



Influence of C–S–Hs–PCE and Na₂SO₄ on the fluidity and mechanical performance of cement–lithium slag binder

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Abstract Application of C–S–Hs–PCE and sodium sulfate into Portland cement containing 20 wt% lithium slag (LS) powder was investigated, in order to strengthen early mechanical properties. Hydration properties and microstructure of cement–LS system were analyzed. Results showed that C–S–Hs–PCE was advantageous for modifying fluidity of fresh LS–cement binder, while increased dosage of sodium sulfate decreased dispersibility of fresh paste. C–S–Hs–PCE and sodium sulfate exhibited a synergistic effect on strength enhancement, hydration acceleration as well as setting behavior of LS–cement binder. Sodium sulfate increased alkalinity of interstitial solution and promoted dissolution of LS. Dissolved Al and Si from LS powder reacted with dissolved sulfate ions from sodium sulfate to produce extra hydrates, and C–S–Hs–PCE accelerated pozzolanic reaction and hydration reaction via nucleation effect collaborated with dispersing effect. The accelerated

hydration generated more AFt and C–S–H gel in the matrix. Newly formed hydrates promoted exceedingly the appearance of network, leading to a refinement of pore structure as well as enhancement in mechanical strength. Application of LS into cement as a greener binder could be obtained by synergistic adoption of C–S–Hs–PCE and sodium sulfate.

Keywords Lithium slag · Cement · C–S–Hs–PCE · Sodium sulfate · Fluidity · Mechanical strength

1 Introduction

Due to the outstanding electrochemical properties, lithium has been applied widely in glass, pharmaceuticals, ceramic as well as lubrication industries, and demand quantity for lithium salts was continuously expanding recently [1, 2]. During production process of lithium salts, enormous lithium slag (LS) produced from spodumene and lithium mica was emerged as industrial waste material [3–9], and more than 1 million tons of LS was released worldwide annually [4, 7, 10, 11]. The discharged LS was heaped up outdoors, which occupied huge land resources, caused serious waste of natural resources and brought serious pollution [5, 12–15]. With a mass of LS piling up annually, it is urgently vital to explore environmental methods of efficaciously utilizing LS, in order to

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alleviate environmental pressure and achieve sustainable development of lithium industry [3–6, 8, 16, 17].

Recently, LS has been widely investigated to explore the possibility of adopting in cement and concrete to achieve the recycling of resources and benefits [3, 5, 8, 10, 11, 13, 18–22]. LS contained higher than 80 wt% of SiO_2 and Al_2O_3 , more than 6 wt% of SO_3 and a spot of CaO and Fe_2O_3 [2, 17, 20, 23]. Crystalline minerals in LS included quartz (SiO_2), leached spodumene ($\text{LiAlSi}_2\text{O}_6$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [12, 14]. In this way, LS was a potentially reactive waste material, which could be utilized as SCMs to meet the huge demand of the cement industry and bring significant environmental as well as economic benefits [4, 5, 8, 10, 12–15, 24, 25]. A high amount of SiO_2 and Al_2O_3 existed in LS would react with portlandite (CH) to produce extra non-crystalline C–S–H [12, 18], which optimized the hydration mechanism as well as microstructure of cement, and improved mechanical as well as durability properties [5, 7, 14, 18, 19]. It has been widely admitted that application of SCMs to replace cement could obviously reduce CO_2 emission by higher than 40% [26, 27], along with reduction in energy consumption as well as natural raw materials consumption.

Noticeably, LS contained abundant zeolites, and possessed glassy pore structure with high internal surface area [2, 9, 28]. The application of LS would have a remarkable negative impact on workability, and lead to a slow early strength development and prolonged setting time [5, 22, 29, 30]. To achieve higher early strength, previous scholars have done a lot of improvement works. The reactivity of LS could be enhanced via curing at high temperature [10, 14], grinding to be finer particles [3, 18, 31] or utilizing chemical activators [5, 20, 22, 29]. Overall, the application of early strength agent is recognized as the most effective technology for enhancing early strength [32, 33], among which sodium silicate, sodium hydroxide, sodium sulfate and other alkali compounds were widely adopted as chemical additives [34–37]. However, sodium silicate, sodium hydroxide and other traditional alkaline activators represented obvious energy depletion and possessed a substantial CO_2 footprint [38–40]. By far, sodium sulfate was considered as the most widely used accelerator. Compared to conventional activators, sodium sulfate was a safe, cheap, environmentally

friendly, and water-soluble inorganic mineral, which can be found in the nature or in the industrial production [26, 41, 42].

It has been reported that sodium sulfate can improve alkalinity for accelerating release of active Al_2O_3 and SiO_2 from SCMs to form extra hydrates [43–45]. The addition of sodium sulfate boosted hydration and early-age strength development of fly ash–cement binder, and the mechanical strength did not reversal at later ages [45–48]. Generally, the presence of sodium sulfate as an activator could raise the content of sulfate ions and correspondingly promote the production of AFt [49]. The formation of additional AFt would lead to microstructure densification as well as strength enhancement. Moreover, increased content of sodium sulfate yielded higher dissolution of minerals and correspondingly increased the activation [41, 43]. However, it has been found that setting times of binders admixed with sodium sulfate were found to be shorter, compared with those activated with sodium silicate or sodium hydroxide. It has also been found that sodium sulfate could strengthen the retarding effect of retarders [50]. Sodium sulfate delayed the hydration of C_3A , decreased the production of AFt, and decreased the adsorbing capacity of retarder molecules on surfaces of cement particles [50]. It has been reported that slag cement activated by sodium sulfate had higher mechanical strength of hardened paste than that activated by sodium hydroxide [51]. Sodium sulfate added to different mixtures might vary in its function, as has been reported that sodium sulfate could enhance mechanical strength of alite paste, while results in Portland cement paste might differ. Moreover, sodium sulfate adopted into slag–cement binder might heighten [52] or decrease [53] the mechanical strength. Acceleration seemed slow because the initial pH value was low [54, 55]. Recent researches have also shown that the performance of sodium sulfate as an activator was further enhanced when it was simultaneously utilized with nano/micro silica in fly ash–cement composite binder [43, 46]. Nevertheless, there existed few researches on activation mechanism of sodium sulfate, and hence, it was vital to conduct more researches in this field.

