



Influence of alkali sulfates in clinker on the hydration and hardening of Portland cement

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HIGHLIGHTS

- The effects of alkali sulfate on cement hydration and hardening were studied.
- The adverse effect of alkali sulfate originated from clinker is significantly.
- The $\text{Na}_2\text{O}_{\text{eq}}/\text{SO}_3$ molar ratio in cement is better <0.5 for good properties.
- Ca-langbeinite could play a good role as gypsum in mortar.

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ABSTRACT

Alkali sulfates originate from cement clinker, occurring as arcanite (K_2SO_4), thenardite (Na_2SO_4), apthitalite (K_3NS_4) and Ca-langbeinite (KC_2S_3). The impacts of alkali sulfates, prepared through high temperature heating in the laboratory, on cement hydration and hardening properties were studied. Results show that the initial setting time would not significantly shorten or extend with the increase of alkali sulfates/ SO_3 molar ratio. Alkali sulfates cannot promote 1 d compressive strength, and result in significantly linear decrease of 28 d compressive strength and increase of drying shrinkage with increasing of the molar ratio of $\text{Na}_2\text{O}_{\text{eq}}/\text{SO}_3$. The adverse effect of alkali sulfate on cement hydration and hardening properties is significant, and the content is better less than 0.5 of $\text{Na}_2\text{O}_{\text{eq}}/\text{SO}_3$ molar ratio. Ca-langbeinite in cement slightly decreases compressive strength and increases drying shrinkage, but can replace gypsum to play a good role in cement. Besides, it is found that alkali sulfates would promote the growth of C-S-H and portlandite during cement hydration.

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1. Introduction

Sulfate, a minor but important component, in Portland cement plays a significant role in cement concrete. The reaction of sulfate in cement with calcium aluminate affects the setting time, fluidity, compressive strength, volume stability and durability [1,2]. Adequate sulfate in cement would be beneficial to the setting time, development of compressive strength and volume stability. However, a high content of sulfate in cement would result in expansion or destructive behavior of concrete, induced by the delayed ettringite formation (DEF) which was reported on heat-cured concretes [3,4], the recrystallization of calcium sulfate [5], and the formation of thaumasite which was reported on carbonated concrete at low temperatures [6,7]. The phase and content of sulfate in cement also affect the compatibility between cement and superplasticizers

with respect to the problems of quick stiffness, variation of initial slump and large slump loss occurred in concrete production [8–10].

As one of the most variable components, sulfate in cement derives from clinker, added gypsum and supplementary materials. Researchers have paid much attention on the content of gypsum as well as its impact on cement hydration and hardening properties, but less attention on the content and impact of sulfate phases originated in cement clinker. It has been recognized that sulfate in Portland cement clinker occurs as alkali sulfates including arcanite (K_2SO_4), thenardite (Na_2SO_4), apthitalite (K_3NS_4) and Ca-langbeinite (KC_2S_3), as a substitute in major phases of silicates and aluminates, along with anhydrite [11,12]. The amount of SO_3 both in alite and belite is low, less than 0.3%. The amount of sulfate in the aluminates and ferrites is quite small and probably ignored [13]. The existence of anhydrite was disputed, and at a low amount if presents [14]. Alkali sulfate is the main sulfate phase in cement clinker, at an amount of typically between 0.5% and 1%

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SO₃ [15,16]. The use of alternative fuels is responsible for the increase in alkali sulfates in clinker. Even though lower content and less importance than added gypsum, alkali sulfate from clinker is still an important sulfate and alkali phase in cement, leading to sensitive and important effects on the properties of cement concrete [17].

An addition of reagent-grade K₂SO₄ or Na₂SO₄ was typically used for investigating the role of alkali sulfates in cement hydration and hardening in previous works [18–21]. The effects of alkali sulfates on the hydration rate and setting time of cement were primarily investigated, but different opinions were still remaining. Odler and Wonnemann [22] reported that the reactivity of C₃A would increase when clinker was doped with K₂O, but not altered when doped with Na₂O. With high amount of alkali sulfates, the hydration rate of C₃A increases, which may lead to rapid setting. Collepari et al. [23] found that Na₂SO₄ would shorten the setting time through investigating the hydration heat of C₃A reacting with Na₂SO₄ compared with pure C₃A. Kumar and Rao [24] reported that the addition of K₂SO₄ and Na₂SO₄ would retard the setting time. Samat and Sarkar [25] pointed out that alkali ion in alkali sulfates tends to accelerate setting, but sulfate ion in alkali sulfates tends to retard setting. Most of literatures reported that alkali sulfate favors early strength development, but decreases 28 d compressive strength [20,26]. Other researchers proposed a positive effect of alkali sulfate on strength development. The absence of alkalis would result in an abnormally low early strength [27]. Furthermore, high amount of alkali sulfates in cement would lead to large drying shrinkage and water expansion. The effect of alkali sulfates on the linear expansion of cement concrete would be much associated with the content of SO₃ and C₃A in cement [28]. It should be noticed that the reagent-grade K₂SO₄ and Na₂SO₄ used in previous research works in some cases could provide references for the impacts on cement properties. Considering that alkali sulfate in clinker, went through high temperature heating, has distinct crystal morphology and dissolution rate from reagent-grade sulfates.

