Construction and Building Materials 138 (2017) 26–34

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Investigation on preparation of pyrite tailings-based mineral admixture with photocatalytic activity

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HIGHLIGHTS

- A photocatalytic mineral admixture was prepared using waste pyrite tailings.
- Cementitious materials with this admixture have obvious photocatalysis.
- The strength of the cementitious with this admixture have a greater improvement.
- We reduce the cost for use high titanium slag as the source of titanium.

ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form 26 December 2016
Accepted 27 January 2017

Keywords:
Pyrite tailings
High titanium slag
Admixture
Photocatalytic

ABSTRACT

In this study, we prepared a mineral admixture with photocatalytic activity by acid leaching-hydrolyzation and single calcination method, using industrial waste pyrite tailings and high titanium slag as raw materials in which pyrite tailings were substrate and high titanium slag was the source of titanium. The compressive strength of the cementitious materials with the admixture, and the photocatalytic activity of the admixture and white cement with admixture were also studied. The results demonstrated that the optimum conditions for preparing admixture were that the mass ratio of acid and slag is 8:1; the temperature of acid leaching is 85 °C; the time of acid leaching is 250 min; the content of distilled water is 40%; the mass ratio of filtrate and tailings is 8:1; the loading temperature is 105 °C; the loading time is 3.5 h; at last, the precursor of admixture is calcined in 800 °C for 2 h. The admixture prepared in this method showed a superior crystallinity of anatase with the particle size of about 100 nm. Comparing with the cement paste without the admixture, the 3, 7 and 28 days compressive strength of the cement paste with 30% admixture were found to be increased by 40.92%, 44.57% and 37.74%, respectively. The photocatalytic degradation rate of methylene blue(MB) reached 95.28% after irradiation for 5 h, and white cement with the admixture manifested perfect photocatalytic performance under irradiation by 300 W high-pressure mercury lamp.

1. Introduction

Titanium dioxide ensures its wide application in photocatalysis field such as self-cleaning and environmental pollution remediation with favorable features of durability, stability and efficient photocatalytic efficiency [1,2]. As a photosensitive semiconductor, TiO_2 has unoccupied conduction band and occupied valence band, the band gap amounts 3.2 and 3.0 eV for anatase and rutile TiO_2, respectively [3,4]. When irradiating the TiO_2 with light having an energy content higher than the band gap, electrons from the valence band are excited to the conduction band, resulting in the formation of e^-_{CB}/h^+_{VB} pairs, and then form reactive hydroxyl radicals ($^{\cdot}OH$) in the presence of oxygen and water vapor. These free radicals undertake a series of reactions with pollutants, such as containing bond cleavage, substitution, and electron transfer, to mineralize them into CO_2 and water [5–7].

In recent years, environment pollution, especially air pollution is increasing seriousness in the city. Buildings in the city are the best place for photocatalytic reaction due to the huge exterior surface area of these buildings exposed to sunlight. Consequently, on account of the degradation function to the harmful substances in the air, the photocatalytic building materials has attracted the increasing attention in the past few years [8,10,11]. In the traditional preparation process, the photocatalytic cementitious materials were obtained by mixing the TiO_2 nanoparticles into the cementitious materials [2,8,9], applying TiO_2 to the surface of traditional concrete pavement [12,13], coating the TiO_2 to the

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http://dx.doi.org/10.1016/j.conbuildmat.2017.01.134
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exposed aggregate of expanded shale to prepare a photocatalytic concrete [14], and preparing titanium dioxide clear paint coated architectural mortar [15], etc. In order to get a preferable photocatalytic effect, these materials are all made from P25, which is made by CVD (chemical vapor deposition), this kind of TiO_2 production cost is high and the price is too expensive for practical application.

In addition, with the purpose of immobilization of the TiO_2 and improvement of the photocatalytic activity, many researchers have been investigated immobilization of TiO_2 in different support materials [16–18]. The load-type TiO_2 particles show a better photocatalytic performance than the pure TiO_2 particles in the same particle size in virtue of the smaller particle size and the bigger specific surface (Fig. 1) and a certain degree of ion doping. The research demonstrated that TiO_2 nanoparticles doped iron and silica revealed higher photocatalytic activity and remarkable degradation efficiency to the pollution in the presence of sunlight [4,19]. Phyllosilicates represent a suitable substrate for immobilization of TiO_2 ascribe to their unique crystallochemical properties and wide scale of practical applications. As a kind of phyllosilicates, kaolinite is used for immobilizing TiO_2 according to several researchers. Chong et al. [20] prepare titania impregnated kaolinite nano-photocatalyst using titanium butoxide, the prepared composite shows enhanced photodegradation ability. A kind of kaolinite-titanium oxide nanocomposites is prepared with titanium isopropoxide via sol-gel and acts as heterogeneous photocatalyst for dyes degradation by Lorrana et al. [21]. The composite shows better photocatalytic activity when compared with titanium oxide P25. Zhang et al. [22] prepare an acidic Ti sol impregnated kaolin photocatalyst which had photocatalytic properties under visible light irradiation. All the photocatalysts manifest a positive photocatalysis activity when immobilization of TiO_2 in kaolinite, but face the problem of the expensive titanium precursors used for preparation of photocatalysts and the finite pure kaolinite resource.

