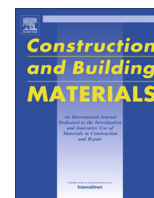




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Valorization of Dried Olive Pomace as an alternative fuel resource in cement clinkerization

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HIGHLIGHTS

- Dried Olive Pomace (DOP) was examined as alternative fuel in cement clinkerization.
- Different amounts of DOP ashes were introduced in raw meal.
- DOP presence didn't affect clinkers main mineralogical phases.
- All syntheses satisfied the requirements for the strength class 52.5 as per standard EN 197-1.

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ABSTRACT

The aim of the present investigation is to examine the potential utilization of Dried Olive Pomace (DOP) as an alternative fuel in cement clinkerization, determining the effects on the properties of the cement clinker produced, by substituting coal on the burning process for DOP by 50 and 100 wt%. Different amounts of DOP and coal ashes were introduced in the raw meal before sintering at 1450 °C and the clinkers produced were characterized by means of chemical analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). After co-grinding with suitable amount of gypsum, the produced cements were evaluated by determining setting times, standard consistency, expansibility and compressive strength at 2, 7, 28 and 90 days, whereas XRD and TG/DTG analysis were carried out for the hydration study evolution. According to the results, DOP presents a promising alternative as a secondary fuel resource, as the presence of its ash in the raw mixes did not affect negatively neither the clinker mineralogical composition, nor the physico-mechanical properties of the final cements produced.

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1. Introduction

In last decades, the fossil fuel reserves have presented a rapid decrement, as their consumption degree in industry and transports has remained almost unchanged. It has been estimated that in the next twenty to thirty years the consumption will grow exponentially and, as the substitution possibilities will be gradually exhausted, the coverage of the energy requirements will require the use of alternative fuels and the implementation of new technologies. Today, the need of using alternative and renewable fuels, over the traditional energy resources, has begun to play a very important role in the developed world, both for environmental and economic reasons [1,2].

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The depletion of high purity natural resources and the urgent requirement for their preservation, created the imperative need to explore ways in order to use lower purity materials, mainly minerals, agricultural and industrial wastes or by-products. According to the International Energy Agency, there is an urgent need for a gradual fossil fuels substitution in combination with the corresponding promotion of alternative fuels, while the European Union has already proposed the target of producing renewable resources from 20% by 2020 to 27% by 2030 (renewable energy can be produced from a wide variety of sources including wind, solar, hydro, tidal, geothermal, and biomass) [3]. To this effect, different types of urban, agricultural and industrial waste have been proposed and used as alternative energy resources for the replacement of the traditional fossil fuels such as coal, petroleum coke and fuel oil. Much progress has been reported in designing and developing facilities for the valorization of waste and by-products such as sewage sludge, waste oil shale, bituminous sludge, tires, plastic, rice husk

and straw, dust from the bamboo processing (bamboo dust) as secondary fuels [4].

The alternative of biomass exhibits many advantages, as the recovery of the contained energy can be carried out by using existing technologies, thus reducing the dependence on conventional energy sources and thereby the environmental pollution by CO₂ and other emissions. In particular, the biomass and coal co-combustion, in existing industrial installations, helps both to extend the life of coal reserves and to overcome the seasonality problem that characterizes the biomass. On the other hand, promising is also the case of waste from petroleum, such as heavy fuel separation waste, oil, tank washings ships, sediment water that contain hydrocarbons (bilge water), oil from oil slick, heavy and lighter distillation residue oils, fatty acids etc.

The use of alternative fuels in the cement industry has been established in many countries in the last 10–15 years [5,6]. However, only about 10% of the fuel consumed by the cement industry in Europe is unconventional [7,8]. In rotary kilns, the ground raw materials (about 75 wt% limestone and 25 wt% aluminium-silicates) are sintered, using as a source of energy gas, oil, coal, or alternative fuels. The clinkering temperature is in the range of 1420–1450 °C. It is well known that the limestone decomposition process, as highly endothermic reaction, is the primary energy consumption of the process, whereas the transformation reactions for the formation of the final cement clinker mineralogical phases are predominantly exothermic reactions. As a result, one of the main cost factors of the cement production is the type of fuel used for the raw materials sintering, as 4000–4200 MJ are required in order to produce 1 kg of clinker. Depending on the price of fuel and because of the coal availability (global coal reserves are much higher than those of oil) fuel costs in cement production has been decreased considerably and today its participation in the shaping of the final factory cost is about 25% [5,7,9].