Recent years, researchers did some studies on the mechanisms of sulfate and alkali affecting on hydration of alite and cement, as well as the structure of C-S-H and portlandite. Kirchheim et al. [29] reported that sulfate reacts faster with orthorhombic C₃A than the cubic phase, forming longer ettringite needles. Quennoz and Scrivener [30] proposed that alite reaction is accelerated in the presence of sulfate, which is attributed to the interaction of sulfate with aluminium ions present in alite. Mota et al. [31] shows that sulfate promotes the formation of hexagonal platelets of portlandite and a divergent needled structure of C-S-H due to the uptake of sulfate on C-S-H. In our study, we are concerned with whether or not the alkali sulfate derived from cement clinker can play a good role as added gypsum to adjust the setting time of cement, promote the development of compressive strength and decrease drying shrinkage, then the dosage of added gypsum could be reduced during cement production, or not the content of alkali sulfate should be controlled due to its adverse effect on cement concrete.

The aim of this paper is to examine how the alkali sulfate in clinker influences cement hydration and hardening properties, and to discover the optimum content of sulfate in cement. Arcanite (K₂SO₄), thenardite (Na₂SO₄), apthitalite (K₃N₂S₄) and Ca-langbeinite (KC₂S₃), prepared in the laboratory, were used in this study. The differences of hydration reactivity of C₃A with arcantite, thenardite, apthitalite and Ca-langbeinite comparing with reagent-grade sulfates were measured respectively. The impacts of each of alkali sulfates on the hydration heat, setting time, compressive strength, drying shrinkage, water expansion, hydration degree and products were fully investigated. Ca-langbeinite (K₂SO₄·2CaSO₄) has main CaSO₄ structure in molecular formula, and may

lead to similar effects as gypsum on cement properties. The impacts of Ca-langbeinite on cement hydration and hardening properties were studied compared with gypsum. The effects of alkali sulfates on cement properties would also much depend on other factors associated with cement such as the content of C₃A and fineness, and curing conditions. Related research works have been carried out continually.

2. Experimental

2.1. Materials

Arcanite (K₂SO₄), thenardite (Na₂SO₄), apthitalite (K₃N₂S₄) along with Ca-langbeinite (KC₂S₃) were prepared through high temperature heating in the laboratory and used in this investigation. The preparations of alkali sulfates were performed under different heating regimes, then optimum regimes were selected according to X-ray diffraction (XRD) analysis and used in this paper. The XRD patterns of arcantite, thenardite, apthitalite and Ca-langbeinite are shown in Fig. 1. Arcanite was produced by heating the reagent-grade K₂SO₄ at 1000 °C for 2 h. Thenardite, the stable phase, was achieved through the transformation from the sodium sulfate phase which was produced by heating the reagent-grade Na₂SO₄ at 800 °C for 2 h in the presence of moisture at room temperature during the storage. Apthitalite was prepared by heating the mixture of reagent-grade K₂SO₄ and Na₂SO₄ with a Na/K molar ratio of 1:3 at 920 °C for 2 h. Ca-langbeinite was prepared by heating the mixture of reagent-grade K₂SO₄ and CaSO₄ with a K/Ca molar ratio of 1:2 at 920 °C for 2 h. The alkali sulfate samples were cooled in air and stored in a storage box at room temperature.

Portland cement clinker with a lower content of SO₃ was used in this study. The content of original alkali sulfate in clinker is 0.24% in the form of SO₃ and 0.19% in form of Na₂O_{eq} measured by 50% ethanol method [24]. The clinker was ground by a grinding mill, and passed through a 75 μm sieve. The chemical compositions of clinker and natural gypsum are listed in Table 1. There is a little anhydrite, but most of dihydrate in natural gypsum. Alkali sulfates were added into clinker to investigate the impacts on cement hydration and hardening properties. The addition of arcantite, thenardite and apthitalite leads to higher contents of total alkali, 0.64, 0.8, 1.0 and 1.2 wt% in form of Na₂O_{eq} in cement, meanwhile introducing 0.00, 0.21, 0.46 and 0.72 wt% SO₃. Gypsum was used to adjust sulfate in cement, and the SO₃ content was 1.0, 1.5, 2.0, 2.5,

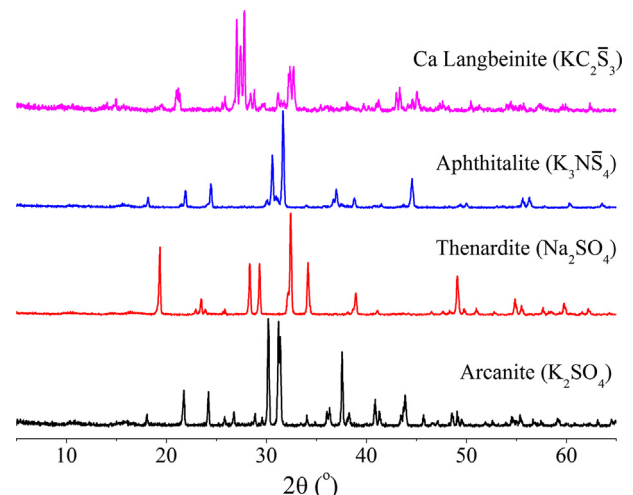


Fig. 1. XRD patterns of arcantite (K₂SO₄), thenardite (Na₂SO₄), apthitalite (K₃N₂S₄) and Ca-langbeinite (KC₂S₃) prepared in the laboratory.

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