



Effects of apththalite on the formation of clinker minerals and hydration properties

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HIGHLIGHTS

- Samples of clinker with different apththalite content were investigated.
- Apththalite influences the sintering progress of clinker.
- Increasing apththalite content transforms R-C₃S to the other polymorphs.
- The hydration in acceleration period becomes faster as the apththalite content increases.

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ABSTRACT

This paper aims to explore the mechanisms of apththalite in clinker sintering and hydration process, in order that wastes containing sulfates can be effectively utilized in cement production. TG-DTA, XRD, XRF and SEM were applied to investigate the sintering process, mineral composition, polymorphs and hydration products of clinker. Hydration reactivity of sintered clinker was analyzed by TA. Results show that apththalite increases the initial decomposition temperature of CaCO₃ and the viscosity of liquid phase. Apththalite negatively affects the reaction of CaO and C₂S into C₃S. β-C₂S is detected and R-C₃S is transformed into the T₁, M₃, and T₂ along with M₂-C₃S as the apththalite content rises. The morphology of clinker with different apththalite content show clearly heterogeneous characteristic. The early hydration of clinker is suppressed, but the induction period is shortened as the apththalite is introduced. Moreover, hydration of clinker in the acceleration period is increased by apththalite. Portlandite shows earlier after the induction period in the hydration of clinker as the apththalite content increases.

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1. Introduction

Over the last 20 years, interest in diverting waste from landfills into useful resource and recovering energy from waste materials has grown significantly. The cement industry in particular has adapted its production methods to accommodate a wide variety of waste materials as alternative fuels or raw materials in order to lower both cost and environmental footprint [1–3]. Manufacturers even use waste incineration, fly ash, sewage sludge as raw material or fuel [4]. Some wastes usually contain a certain amount of alkali and sulfur, both sulfide and organic sulfur in those wastes materials would be transferred into sulfate under high temperature cementation [5], which makes sulfates in cement clinker include not only K₂SO₄, Na₂SO₄ and CaSO₄, but also 2CaSO₄·K₂SO₄ and apththalite [6]. In addition, the emission of foul gas containing

sulfur in the cement production has been significantly reduced, as a result of the popularization and application of new technology of kiln outside decompose [7,8], so that more and more remained sulfur is introduced into cement clinker. SO₃ in clinker was about 0.5% in the 70s and 80s of last century. By now, it is common that SO₃ in clinker exceeds 1%, and it may reach 3% in the extreme cases [6,9,10].

Trace elements like Na, K and S in the fuel or raw materials will alter the sintering process of raw materials [11–13]. The mineral composition and crystal structure of mineral in clinker are influenced by those elements, which finally changes the hydration of cement. In accordance with the electronegativity principle, strong electropositive elements, such as K⁺ and Na⁺, can increase the viscosity of liquid [14]. The formation temperature and viscosity of the liquid phase significantly affect the compositions, crystal structure and properties of the mineral in cement clinker. Gypsum used as a mineralization agent in the cement production has been fully investigated, a small amount of SO₃ facilitates the formation of

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clinker, conversely, an excessive amount of SO_3 would hinder the formation of C_3S [15,16]. K. Kolovos [11] found that SO_4^{2-} reduces f-CaO in clinker and that effect is better than S^{2-} , HPO_4^{3-} , F^- and other anions. SO_3 is favorable for the stable existence of C_2S and CaO. MgO favors the formation of $\text{M}_3\text{-C}_3\text{S}$, while SO_3 stabilizes the $\text{M}_1\text{-C}_3\text{S}$ [17,18]. C_3S in commercial cement mainly exists in M_1 and M_3 due to the incorporation of some ions. The polymorph of C_3S will change, since K^+ , Na^+ , Al^{3+} , Mg^{2+} , and Fe^{3+} replacing Ca^{2+} in the C_3S crystal structure [19]. Ca^{2+} in belite is replaced by K^+ , Na^+ , etc. which favors C_2S exist stably as $\beta\text{-C}_2\text{S}$ [20].

C_3S in different polymorphs have different hydration performance. the early hydration properties of three C_3S polymorphs was observed by Stewart [21], the sequence of hydration reactivity from high to low is monoclinic, triclinic and trigonal C_3S , but the morphologies of the hydration products of all C_3S are unanimous. The hydration will be accelerated, when Na^+ is dissolved in cement clinker, and it forms transitional hydration products, a large amount of Na^+ will be detrimental to the microstructure of the hydration products [22]. The ions introduced into clinker increase the defects of the lattice and shorten the induction period [23].