Except chemical accelerators, nanoparticles serving as nuclei seeds, including nano SiO_2 [56–58], nano TiO_2 [56–62], nano ZnO [59, 61], nano Fe_2O_3 [58], nano CaCO_3 [56, 57], carbon nanotubes (CNTs) [60]



and calcium silicate hydrate seeds (C–S–Hs) [43, 63–74] recently have been adopted to improve mechanical strength of cementitious materials. Nanoparticles could serve as nucleation seeds to boost hydrates formation at the early age, and nanoparticles with lower particle size and similar chemical compositions to hydrates had greater potential to be adopted as early-strength agents in cementitious materials. Therefore, there existed an elevated interest in analyzing synthetic C–S–Hs as an accelerating agent during the past decade, due to the economic and environmental benefits [63, 68, 70, 71, 73–76]. C–S–Hs would serve as heterogeneous nucleation sites for hydration products, beneficial for seeding in facilitation of hydration kinetics through expedited nucleation and growth of hydrates, and thus efficaciously promoted cement hydration to produce hydrates [43, 70, 72, 74, 75, 77]. C–S–Hs not only reduced or even eliminated the induction period through homogeneous nucleation effect, but also provided excellent physical filling effect. Particularly, the superiority of C–S–Hs in comparison with traditional accelerators is that it did not compromise long-term performance of hydrated matrix [67, 73, 78].

However, the accelerating efficiency of C–S–Hs was highly impaired due to the agglomeration. In order to regulate dispersion retention behavior of C–S–Hs, polycarboxylate (PCE) superplasticizer was injected to the co-precipitation methods [64, 68–70]. C–S–Hs stabilized by PCE showed low aggregation [79]. Finer sized and more stable C–S–H nanoparticles with higher surface area and low aggregation could be generated [68, 78–80]. Moreover, PCE remarkably delayed the transformation of C–S–H from globular to nanofoil-like, and maintained nucleation productivity of C–S–H [66, 68–70]. Applying well-dispersed nano-sized C–S–Hs would obviously expedite hydration kinetics and increase mechanical strength [71, 74–76]. C–S–Hs reduced the free activation energy of hydration crystallization to zero, and multiplied hydration formation on clinker and C–S–Hs surface, which declined the hydrates layer thickness and increased ion concentration gradient [69, 70, 74]. Furthermore, C–S–Hs could not only promote hydration of silicates in clinker [81, 82], but also accelerate pozzolanic reaction of fly ash [68], metakaolin [82], blast furnace slag [80, 83], calcined clay [80]. However, up to now researches into adoption of C–S–Hs–PCE to generate

strength enhancement of LS-cement binder remained scarce.

In spite of increased analytical results with regard to hydration of composite cement in the function of different acceleration methods, researches concentrating on combined action of sodium sulfate and C–S–Hs–PCE on performances of LS blended cement merited investigation. Simple utilization of chemicals or nanoseeds was difficult to obtain high enough mechanical strength at early stage [43]. It was vitally important to excavate highly-efficient and environmentally friendly early-age strength enhancement method of LS-cement composite binder.

The primary purpose of this study was to enhance mechanical strength of cement-LS system by incorporating C–S–Hs–PCE and sodium sulfate. Mortars and pastes containing 20% LS and different dosages of C–S–Hs–PCE and sodium sulfate were prepared. Fluidity, setting time and mechanical strength were investigated, and multiple techniques were applied to reveal underlying mechanism in detail. The main results of this investigation would provide scientific guidance for the preparation of LS-based cementitious materials.

2 Experimental

2.1 Materials

PII52.5 Portland cement was supplied by Anhui Hailuo Cement Company, and LS was provided by Jiangxi Lithium Company. The chemical compositions of cement and LS are shown in Table 1. LS was ground for 10 min via a ball mill. The volume average size (d_{50}) of cement and LS were 16.54 and 11.08 μm , respectively. LS particles were mainly in the form of crushed stone, and a small amount of rod-like crystals can be seen. Mineral compositions of LS powder were mainly lithopone, quartz and gypsum, and their contents were respectively 63.4%, 8.5 and 12.5% analyzed via XRD/Rietveld methods.

Chemical reagent sodium sulfate, calcium nitrate, and sodium hydroxide were provided by Chinese Sinopharm Chemical Reagent Co., Ltd. Methyl allyl polyethenoxy ether, acrylic acid, ammonium persulfate and thiohydracrylic acid used for the synthesis of PCE polymer were provided by Sanrui Polymer Materials Co., Ltd.



2.2 Mix proportion and sample preparation

Blended binders contained 80 wt% PII52.5 cement and 20 wt% LS. Samples for hydration analysis as well as compressive strength measurement were prepared following former reports [63, 66, 84–86]. Sodium sulfate and C–S–Hs–PCE suspension were dissolved in deionized water. Cement-LS binder was mixed at W/B of 0.29, and cement-LS mortars were prepared at a ratio of water to binder of 0.5, and a ratio of binder to sand of 1:3 (as shown in Table 2).

For ion dissolution analysis, pore solutions with various dosages of C–S–Hs–PCE and sodium sulfate were firstly prepared following Table 3. And then 3.0 g LS powder was mixed with these solutions. The suspensions were sealed and cured at $(20 \pm 1)^\circ\text{C}$, and then separated by centrifugation at 3000 r/min for 3 min. The supernatant was filtered, and 10 mL of each sample was adopted for ICP measurement [87].

2.3 Test procedure

Setting time of composite binders was measured by Vicat apparatus following Chinese Standard GB/T 1346–2011 [66, 88]. The fluidity of fresh binder was measured via a mini-slump cone (a height of 60 mm, upper diameter of 36 mm and a bottom diameter of 60 mm), according to Chinese standard GB/T 8077–2000. Compressive strength was measured following GB/T 17671–2021 [89]. Mortars of 40 mm \times 40 mm \times 160 mm were prepared for compressive strength measurement. The specimens were cured at $20 \pm 1^\circ\text{C}$ and $95 \pm 5\%$ RH. At the ages of 12 h, 1d, 3d and 28d, the compressive strengths of mortar were measured [90–94].

Ion dissolution was tested via inductively coupled plasma (ICP). The mix proportion of pore solution as well as the sample preparation has been expatiated in Sect. 2.3. The concentrations of Si^{4+} , Al^{3+} , Fe^{3+} and Ca^{2+} in the upper solution were measured [8, 87].

