



Incorporation mechanism of titanium in Portland cement clinker and its effects on hydration properties



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HIGHLIGHTS

- Ti was preferentially incorporated in C₄AF followed by C₃A, C₂S and C₃S.
- The crystal pattern of C₃A translated into orthorhombic from cubic as the TiO₂ dosage reached to 1.5%.
- TiO₂ promoted the hydraulic activity of clinker in initial period.

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ABSTRACT

Titanium is a trace element that might be introduced by industrial wastes to the cement kilns. In this study, the effect of TiO₂ on cement clinker phase formation, ion substitution as well as hydration properties were evaluated by free lime test, X-ray diffraction (XRD), scanning electron microscope-energy dispersive spectrometer (SEM-EDS), isothermal heat-conduction and nuclear magnetic resonance (NMR). Results indicated that titanium was preferentially incorporated in the interstitial phases, especially in C₄AF, then C₃A, C₂S and C₃S, which could be attributed to the lattice substitution of Ti⁴⁺ to Fe³⁺ in C₄AF and consequently weakened its crystallinity. Meanwhile, the threshold limit for TiO₂ incorporated into clinker was 1.5 wt%, beyond which, the crystal form of C₃A transformed from cubic to orthorhombic. These changes of C₃A and C₄AF promoted the formation of C₃S by decreasing the liquid phase viscosity during the sintering process. TiO₂-doped promoted the hydraulic activity of clinker in initial period while postponed the hydration process of C₃S in later period. However, after 28 days hydration, C–S–H gel polymerization degree did not decrease but improved as the TiO₂ dosage was below 1.5 wt%.

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1. Introduction

In recent years, pollution issues caused by municipal solid and industry wastes have aroused far-ranging concern [1–4]. Seeking for waste treatment methods that are environmentally friendly and beneficial are urgent. The cement industry, which is known to consume a large quantity of raw mixes and energy, integrated these problems by replacing part of traditional materials during the manufacturing process could alleviate these issues effectively [5,6]. Many industrial by-products, for example, sewage sludge, oil-based mud, furnace slag and stainless steel slag could be used as alternative fuels and raw materials [7–9]. These wastes usually contain a certain amount of heavy metal elements, however, which could alter the performance of final clinker [10]. Therefore, before

utilizing the substitutions, more cautious needs to be noticed and ensure the quality and performance of clinker is not adversely affected. Fortunately, many ongoing studies on heavy metal elements focused on enhancing the security of cement manufacture and application, especially for titanium, one of the most common trace elements that mainly introduced by alternative raw mixes and fuels. In typical cement raw material, Titanium (Ti) as oxide could be present at the 0.02–0.4% level by weight [11], and even a higher concentration of 0.1–1.0% TiO₂, which was reported by Gartner [12].

As a low volatility element [13], the effect of a small amount (0.5–1.0 wt%) of titania was generally regarded to be that of mineralizer, which could lower the viscosity of liquid phases and stabilize belite [14,15], but Miller believed the effect was negligible [16]. At high dosage (≥5.0%), new compounds were found [14,17], such as CaO·TiO₂, 2CaO·TiO₂, 3CaO·TiO₂, and even 4CaO·3TiO₂. For hydration properties, a small quantity of TiO₂ apparently enhanced the hydraulic activity of cement and affected

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in consequence the compressive strength that increased, which can be ascribed to the distortion of alite and belite as a result of substitution of the Si^{4+} ion by Ti^{4+} ion and formation of the corresponding solid solutions [18]. However, Glasser ever studied effect of TiO_2 on ferrite structure and concluded that Fe^{3+} was substituted by Ti^{4+} , charge being balanced by incorporation of additional oxygen atoms, forming the solid solution which was given as $\text{Ca}_5(\text{Fe}_{4-x}\text{Al}_x)\text{TiO}_{13}$ [19]. No doubt that the latter substitution could contribute more to the cement activity for the greater defects of clinker phases, this is because of the change of ferrite structure could influence the properties of the melts and then affect the sintering process of silicate phases. At high concentrations, the formation of $\text{CaO}\cdot\text{TiO}_2$ resulted in the rate of hydration decreased for it does not possess hydraulic properties [20]. Kakali held different opinion, however, who thought addition of TiO_2 did not show any significant increase in the hydration rate of Portland cement, though the dosage was up to 2.0% by weight [21].

