burned ginger nut made it a suitable material for the protection for cultural relics in

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humid environment. Hydraulicity characteristics of burned ginger nut were similar to that of NHL.

Recent years, as the demand of cementitious material such as cement and NHL increased, resource and environmental problem brought by their production was increasingly serious [18]. Substitution of cementitious material by certain pozzolan was a feasible method to alleviate above mentioned problem [19,20]. According to previous research, partial substitution of cement by diatomite improved mechanical strength of mortars [21]. However, partial replacement of cement by diatomite reduced mortars' strength according to another research [22]. Some researchers [23,24] improved mortars' mechanical strength by using fly ash as partial replacement of cement. But, Gesoğlu et al. [25] and Rajamma et al. [26] concluded that the use of fly ash as partial substitution of cement led to the decrease of mortars' strength. So, one certain pozzolan was not suitable for all cementitious system and it should be designed and evaluated. Silane, siloxane and tetraethyl orthosilicate were also employed to modify cement mortars. Silane modification can improve the flowability and mechanical strength of cement mortars [27]. CS and sulfate resistance of cement mortars were enhanced by introducing tetraethyl orthosilicate [28]. Collodetti et al. [29] studied the effect of surface modification of nanosilica by siloxane on the hydration of cement mortars. Siloxane modification changed surface functional groups of nanosilica and hydration degree of cement mortars after 100 h was not greatly influenced.

So far, the employment of pozzolan as partial substitution of NHL has been rarely studied. Grilo et al. [30,31] employed metakaolin as partial substitution of NHL and they found that mechanical strength of mortars incorporating metakaolin increased. Mechanical properties, pore structure and durability of NHL-based mortars were improved by using diatomite as partial replacement of NHL. Compared with diatomite, fly ash had faint modification effect and even reduced the strength of mortars [32,33].

SF is a pozzolan containing high active silica. It can effectively modify the interfacial zone between cement and aggregate, thus to enhance mechanical strength and durability of concrete mortars. SF has gained a wide and increasing application recently [34]. But, there was few study and report on modification of NHL by SF. So, in this paper, SF was considered to replace partial NHL.

The aim of the research was to obtain appropriate material for the restoration of earthen structure. In most cases, earthen structure is vulnerable to salt erosion due to iterative dissolution and crystallization of soluble salt, especially sodium sulfate, leading to severe weathering of the structure [35]. Freeze and thaw cycle is another key weathering factor in cold regions and influences life cycle performance of earthen structure. Besides, earthen structure may be attacked by acidic medium such as acid rain, leading to incomplete and unstable state of earthen structure [36]. So, the issues related to above natural weathering must be considered when NHL-based mortars were employed in the repair of earthen structure. All of above mentioned weathering damages require water as medium, water is an important factor for the degradation of porous construction materials [37]. Water repellency should be considered and properly enhanced in the design of mortars. Several kinds of chemicals have been employed to improve waterproof property of concrete mortars, such as silane-siloxane, silicone and silicate. Application of soluble sodium silicate improved permeability, hardness, abrasion resistance and chemical durability of concrete mortars [38]. Hagen [39] applied several kinds of concrete sealers on concrete bridge decks. After 3 years, the field performance of water based silane, solvent based silane and siloxane was better than the others. Besides, corrosion rate of concrete mortars was reduced when silane-siloxane was coated on the surface of concrete [40]. Silane based sealers are called as penetrating sealers. Significant penetration depth could be achieved with sealers of alkoxysilanes while other sealers were hard to penetrate the concrete to measurable extent according to Aitken et al.'s research [41]. Additionally, solvent based silane performed better than soluble reactive silicates in improving chloride permeability property of concrete mortars [42].

Alkyltriethoxysilane was widely used in the surface coating of concrete mortars and generated beneficial protection effect [43,44]. In this paper, one kind of alkyltriethoxysilane (SO) and SF were employed to modify NHL-based mortars. The feasibility of modification by SF and SO was evaluated through testing and comparing physical, mechanical and durability properties of prepared mortars. The mechanism of the property improvement was also proposed and discussed.

2. Materials and methods

2.1. Materials

The binder material used in this paper was NHL2, and it was purchased from Chaux De Saint-Astier Company, France. The mineralogical phases of NHL2 were detected by Rigaku D/max 2200 X-ray diffractometer. Portlandite, dicalcium silicate (C_2S), calcite and quartz are main phases in NHL2. Undensified SF was used in this research and it was supplied by Beijing sino-sina Construction Technology Company. The oxide compositions of NHL2 and SF were obtained by using Philips PW1010 X-ray fluorescence spectrometer and the results were shown in Table 1. SO was supplied by Xinghuo silicone factory in Jiangxi Province, China. Its molecular structure was shown in Fig. 1. The research was carried out on restoration materials for one earthen site structure, so the soil of the earthen structure was used as aggregate. Quartz, albite, chlorite, dolomite, tremolite and calcite were main components in the soil based on XRD results. Fig. 2 depicted its particle size distribution.

2.2. Mortars preparation

In order to preliminarily investigate the modification effect of the sole use of SF, SO, and the combined use of SF and SO, several appropriate formulas were designed shown in Table 2 based on test results from grope experiment. The mortars were named as Blank, SF, SO and SF-SO, respectively. The flow table consistency was determined based on EN 1015-3:1999/A2:2006 and the average value for each mortar was also presented in Table 2.

Ingredients for different mortars in Table 2 were weighed and dry-homogenised in Hobart mixer. Then, required amount of water was added. After that, slow mixing with speed of 62 ± 5 r/min for first 30 s, the aggregate soil and SO was added gradually during second 30 s slow mixing process. Rapid mixing with speed of 125 ± 10 r/min for 30 s and then stop mixing for 90 s. Rapid mixing for another 60 s and then completed the mixing process. The mortar mixtures were compacted by a vibration table operating at 12,000 ± 400 rpm for 1 min. Then, the fresh mortars were molded in prismatic 40 × 40 × 160 mm^3 casts. Mortars were placed in 20 °C and 90% RH for 72 h and then demolded. Curing was carried out in a constant temperature & humidity incubator (20 °C and 70% RH) until the test day.

Table 1
Main oxide compositions (wt.%) of NHL2 and SF.

Material	SiO_2	CaO	Fe_2O_3	Al_2O_3	K_2O
NHL2	15.18	74.42	4.36	2.35	2.28
SF	94.78	0.37	0.56	1.02	1.51

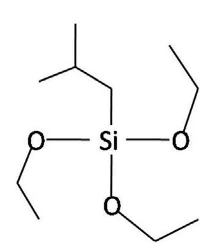

Fig. 1. Molecular structure of SO.