Table 1 Compositions of cement and LS (wt%)

| Oxide | CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | SO ₃ | TiO ₂ | K ₂ O | Li ₂ O | F | MnO | Na ₂ O |
|--------|-------|------------------|--------------------------------|--------------------------------|------|-----------------|------------------|------------------|-------------------|------|------|-------------------|
| Cement | 61.43 | 20.92 | 6.44 | 3.12 | 1.08 | 2.19 | 0.30 | 0.88 | – | – | – | – |
| LS | 4.45 | 48.19 | 16.35 | 0.67 | 1.35 | 3.88 | – | 8.15 | 0.74 | 4.96 | 0.45 | 6.95 |

Table 2 Mass percentage of cement, LS, C–S–Hs–PCE and sodium sulfate of pastes and mortars

| Sample | C/g | LS/g | W/g | C–S–Hs–PCE/g | Na ₂ SO ₄ /g |
|--------|-----|------|-----|--------------|------------------------------------|
| N0-0 | 80 | 20 | 29 | 0 | 0 |
| N0-1 | 80 | 20 | 29 | 0 | 1 |
| N0-2 | 80 | 20 | 29 | 0 | 2 |
| N1-0 | 80 | 20 | 29 | 1 | 0 |
| N1-1 | 80 | 20 | 29 | 1 | 1 |
| N1-2 | 80 | 20 | 29 | 1 | 2 |
| N2-0 | 80 | 20 | 29 | 2 | 0 |
| N2-1 | 80 | 20 | 29 | 2 | 1 |
| N2-2 | 80 | 20 | 29 | 2 | 2 |

Hydration heat evolution was tested via TAM Air isothermal calorimeter (3114/3236 TAM 83), and hydration products of composite binder were analyzed by XRD [84, 95, 96]. Microstructure observation was observed via SEM [97, 98].

3 Results

3.1 Fluidity

Fluidity of cement-LS fresh binder were measured (shown in Fig. 1). In comparison with reference sample, increased dosage of C–S–Hs–PCE led to improved fluidity of fresh LS-cement paste. This might be ascribed to physically adsorbed PCE onto C–S–H seeds, which dissolved into pore solutions and then adsorbed onto mineral surfaces and modified the dispersity of fresh paste. This inferred that C–S–Hs–PCE was advantageous for modifying the workability of fresh binder, which was essentially different from those traditional nanoparticles, such as nano SiO₂, nano CaCO₃, et al. And this finding was coincident with previous reports. Plank et al. [68] and Sun et al.



Table 3 Mix proportions of ion dissolution measurement

| No | Deionized water/g | Ca(OH) ₂ /g | C–S–Hs–PCE/g | Na ₂ SO ₄ /g | LS/g |
|------------------------------|-------------------|------------------------|--------------|------------------------------------|------|
| P1 (supersaturated CH) | 1000 | 40 | 0 | 0 | 30 |
| P2 (1% C–S–Hs–PCE) | 1000 | 0 | 10 | 0 | 30 |
| P3 (1% C–S–Hs–PCE-20 g/L SS) | 1000 | 0 | 10 | 20 | 30 |

[82] have also affirmed that C–S–Hs–PCE could raise fluidity of fresh paste as well as the slump of fresh concrete. As a leaching residue [1, 10, 12, 23], LS contains a substantial zeolites and has a large internal surface area as well as porous structures [4, 5, 10, 17, 18, 22, 25, 29], and is obviously disadvantageous for dispersing of fresh binder. C–S–Hs–PCE was advantageous for modifying fluidity of fresh LS-cement binder. According to the fabrication process, PCE polymer and C–S–H seeds are physically combined, and plentiful amount of PCE would dissolve into pore solution during stirring fresh binder. The dissolved PCE adsorbed onto positive-charged surface through electrostatic attraction [99], and adsorb onto negative-charged surface via bridge effect of Ca²⁺ ions [86, 91, 92, 94, 100–102]. The larger adsorption amount of PCE onto cement as well as LS surfaces brings about higher dispersibility of fresh binder.

However, the addition of sodium sulfate performed a negative role in improving fluidity of LS-cement paste. Increased dosage of sodium sulfate intensified the negative effect on fluidity. When 1% C–S–Hs–PCE was added into LS-cement blended binder, the increased content of sodium sulfate (from 0 to 2%) gradually decreased the fluidity of the fresh binder. Similarly, with 2% C–S–Hs–PCE added into composite binder, increased dosage of sodium sulfate gradually led to decreased fluidity. We can also observe that the increased dosage of sodium sulfate led to the loss of consistency rapidly and the form of denser matrix.

3.2 Mechanical strength

Compressive strengths of hardened LS-cement composite mortars were tested (Fig. 2). In comparison with reference (N0-0), compressive strength increased observably with increased dosage of C–S–Hs–PCE

adopted. With the dosage of C–S–Hs–PCE increased from 0 to 2%, compressive strengths at 12 h, 1d, 3d and 28d increased respectively by 38.5%, 67.0%, 5.8%, and 6.2%. This indicated that C–S–Hs–PCE promoted the mechanical strength enhancement especially at early ages. C–S–Hs–PCE promoted hydration evolution ascribing to nucleation effect [63, 65, 66, 68–70, 80] as well as dispersing behavior of PCE superplasticizer [84, 92, 103–106], which contributed to intensified formation of hydrates and compacter microstructure [107].

The increased content of sodium sulfate also promoted the enhancement of compressive strength of LS-cement binder, especially early-age strength (at 12 h, 1d and 3d). With 2% sodium sulfate adopted, compressive strength at 12 h, 1d and 3d increased respectively by 28.8, 51.8 and 20.9% relative to the control sample (N0-0), while compressive strength at 28d did not increase. Sodium sulfate could react with CH to produce CaSO₄·2H₂O, and a great deal of AFt crystals were produced by rapid reaction of highly dispersed CaSO₄·2H₂O with C₃A, leading to development of early-age strength [63]. Indeed, as reported in previous studies, sodium sulfate would reduce late hydration rates and hence decrease late age strengths [41].