There are a large number of sedimentary pyrite resources in southwest china. The explored reserves accounts for 30% of the countrywide pyrite resources. The pyrite occurs accompanying the sedimentary kaolinite clay and the proportion of the pyrite is 25% to 30% and the kaolinite clay is 70% to 75%. The mining and processing in the past years lead to the production of millions of tons of kaolinite tailings. At present, most of kaolinite tailings are accumulated as waste, resulting not only in wasting resources but also in polluting the environment [23,24]. As discussed in Ref. [25], after calcining at high temperature, the kaolinite is dehydrated to form metakaolinite which is excellent admixture for cement and concrete, meanwhile the pyrite tailings contain a large number of iron and silica. Thus, loading the TiO_2 in the pyrite tailings not only improve the photocatalytic efficiency but also improve the strength of cementitious materials when used in some building materials.

In this work, the mineral admixture with photocatalytic activity was prepared by the process of acid leaching-hydrolyzation and single calcination method. The pyrite tailings and high titanium slag were used as the source of titanium and substrate, respectively. The cementitious materials mixed the mineral admixture showed a remarkable improvement in compressive strength and photocatalytic performance. Moreover, the titanium content of admixture, the phase composition of admixture, the photocatalytic degradation efficiency of the admixture, cementitious with the admixture and the mechanical performance of the cementitious with admixture were characterized.

2. Experimental procedure

2.1. Materials

High titanium slag is from Chengde Tianfu Titanium Co., Ltd, China, the chemical properties and the phase composition are shown in Table 1 and Fig. 2 . Pyrite tailings come from Xuyong County, Luzhou City, Sichuan Province of China, and its chemical properties and the phase composition are provided in Table 1 and Fig. 3. The cement was 42.5 ordinary Portland cement (P.O 42.5) from CUCC of China.

2.2. The preparation principle of mineral admixture

Fig. 4 manifests the process of the preparation of admixture. As titanium source, high titanium slag was blended with NaOH and modified at high temperature. $Fe_3Ti_3O_{10}$ and Ti_3O_5 in high titanium slag transformed into Na_2TiO_3 [26], the phase composition of slag after alkali fusion is shown in Fig. 5. In the process of washing the alkali modified slag by a three-stage counter current, ion-exchange of Na^+ in Na_2TiO_3 and H^+ in water occurs. Na^+ gets into liquid phase, and the solid phase transforms into amorphous $Na_xH_{2-x}TiO_3$. After being dried, the solid phase reacted to form titanyl sulfate in high temperature when blended in sulfate solution of high concentration. In reducing the acidity and rising the temperature of the solution, titanyl sulfate can hydrolyze into hydrated titania [27]. Therefore, adding a suitable amount of distilled water simultaneously blending the solution with pyrite tailings and reacting at a higher temperature, the acidity of system is reduction to promote the hydrolysis of titanyl sulfate because of the reaction of the surplus sulfuric acid in solution and the aluminum in tailings consume some sulfuric acid. After the former step, tailings were added in the acidic leaching solution and stirred constantly so that hydrated titanium dioxide particles loaded onto the tailings to avoid grain growth. Thereby the precursor admixture containing nanoscale hydrated titanium dioxide was prepared. The mineral admixture with photocatalytic activity was prepared by calcining the precursor at a high temperature so that the hydrated titanium dioxide dehydrate to anatase while kaolin tailings dewatering to metakaolin.

2.3. Test methods

Ultra55 field emission gun scanning electron microscopy (FSEM) was used to observe the microstructure of admixture, X'Pert Pro X-ray diffraction photometer was employed to analysis the phase of the samples, Axions X-ray fluorescence spectrometer was used to analysis the titanium content in the samples.The compressive property was measured by mixing the admixture and the ordinary Portland cement in mold with the size $10*10*10\ mm^3$.

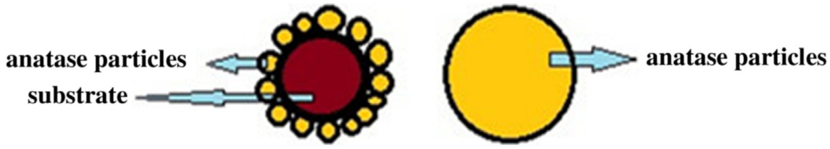

Fig. 1. Load-type TiO_2 particles and pure TiO_2 particles sketche.