The production capacity installed in cement industries in Greece is about 15 million t/year and the total fuel consumption has been estimated at about 1.5 million tons of coal. Taking into account that the average calorific value of secondary fuels is about 3000 kcal/kg (1 ton of coal equals to two tons of secondary fuel), 1–2 million tons of alternative fuels could be used in cement industry, if the traditional energy sources would be replaced by 50–70% [1,5,7]. The main benefits arising from the alternative fuels valorisation in cement industry are primary related not only with the cost reduction, but also with environmental reasons, as it would give solutions to many problems associated with wastes and by-products disposal.

Certainly, alternative fuels present some disadvantages. One of the main drawbacks is the lower content of volatile compounds. The volatile components of the coal are flammable gases (CH₄, H₂, CO) and non-combustible, such as CO₂, NO_x. Obviously higher volatile content contributes to the easier ignition of the carbon. The lower content of volatile compounds could lead to the combustion delay and, consequently, to higher flame and temperatures, thus creating products of lower granulometric quality. Furthermore, their higher moisture content replaces part of the fuel and reduces the calorific power. Also, the composition of the combustion solid residue (ash), in relation with the corresponding of coal, may vary significantly (presence of higher sulphates and alkalis content) and should be taken into account during the raw meal design [9,10].

Several investigations have been carried out, burning wastes as an industrial resource. Most of these studies have been based on the sintering process simulation in a cement kiln, by designing the raw meal with different amounts of ashes, produced during the waste fuels combustion, as only the inorganic constituents are absorbed in clinker phases, while the organic matter is consumed. Trezza and Scian studied the effect of the addition of small

amounts of ashes from used car oils in the clinkering process and according to the results, their presence in the raw meal did not seem to alter neither the mechanical nor the hydration characteristics of final cement clinker [11]. Used oils from different sources (industrial lubricants, oil sludges etc) have been also tested by other investigators with very promising results, due to their high calorific value content (about 32.000 kJ/kg) and to the fact that they could be used in cement kilns with minimal processing cost [12,13]. A lot of work has been carried on the utilization of tire derived fuels (TDF) as supplement fuel in rotary kilns, due to significant high calorific value of tires (approximately 31.400 kJ/kg) [14–16]. It has been estimated that the maximum percentage of TDF during raw meal sintering cannot exceed the 30 wt% of the fuel, as strong modification in clinker mineralogy and chemistry have been observed due to the clinker phases enrichment with zinc [15]. Corresponding work has been carried out with different types of carbon, such as spent activated carbon from drinking water treatment plants, or black carbon from pyrolysis process [17,18], the calorific values of which are in the range of 30.000 kJ/kg (similar to those of natural coal). In all cases the results showed that these types of fuels did not affect the final product quality. Another interesting alternative fuel resource has been proved the previously dried sewage sludges, with a calorific value of 8000 kJ/kg, meeting the corresponding cement industry requirements [19,20]. It has been estimated that their use in cement kiln as an alternative fuel could substitute the natural fossil resources by 70%. Finally trials have been accomplished with refuse-derived fuel (RDF) from shredding and dehydrating municipal solid waste. Karagiannis et al. have investigated the combinational action of RDF with cotton stalks, by replacing coal by 100 wt% and consequently introducing the corresponding ashes proportions in the raw meal before sintering [21]. The results suggested that both waste materials could be used as an alternative fuel in rotary kilns.

To the authors' best knowledge little attention has been given to the utilization of olive pomace as an alternative fuel during the clinker production in cement rotary kilns. Olive pomace (or olive cake) is the main by-product obtained during the production of olive oil in two or three phases centrifugation system and it consists of about 65% of water, added during the olive oil extraction process, 20 wt% of olive pulp and 15 wt% of crushed olive stones [10]. It is rich in organic matter, presenting a heating value of about 15–20 MJ/kg and as a result could be used as an alternative fuel for electrical or thermal production. However, one of its main disadvantages is the relatively high amount of ash production (5–8 wt %) during combustion, which is rich in alkalis (especially potassium). On the other hand, its CO₂ emissions excluded from the greenhouse global gas emissions, as the carbon contained in alternative fuels is considered carbon-neutral and do not count to the Emission Trading System [22].

The aim of the present investigation is to determine the effects on the properties of the cement clinker produced, by replacing coal on the burning process by different amounts of Dried Olive Pomace (DOP). For that reason different amounts of DOP and coal ashes were introduced in the raw meal before sintering at 1450 °C and the clinkers produced were studied by means of chemical analyses, X-ray diffraction, scanning electron microscopy, whereas the corresponding cements were tested for water demand, setting times, soundness and compressive strengths at 2, 7, 28 and 90 days.

2. Experimental

2.1. Materials, raw meal preparation & sintering process

In all cases, one initial Raw Meal (RM) was used, prepared by ordinary natural raw materials, such as limestone, schist, bauxite and silica sand. Before sintering process, the raw meal synthesis was modified by adding different amounts of DOP and coal ashes. The fuels analyses was based on the determination of their

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