Moreover, the synergistic adoption of C–S–Hs–PCE and sodium sulfate was also analyzed. With union usage of 1% C–S–Hs–PCE and 1% sodium sulfate, compressive strength exceeded that of only adopting 1% C–S–Hs–PCE as well as that only adopting 2% C–S–Hs–PCE. And with the increased dosage of both sodium sulfate and C–S–Hs–PCE, compressive strengths increased obviously. The compressive strengths of LS-cement binder with adoption of 2% C–S–Hs–PCE and 2% sodium sulfate were enhanced by 69.2, 91.8, 48.3, and 15.2% at 12 h, 1d, 3d and 28d. The compressive strength of all mortars enhanced over time, and enhancement effect of C–S–



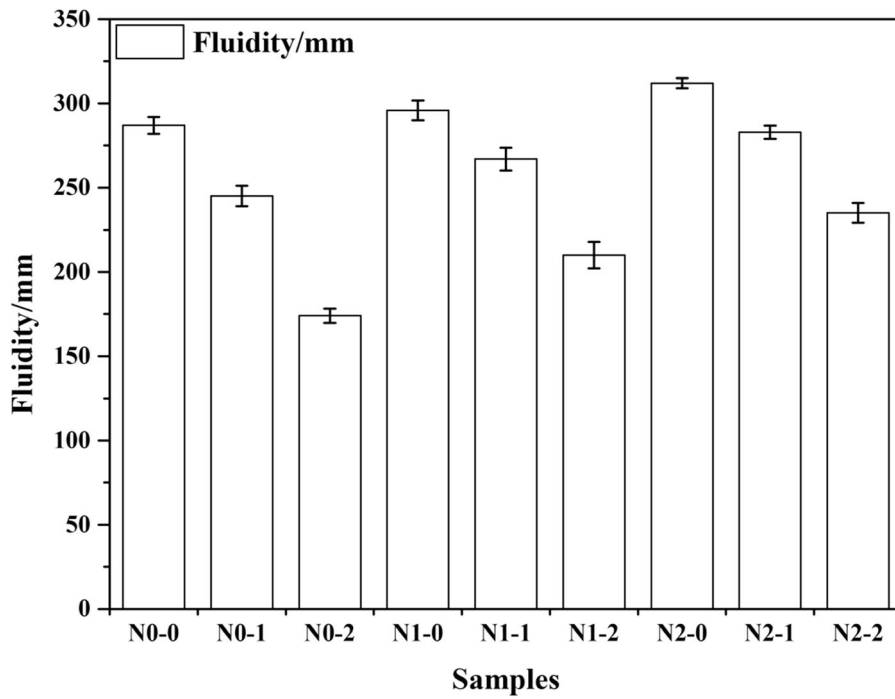


Fig. 1 Fluidity of fresh LS-cement blended binder

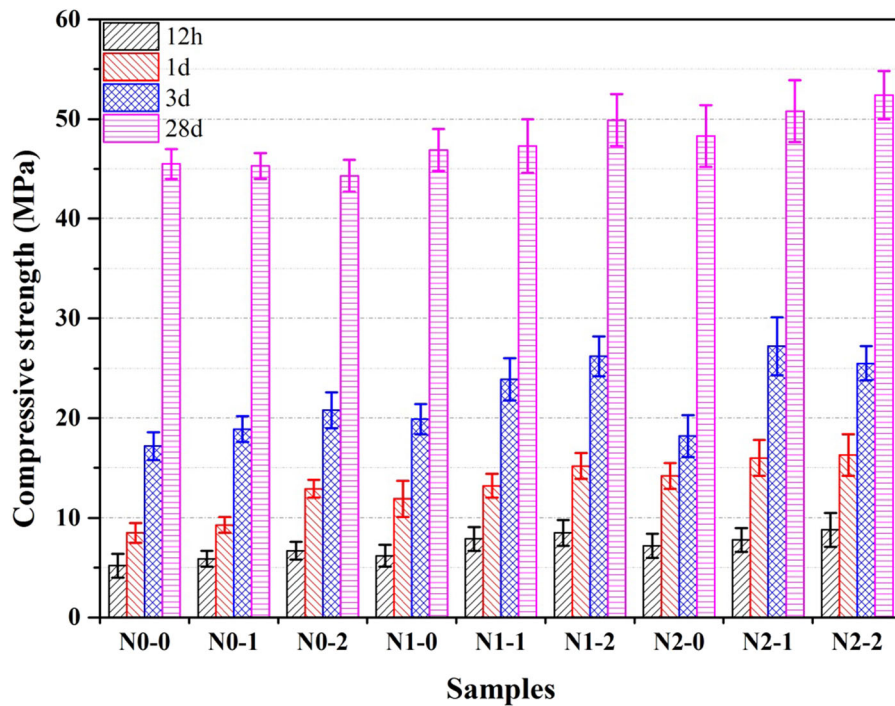


Fig. 2 Compressive strengths of LS-cement composite mortar



Hs–PCE and sodium sulfate on compressive strength was obviously overt, in comparison with simply adopting C–S–Hs–PCE or sodium sulfate. This indicated that combined usage of C–S–Hs–PCE and sodium sulfate exhibited a synergistic effect on strength enhancement of LS-cement binder.

3.3 Hydration heat

Hydration heat evolution of LS-cement composite binder was analyzed (Fig. 3), which supplied high resolution information concerning influences of C–S–Hs–PCE and sodium sulfate on hydration progression of LS-cement binder.

Binders that differed in dosages of C–S–Hs–PCE and sodium sulfate exhibited various heat flows and hydration heat over 72 h. All the binders presented massive heat flow at the very beginning, ascribing to rapid dissolution of minerals and rapid reaction of aluminates. After induction period, the secondary exothermic peak was ascribed to the silicate reaction. C–S–Hs–PCE (see N1-0, N2-0) remarkably affected the secondary exothermic peak (see Fig. 3a), showing as elevated exothermic peak, suggesting C–S–Hs–PCE would effectively enhance hydration of silicates. This was in agreement with previous reports that C–S–Hs–PCE accelerated cement hydration [69, 80, 108].

