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Evaluation of oil sludge as an alternative fuel in the production of Portland cement clinker

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HIGHLIGHTS

- Oil sludge was used as alternative fuel in cement clinker production.
- Effect of adding modes on cement clinker production were investigated.
- High temperature in cement kiln significantly reduce the discharge of VOCs.

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ABSTRACT

The use of oil sludge as an alternative fuel during clinker production was evaluated. It was found that 14% oil sludge could be added to raw mixture and that variations in the mode of oil sludge addition had no obvious effect on the combustibility of the mixture or the cement quality, such that all cement samples satisfied the P.O 42.5 standard. It was also determined that 90.98% of coal could be replaced by oil sludge. The concentration of VOCs decreased as the calcination temperature was raised. So the adding points with high temperature (>1450 °C) are recommended for oil sludge utilization.

1. Introduction

The majority of the oil sludge generated in China comes from the cleaning of oil storage tanks, and more than 1×10^6 tons of this material are generated annually [1]. Oil sludge typically consists of water, oil and various solids and generally contains many toxic, mutagenic and carcinogenic compounds. This sludge thus has the risk to pollute soil and ground water (such as with petroleum hydrocarbons) as well as the atmosphere (such as with volatile organic compounds, or VOCs), and so has been included in the national catalogue of hazardous wastes [1]. At the same time, the treatment of oil sludge to render it harmless remains challenging. Typically, oil sludge can be disposed of by oxidation [2], microbial degradation [3–5] and by recycling into reusable oils [6–9]. However, these methods have limited capacities and can also generate secondary pollutants.

Because oil sludge is primarily composed of high molecular weight organic compounds and a high proportion of combustible matter, it has been recognized as a potential energy resource that can be recycled as an alternative fuel for use in various industrial processes. Cement production is one such industry; the average energy demand for the production of one ton of clinker is approximately 3.52 GJ, which corresponds to 0.12 tons of coal with a calorific value of 29.31 MJ/kg [10]. Energy costs account for about 35% of the total costs of cement production and so cement plants are currently attempting to reduce energy expenditures.

The rotary cement kiln has numerous advantages, including the generation of high temperatures in conjunction with an alkaline environment and an oxidizing atmosphere, as well as a large heat-exchange surface and good mixing of gases and products [1]. Many types of wastes, such as sewage sludge [11], glyphosate neutralization liquor [12], scrap tires [13], and activated carbon [14], have been shown to be feasible as alternative fuels for cement clinker production. The calorific value of oil sludge is relatively low (between 8.53 and 20.25 MJ/kg [1,15]) but still easily meets the

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cement industry requirement of 6.25 MJ/kg [16]. In addition, because oil sludge produces a very high yields of volatiles (about 93 wt% on a free ash basis) and very low fixed carbon [17], it has the potential to serve as an alternative fuel for cement production.

To the best of our knowledge, there has been little research regarding the use of oil sludge as an alternative fuel in cement production. In addition, there have been few studies concerning the effects of different fuel addition modes on the clinker quality. Finally, little attention has been paid to the quantities of VOCs generated during off-gassing throughout the alternative fuel processing. For these reasons, the objective of the present work was to evaluate the effects of two modes of adding oil sludge to the raw ingredients mixture on the clinker quality, as well as to track the concentrations of VOCs in off-gassing during the oil sludge processing.

2. Material and methods

2.1. Material

The oil sludge used in this work was obtained from a refinery in Zhoushan, Zhejiang, China (Fig. S1), while the limestone, clay, copper slag and shale were collected from a cement plant in Jinhua, Zhejiang, China. These raw materials were dried at 105 °C to a constant weight and then ground to ASTM 200 mesh size with a ball mill. The chemical composition of the oil sludge is summarized in Table 1. The actual calorific value of the sludge can be considered to have two components: the heat of vaporization of water and the heat of combustion of the sludge. And the calorific value of the oil sludge was estimated to be 14.29 MJ/kg.

2.2. Clinker and mortar preparation

Typically, the moduli of Chinese cement clinkers are controlled by varying the lime saturation ratio (between 0.87 and 0.96), the silica ratio (between 1.7 and 2.7) and the alumina ratio (between 0.9 and 1.9) [18].

When the raw materials (including the oil sludge) were mixed according to the set of parameters above, we defined this mode as M1 whereas, in the case that the oil sludge was directly added to the control raw ingredient mixture, we defined this mode as M2. The oil sludge proportions in the raw mix ranged from 0% to 14% for both of the addition modes. When employing mode M1, the specimens containing 0%, 2%, 6%, 10% and 14% oil sludge are termed R0, R1, R2, R3 and R4 (Table S1), while the M2 mode mixtures containing these same quantities are referred to as Q0, Q1, Q2, Q3 and Q4 (Table S2).