Hitherto, investigation of Portland cement incorporated with sulfates mainly concentrates on the influence of anions or cations separately [24–26]. Effects of Na^+ , K^+ and SO_4^{2-} in cement clinker have not been fully performed. Different effects could be engendered, when these ions are mixed together. For instance, the $\text{R}_2\text{O}/\text{SO}_3$ has an influence on the mineral composition and the crystalline of mineral in sintered clinker [17,27]. It is an integral part required to evaluate the utilization of alternative fuels and waste materials with high sulfur. Herein, the different amounts of apththalite were added into four kinds of analytical grade reagents. Portland cement clinker was synthesized in the lab. The sintering progress, the mineral composition of clinker and the polymorph of mineral were investigated, hydration calorimetry and products of clinker with apththalite were also discussed in this paper.

2. Experimental procedure

2.1. Materials

Analytical grade reagents CaCO_3 , SiO_2 , Al_2O_3 , Fe_2O_3 , K_2SO_4 and Na_2SO_4 were used as raw materials in order to eliminate the influence of other impurities. The lime saturation factor (LSF), silica modulus (SM) and the iron modulus (IM) of control sample used in this experiment were mainly referred to the common values of cement production plants. Three parameters are $LSF = 95.1$, $SM = 2.50$ and $IM = 1.76$. The proportion of raw materials of the control group was calculated (Table 1). Three modified samples were prepared by mixing the control sample with 1.2%, 2.4% and 3.6% apththalite measured by quality percentage of SO_3 , respectively.

K_2SO_4 and Na_2SO_4 (purity over 99%) were mixed with a molar ratio of 3:1, then pressed into round cakes with a diameter of 20 mm and a thickness of 10 mm. Samples were put into the resistance furnace, heated from room temperature to 1000 °C in a constant speed within 1 h and maintained at 1000 °C for 2 h, after that,

Table 1
Raw materials mixing proportion.

Dosage of $\text{SO}_3/\%$	Mass/g				
	CaCO_3	Al_2O_3	SiO_2	Fe_2O_3	Apththalite
Control (0%)	37.38	1.76	6.90	1.00	0
1.2%	37.38	1.76	6.90	1.00	0.80
2.4%	37.38	1.76	6.90	1.00	1.60
3.6%	37.38	1.76	6.90	1.00	2.48

Table 2
Oxide composition of synthesized clinker.

Oxide composition/%	Samples			
	Control (0%)	1.2%	2.4%	3.6%
Na_2O	0.00	0.15	0.69	1.35
Al_2O_3	4.64	6.66	4.86	4.60
SiO_2	20.56	21.20	20.10	19.60
SO_3	0.00	0.13	1.32	3.10
K_2O	0.01	0.04	1.25	2.93
CaO	64.70	65.00	63.50	62.00
Fe_2O_3	3.02	3.29	3.25	3.15
others	7.07	3.53	5.03	3.27

samples were removed out of the furnace, cooled in air, then milled into powder.

Raw materials were uniformly mixed at a rate of 500 r/min for 3 min by the ball mill, then pressed with a pressure of 100 MPa into round cakes with a diameter of 20 mm and a thickness of 10 mm. Samples were placed in Pt crucibles, the heating rate was 10 °C/min and the sample was maintained at 1450 °C for 1 h, then Samples were removed out of the furnace, quenched in the air. Sintered clinker was ground into powder and sifted through a 180 meshes sieve for testing. The oxide composition of sintered clinker was determined by X-ray fluorescence spectrometry (XRF) (Table 2).

2.2. Test methods

2.2.1. TG-DTA

The sintering progress of raw materials was investigated by thermogravimetric and differential thermal analysis (TG-DTA) with a Stanton Redcroft STA 780 Simultaneous Thermal Analyzer. Raw materials were mixed and grounded into powder with a fineness less than 80 μm , the grounded samples were placed in corundum crucible, then were examined at a heating rate of 10 °C/min under flowing nitrogen (50 cm^3/min) from 30 °C to 1450 °C.

2.2.2. XRD

A Rigaku International Corporation D/max 2550 VB3+/PC diffractometer (Cu $\text{K}\alpha$ radiation) was used to determine the mineralogy and hydration products of clinker. The measurements were conducted in the range of 5–75° (2 θ) with a step of 0.05°, a counting time of 4 s per step, a tube voltage of 40 kV, and current of 250 mA.

2.2.3. XRF

Sintered clinker was pulverized into powder with a fineness less than 80 μm and sealed until a Bruker DRS3400X X-ray fluorescence spectrometry (XRF) was used to test the oxide composition of it.

2.2.4. SEM

Selected nodules of the sintered samples were coated with Au to provide a conductive surface for imaging. The mineral morphological feature was observed by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). An accelerating voltage and beam current for images were 20 kV and 0.5nA, respectively. The distribution of Na, K and S in clinker minerals was analyzed by EDS.

2.2.5. Hydration heat test

The hydration heat flow was measured by an isothermal heat-conduction calorimetry (TAM air C80, Thermometric, Sweden). The experiment temperature was 20 ± 1 °C, the quality of each sample was 2.00 g, the weight ratio of water/clinker was 0.5, the

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