As shown in Fig. 3a, C–S–Hs–PCE and sodium sulfate had obvious influence on the nucleation of hydrates during acceleration period. With addition of C–S–Hs–PCE and sodium sulfate, the second hydration peak was shifted to earlier time and the introduction period was cut down obviously, shown as larger and earlier hydration peaks, which was also proved by increased cumulative hydration heat (exhibited in Fig. 3b). And with increased content of C–S–Hs–PCE and sodium sulfate, the introduction period dramatically shortened, and the slope of the acceleration period increased. The slope of acceleration period was highest for N2-2 sample (2% C–S–Hs–PCE and 2% sodium sulfate), indicating that early hydration rate and hydration heat release were prodigiously enhanced. The diffusion rate of various ions from minerals was boosted by the addition of C–S–Hs–PCE and sodium sulfate. Moreover, we can also find that the slope of the acceleration period for N1-2 (1% C–S–Hs–PCE and 2% sodium sulfate) was higher than that for N2-0 (2% C–S–Hs–PCE and 0% SS). This indicated that the combined adoption of C–S–Hs–

PCE and sodium sulfate would significantly promote formation of hydrates, in comparison with simple usage of C–S–Hs–PCE.

From Fig. 3b, union application of C–S–Hs–PCE and sodium sulfate boosted cumulative heat flow. Before 24 h, LS-cement binder added with 1% C–S–Hs–PCE and 2% sodium sulfate generated higher cumulative hydration heat than that only admixed with 2% C–S–Hs–PCE or synergistically adopted with 2% C–S–Hs–PCE and 1% sodium sulfate. However, after hydrating for 72, LS-cement binder admixed with 2% C–S–Hs–PCE or applied with 2% C–S–Hs–PCE and 1% sodium sulfate generated higher cumulative hydration heat than that admixed with 1% C–S–Hs–PCE and 2% sodium sulfate. Indeed, differences in cumulative hydration heat amount increased further and greater plateauing of heat production was evident. This indicated that a high amount of sodium sulfate would be beneficial for the very early-age hydration, while increased dosage of C–S–Hs–PCE would be propitious to boost later-age hydration.

3.4 Setting time

Effect of synergistic adoption of C–S–Hs–PCE and sodium sulfate on setting behavior was analyzed (Fig. 4).

From Fig. 4, C–S–Hs–PCE and sodium sulfate altered setting behavior, highly correlated with their dosages. Simply adding sodium sulfate or C–S–Hs–PCE into LS-cement composite binder shortened the setting time. And increased dosage of sodium sulfate or C–S–Hs–PCE gradually cut down initial setting time and final setting time. With 1% C–S–Hs–PCE added into LS-cement binder, increased dosage of sodium sulfate from 0 to 2% shortened initial setting time by 31.8%, and shortened final setting time by 18.6%. With 2% C–S–Hs–PCE added into LS-cement binder, increased content of sodium sulfate from 0 to 2% shortened the initial setting time by 52.1%, and shortened final setting time by 48.3%. In comparison with simply adding sodium sulfate or C–S–Hs–PCE, union adoption of C–S–Hs–PCE and sodium sulfate presented enhanced acceleration on setting behavior.

3.5 Hydration products

From XRD patterns in Fig. 5, hydrates of blended binder were analyzed, with phases such as C_3S or C_2S