Bogue's calculation [19,20] was used to estimate the amounts of alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A) and brownmillerite (C_4AF) in the raw mix following sintering.

All the clinkers were prepared in the same manner. Deionized water (10–15 mL) was added to 100 g of the raw ingredient mixture, and the combination was stirred vigorously. The resulting material was pressed into cube-shaped specimens with 40 mm sides at a pressure of 49 MPa. Each specimen was heated in a 950 °C furnace for 30 min, then raised to a temperature of 1450 °C at a rate of 10 °C/min, and held at that temperature for 60 min. Following this, the clinker was immediately removed from the furnace and cooled to room temperature to prevent the decomposition of C_3S to C_2S. All the clinkers were ground to ASTM 200 mesh size in preparation for further analysis.

To compare the VOC concentrations generated during off-gassing at different calcination temperatures (950 and 1450 °C) and varying oil sludge concentrations (0% and 14%), five 3 L off-gassing samples were collected following calcination (Table 2).

2.3. Testing methods

The chemical compositions of clinker samples were analyzed according to the GB/T 176-2008 standard [21]. The quality of cement specimens made with these materials (95% clinker and 5% gypsum) was assessed according to standard Chinese methods for water demand, stability, setting time and free lime (f-CaO) (GB1346-2001) [22], and strength testing of standard mortar (GB/T 17671-1999) [23]. The clinker minerals were also examined by X-ray diffraction (XRD) using a Cu anode operating at 35 kV and 20 mA with CuKα radiation and a diffracted-beam graphite monochromator. Each sample, in powder form, was mounted on a quartz holder and scanned over the 2θ range of 5°–80°, with a step size of 0.02°. The crystalline phases were identified by referencing the International Center for Diffraction Data database (JCPDS-ICDD). According to the GB/T 213-2008 [24] and GB/T 384-1981 [25] standards, an oxygen bomb calorimeter was employed to measure the calorific value of the oil sludge. The VOC concentrations generated during processing were measured according to the HJ 732-2014 [26] and HJ 734-2014 standards [27].

Table 2
Procedures of collecting off-gas samples.

Sample	Addition of oil sludge	Furnace temperature	Remarks
A	0%	1450 °C	100 g raw mix was directly put into the furnace and maintained for enough time to collected off-gas
B	14%	1450 °C	
C	0%	950 °C	
D	14%	950 °C	
E	14 g	950 °C	14 g oil sludge was directly put into the furnace and maintained for enough time to collected off-gas

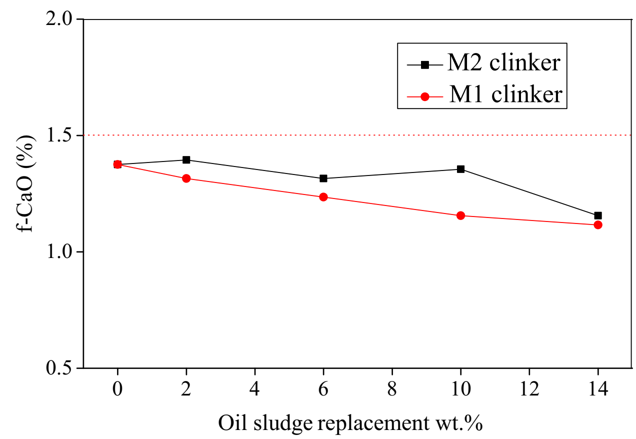

Fig. 1. Free lime (f-CaO) contents of M1 and M2 clinkers at 1450 °C.

3. Results and discussion

3.1. Combustibility of the raw mix

Raw mix combustibility is related to the rate at which CaO combines with SiO_2, Al_2O_3 and Fe_2O_3 to form C_3S, C_2S, C_3A and C_4AF during the sintering process, and is typically evaluated according to the amount of f-CaO in the clinker. The GB/T 21372-2008 standard [28] requires that the f-CaO content in clinker should less than 1.5%. In the case of both the M1 and M2 clinkers (Fig. 1), the f-CaO concentrations met the regulation limit. It was also found that as the oil sludge proportion increased from 0% to 14%, the f-CaO content of all clinkers decreased. These results indicate that the different sludge addition modes had no significant effect on the combustibility of the raw mix, although the addition of the oil sludge did slightly improve the combustibility.

3.2. Clinker quality assessment

The chemical compositions of the M1 clinkers (Table 3) showed no significant differences in the main chemical components (SiO_2, CaO, Al_2O_3 and Fe_2O_3) of each sample. The lime saturation ratio

Table 1
Chemical composition of oil sludge (by wt%).

	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Cl^-	Others
Oil sludge	60.91	2.64	2.16	2.24	18.56	0.42	0.03	0.06	0.036	12.94