Though these existing researches have achieved great progress, effect of TiO_2 on the formation and hydration properties of clinker minerals still has not achieved a general consensus and thus needs to be further clarified. Meanwhile, the threshold limit for titanium incorporated in clinker and ion substitution need to be determined, and the hydration mechanism also needs to be further studied.

In this paper, effect of TiO_2 on cement clinker formation, hydration activity, as well as lattice substitution was fully discussed. Herein, the formation of clinker phase in the sintering process was investigated by chemical analysis and XRD. In addition, the titanium immobilization and ion substitution in clinker were analyzed by SEM-EDS. At last, the influence of TiO_2 on hydration activity of clinker was studied by isothermal heat flow calorimeter and ^{29}Si NMR.

2. Experimental

2.1. Materials

Samples were prepared by mixing analytical grade reagents of $\text{Ca}(\text{OH})_2$, SiO_2 , Al_2O_3 , Fe_2O_3 and TiO_2 to avoid the influence of other impurities. A reference clinker was synthesized basing on the potential mineral compositions of $\text{C}_3\text{S}=65\%$, $\text{C}_2\text{S}=15\%$, $\text{C}_3\text{A}=10\%$, $\text{C}_4\text{AF}=10\%$ by weight according to the Bogue formula. The doped clinkers were prepared by introducing various amounts of TiO_2 into the reference, and the specific dosage was 0.5%, 1.0%, 1.5% and 2.0 wt%, respectively. The raw mixes were homogenized and then pressed at 100 KN into pellets of $\varnothing=25\text{ mm} \times 10\text{ mm}$ to obtain a more regular clinkering process. Finally, the pellets were placed in alumina crucible and fired up to 900 °C at the rate of 10 °C/min, sintering for 1 h, and up to 1450 °C at the rate of 10 °C/min. After 3 h of burning to the clinkering temperature, the clinkers were quickly moved from the furnace and rapidly air quenched. At last, the final clinkers were crushed and grounded to pass a 78- μm sieve until the residue weight less than 3.0%. Chemical and mineral composition of the reference clinker mixture after sintering at 1450 °C (According to Bogue formula 1–4) has been shown in Table 1.

$$\text{C}_3\text{S} = 4.07 * \text{C} - 7.6 * \text{S} - 6.72 * \text{A} - 2.86 * \bar{\text{S}} \quad (1)$$

$$\text{C}_2\text{S} = 2.87 * \text{S} - 0.754 * \text{C}_3\text{S} \quad (2)$$

$$\text{C}_3\text{A} = 2.65 * \text{A} - 1.69 * \text{F} \quad (3)$$

$$\text{C}_4\text{AF} = 3.04 * \text{F} \quad (4)$$

Table 1
Chemical and mineral composition of the reference clinker mixture after sintering at 1450 °C (according to Bogue).

Chemical composition		Mineral composition	
Oxide	Wt (%)	Mineralogical constituent	Wt (%)
CaO	68.08	C_3S	65.0
SiO_2	22.81	C_2S	15.0
Al_2O_3	5.84	C_3A	10.0
Fe_2O_3	3.27	C_4AF	10.0

Where C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , $\bar{\text{S}} = \text{SO}_3$.

2.2. Methods

Free lime (f-CaO) content of final clinker was estimated using glycerin-alcohol method to represent the burnability of clinker.