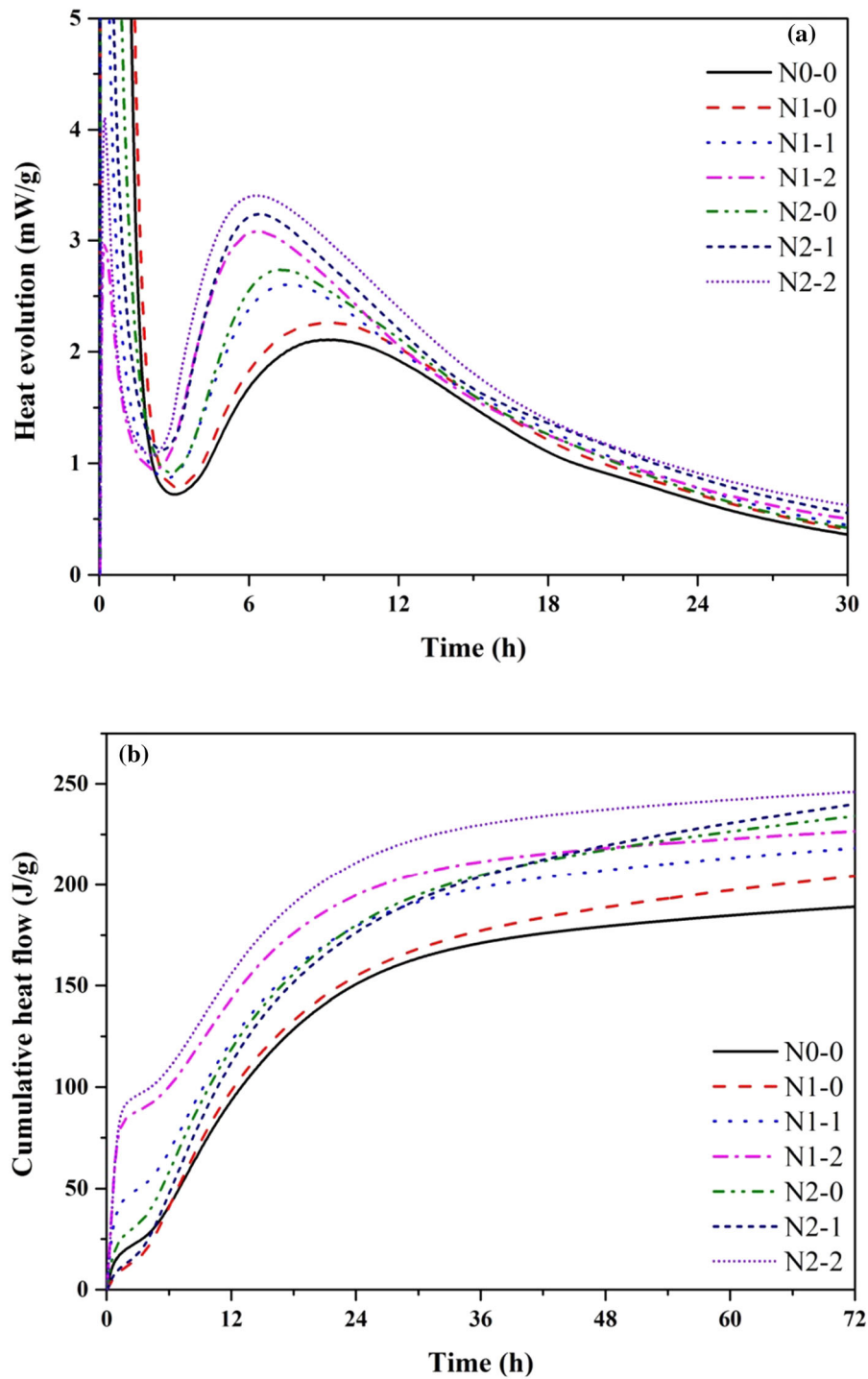


Fig. 3 Hydration heat of LS-cement blended binder



consumed and new phases formed, like CH, AFt. At early ages (1d, 3d, and 7d), compared to reference sample (N0-0), adding C–S–Hs–PCE affected intensity of characteristic peaks of CH, C_3S and AFt. With increased dosage of C–S–Hs–PCE, the intensity of characteristic peaks of CH enhanced remarkably, and the intensity of characteristic peaks of C_3S reduced gradually, which was possibly a consequence of a more effective reaction of cement and regarded that the hydration of cement clinker was accelerated by C–S–Hs–PCE at early age. This agreed with previous reports that C–S–Hs–PCE could facilitate hydration of C_3S [66, 69].

At 28d, intensity of CH peak decreased with increased dosage of C–S–Hs–PCE (see sample of N1-0, N2-0), suggesting enhanced pozzolanic reaction was developed between CH and dissolved silicon and aluminum species from LS, producing extra C–S–H gel. This was because at later age pozzolanic reaction between LS and CH took place, and C–S–Hs–PCE boosted pozzolanic reaction of LS, resulting in a decreased amount of CH formed in the hydrated matrix.

The peak intensity of AFt was augmented significantly by adoption of sodium sulfate. When C–S–Hs–

PCE content was fixed at 1%, with the increased dosage of sodium sulfate (from 0 to 2%), the appearance of AFt peak was observed to be gradually obvious. It was deduced that sodium sulfate expedited production of AFt. The same results were observed for samples containing 2% C–S–Hs–PCE. This indicated that sodium sulfate promoted formation of AFt, and this result was coincident with previous researches [5, 87, 109]. Moreover, at early ages (1d, 3d and 7d), with sodium sulfate incorporated in the binder, the intensity of CH peak increased, indicating enhanced hydration of Portland cement. And the intensity of AFt enhanced, due to the fact increased formation of CH would react with sodium sulfate to produce gypsum as an intermedium reaction product, which then reacted with aluminates from Portland cement or aluminum ions from LS to form additional AFt crystals.

3.6 Reaction of LS

After LS was soaked in various solutions, concentrations of Al and Si were tested (Fig. 6). Compared with CH solution, concentrations of Al and Si in 1% C–S–Hs–PCE solution reduced ascribing to nucleation effect of C–S–Hs–PCE, which facilitated depletion

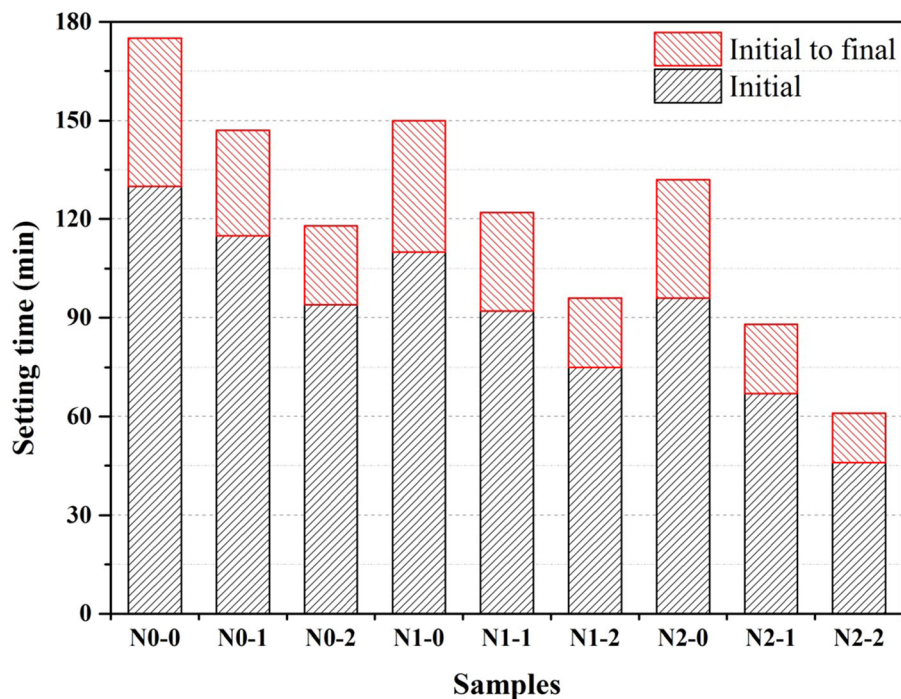
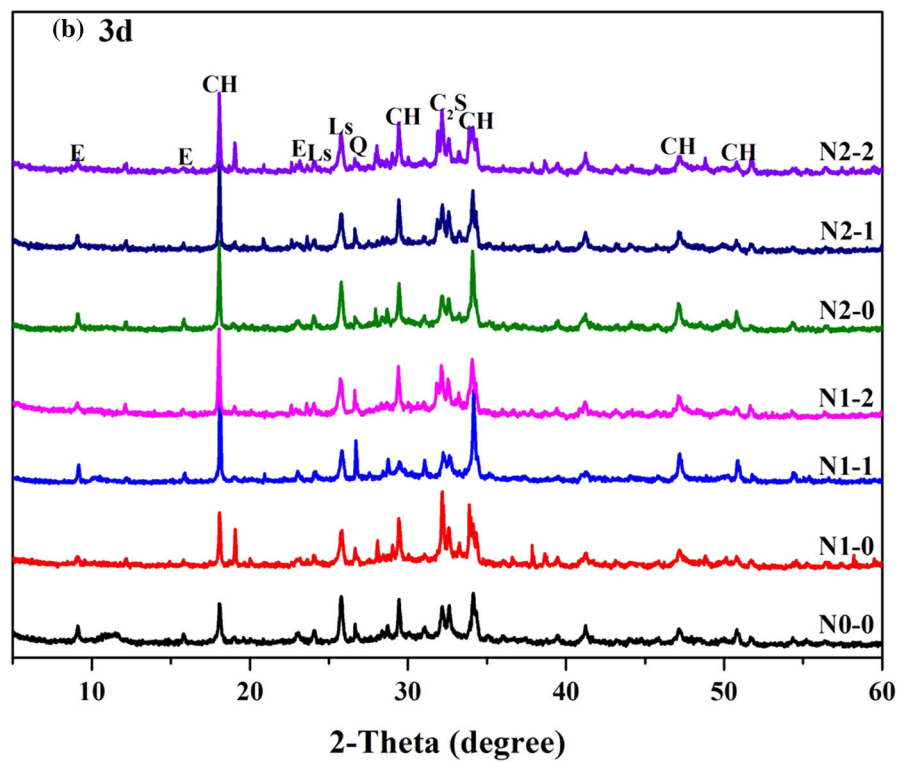
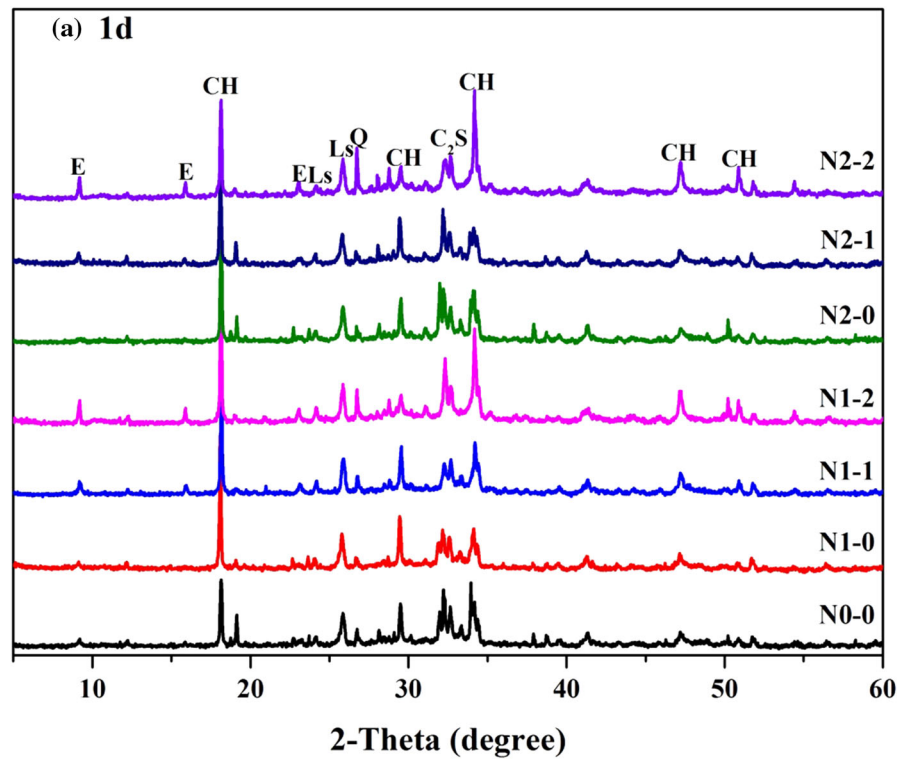


Fig. 4 Setting time of LS-cement blended binder

Fig. 5 XRD patterns of hydrated LS-cement binder



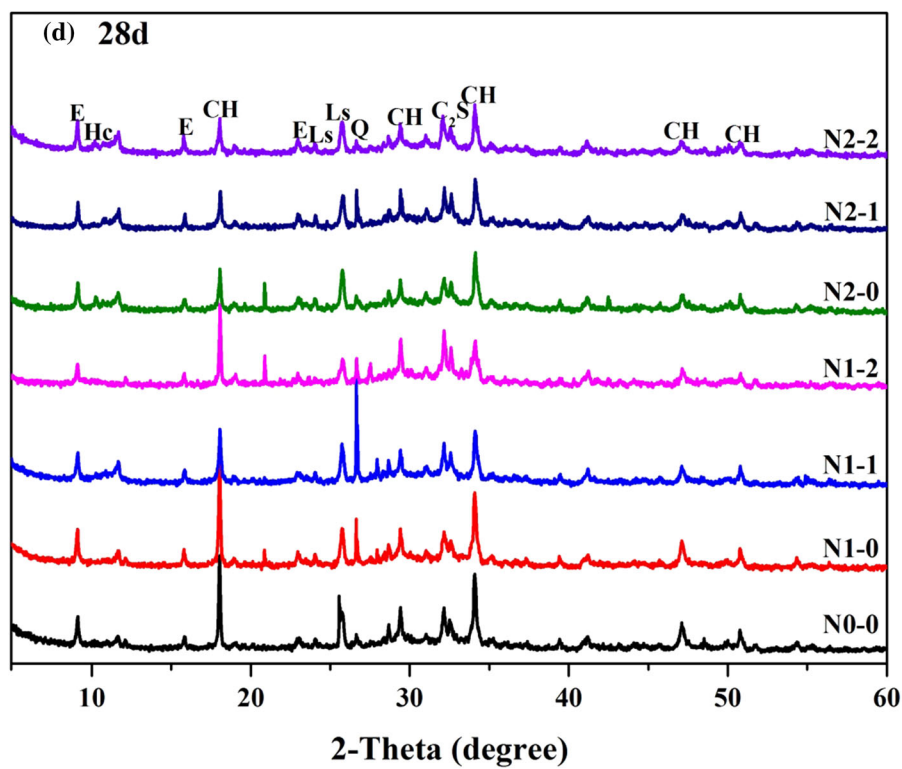
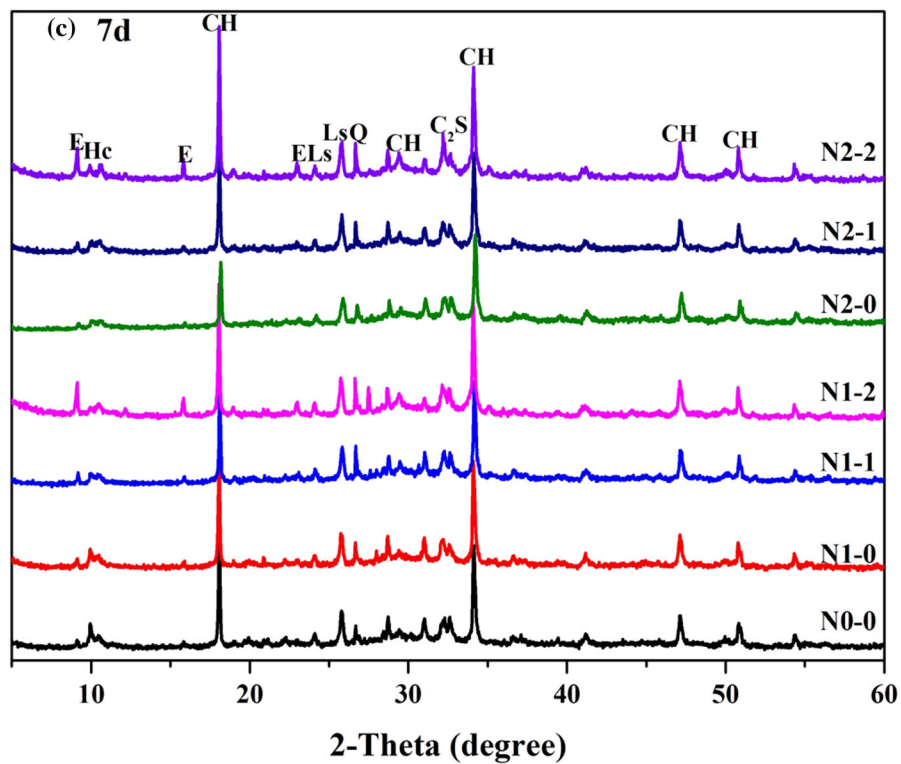