The mineralogical compositions of clinker were determined by means of X-ray diffraction (XRD). A Bruker D8 with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15046\text{ nm}$) was used. The measurement was carried out in the 2θ ($5\text{--}75^\circ$) with a step of 0.02° at $2^\circ/\text{min}$, and the X-ray tube was operated at an accelerating voltage of 40 KV and a current of 40 mA.

The Quanta FEG450 environmental scanning electron microscope (ESEM) and energy dispersive X-ray spectroscopy (EDS) coupled with the ESEM system (20 kV, 60 Pa) were used to investigate the morphology feature and element distribution of clinker phases. SEM was operated in backscattered electron mode which required a polished specimen for optimal observation. A block of sample was vacuum impregnated in epoxy resin and then polished. At last, the polished samples were coated with platinum to generate a conductive surface for observation.

An isothermal heat flow calorimeter (TAM air) was used to characterize the hydraulic reactivity of clinker. In order to avoid the influence of other factors, the hydration process of clinker did not mix gypsum. The heat evolution of samples with water/clinker of 0.45 was measured at $20 \pm 0.1^\circ\text{C}$. In the titration cell, the powder sample and deionized water were thermostated for 3 h before the reaction was started by injecting the water into the reaction vessel and stirring the sample in the calorimeter for 30 s. This procedure could monitor the hydration from the very beginning as water was injected into the sample [22]. The hydration heat-evolution tests measured for 7 days.

Calcium silicate hydrate (C–S–H) is one of the most important hydration products of clinker reacting with water. Whereas, C–S–H is nearly amorphous, which signifies it is a non-stoichiometric composition, thus X-ray diffraction techniques are of limited value [23]. Fortunately, ^{29}Si solid-state Magic Angle Spinning Nuclear Magnetic Resonance (^{29}Si MAS NMR) can solve the problems, which is an ideal tool to get some structure information of C–S–H [24]. In this paper, NMR test was performed on a Bruker Advance 300 using a MAS probe for 7 mm zirconia rotors, a spinning speed of 6 kHz, a relaxation delay of 1 min and 300–500 scans.

3. Results and discussion

3.1. Chemical analysis

The content of free lime (f-CaO) in clinker is a good indicator of the degree of burning [25]. The variation of the f-CaO content in clinker fired at 1450 °C for 3 h is presented in Fig. 1. As the amount of TiO_2 increased, f-CaO content in clinker had an obvious trend of decrease. As an example, there was 0.57% f-CaO in the reference, while it decreased to 0.09% in 1.0% dosage. It also showed the content of f-CaO was negligible as the TiO_2 content was beyond 1.5%. The effect of TiO_2 on clinker sintering process was generally regarded as mineralizer, which could reduce the viscosity and formation temperature of the melt [15,26,27]. In other words, doping TiO_2 played a positive effect on the burnability of the clinker.

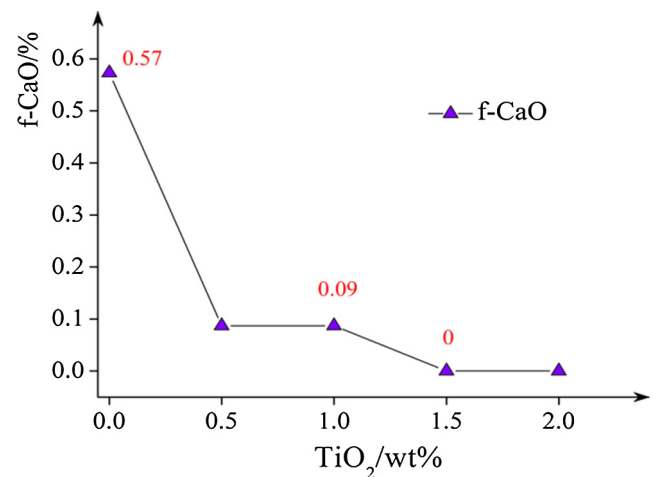


Fig. 1. Change of f-CaO content in the final clinker doped TiO_2 .

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