Fig. 5 continued

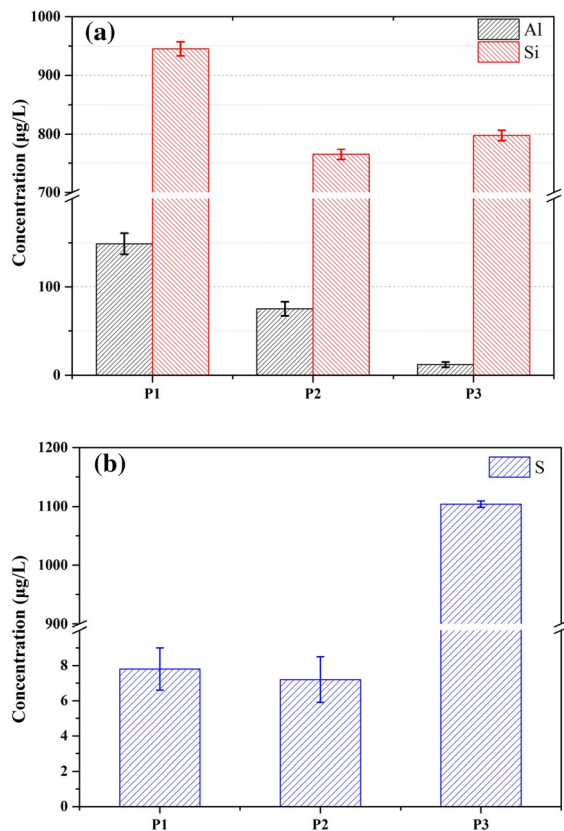


Fig. 6 Element concentrations, i.e. P1: supersaturated $\text{Ca}(\text{OH})_2$ solution; P2: 1% C–S–Hs–PCE solution; P3: 1% C–S–Hs–PCE–2% SS

of free Al and Si. Moreover, concentrations of Al and Si in 1% C–S–Hs–PCE mixed with 2% sodium sulfate decreased further. Because adding sodium sulfate enhanced the alkalinity in solution, dissolution of Al and Si from LS minerals increased at early ages. And then, sulfate ions (SO_4^{2-}) would react with Al to produce AFt and the freshly generated AFt might also act as seeding sites for the production of C–(A)–S–H, leading to reduced content of free Al and Si in interstitial solution. The lowest content of Si and S appeared in the 1% C–S–Hs–PCE–2% sodium sulfate solution, due to boosted depletion of free Al and S due to cooperative effect of sodium sulfate and C–S–Hs–PCE. Because of a high amount of sulfate ions provided by sodium sulfate, the dissolved Al^{3+} from LS reacted with sulfates to form AFt, which led to accelerated consumption of Al^{3+} .

4 Conclusions

In this paper, synergistic effect C–S–Hs–PCE and sodium sulfate on LS-cement binder was analyzed. The setting behavior, dispersing performance, mechanical strength, and hydration evolution of blended binder were evaluated. The main conclusions are shown below:

- (1) The addition of C–S–Hs–PCE is advantageous for modifying fluidity of fresh LS-cement binder, while increased dosage of sodium sulfate decreased fluidity of fresh paste. Compressive strength increased observably with increased dosage of C–S–Hs–PCE adopted. The union usage of C–S–Hs–PCE and sodium sulfate exhibited a synergistic effect on strength enhancement of LS-cement binder. Combined adoption of 1% C–S–Hs–PCE and 1% sodium sulfate generated higher compressive strength than simply admixing 1% C–S–Hs–PCE or simply admixing 2% C–S–Hs–PCE.
- (2) C–S–Hs–PCE and sodium sulfate advanced the hydration of LS-cement binder, shortened introduction period, advanced acceleration period and cut down setting time. Synergistic adoption of sodium sulfate and C–S–Hs–PCE presented enhanced shortening effect on setting time.
- (3) Combined adoption of C–S–Hs–PCE and sodium sulfate significantly promoted generation of C–S–H gel and CH than the application of simple usage of C–S–Hs–PCE, shown with enhanced cumulative hydration heat release. A high amount of sodium sulfate would be beneficial for the very early-age hydration, while increased dosage of C–S–Hs–PCE would be propitious to promote later-age hydration.
- (4) The addition of sodium sulfate increased alkalinity of interstitial solution and promoted the dissolution of LS. The free Al and Si from dissolution of LS reacted with dissolved SO_4^{2-} ions from sodium sulfate to produce hydrates.

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