Activated carbon as an alternative fuel. Effect of carbon ash on cement clinkerization

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ABSTRACT

Spent activated carbon is a by-product of potabilization plants. The present study explored the feasibility of valorizing this waste as an alternative fuel to replace oil coke in portland clinker furnaces. This involved determining its composition, calorific value, and ash and heavy metal content. Since the ash generated by spent activated carbon firing is taken up by the clinker, the possible effect of such uptake on clinkerization or the properties of the clinker obtained were also ascertained.

Although spent activated carbon has an 18% lower calorific value than oil coke, one of the traditional cement kiln fuels, it was found to be apt for the purpose envisaged. Its ash content (10 wt%) is one order of magnitude higher than the ash content in coke.

Spent activated carbon ash contains substantial proportions of anhydrite and quartz, hematite and augite, but consists primarily of amorphous matter (59 wt%).

The effect of this ash on clinker phases was studied by clinkerizing raw meal in which it was used as a replacement for clay. Such meal exhibited high burnability and yielded clinkers with a composition and mineralogy comparable to the properties found in the industrial product. The sulfate present in the ash induced substantial alite crystal growth in the clinker. The loss of minority elements during clinkerization was likewise studied.

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1. Introduction

Since the outset, cement plants have been chiefly fired by coal, although the industry has also used oil coke, natural gas and oil itself as primary fuels. Replacing these sources of energy with calorific industrial waste that would otherwise be incinerated is one way of saving on fossil fuel and reducing global CO_2 emissions.

Many industrial processes generate large amounts of waste that could be used as alternative fuels. If not reused, the spent activated carbon produced in drinking water treatment plants (DWTP), for instance, is sent to sanitary fills at a very high cost. Spain's drinking water plants generated about 8400 t of spent activated carbon in 2009 (http://www.sostaqua.com/publications/publications.php?act=6&task=20, 2009).

A number of methodologies have been used to assess the effect of alternative fuels on clinkerization and the clinkers obtained,

although no literature has been found on the replacement of traditional fuel with spent activated carbon.

Very few papers have been published on the inclusion of coal ash in clinker, the main components of which are silica and alumina. According to Kaminskas and Kubiliuté (2010), the composition of coal ash is as follows (in wt %): SiO_2 (35—60%), Al_2O_3 (15—35%), Fe_2O_3 (5—20%), CaO (0—10 wt%), and traces of MgO, SO_3 and alkalis. Since the major oxides are the same in coal ash and Portland cement, coal ash may react with free lime when burned to form the phases characteristic of cement clinker.

By adding 5, 10 or 15% coal ash to tricalcium silicate raw meal, Kaminskas and Kubiliuté (2010) showed that the ash reacted with lime, reducing the percentage of C3S[1] in the sample and raising the proportion of other phases such as C2S or C3A.

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[1] Cement chemistry notation is used throughout this paper to denominate clinker and cement phases: C = CaO; A = Al_2O_3; S = SiO_2; F = Fe_2O_3; H = H_2O; Ŝ = SO_3; c = CO_2; C3S = Ca_3SiO_5; C2S = Ca_2SiO_4; C3A = $Ca_3Al_2O_6$; C4AF = $Ca_4Al_2Fe_2O_{10}$; CH = $Ca(OH)_2$; Cc = $CaCO_3$.

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Trezza and Scian (2000, 2005, 2009) studied the characteristics of clinkers made with raw meal containing certain percentages (<20 wt%) of different types of alternative ash fuels (pyrolytic carbon, petroleum waste carbon, mixed fuels). These authors showed that at the ash percentages and under the conditions studied, ash did not significantly alter clinker properties. By contrast, fuels such as used automobile oil (Trezza and Scian, 2000) or used tires (Giugliano et al., 1999) have been observed to leave traces of Pb, Zn and other metals in the system, modifying the crystalline structure of the phases formed during clinkerization. This raises the milling energy required but also improves the mechanical properties of the end product (Trezza and Scian, 2000).

According to Giugliano et al. (1999), assuming the calorific value of tires to be approximately 7505 kcal/kg (Pipilikaki et al., 2005), using one ton of this fuel reduces the coal needed by 1.25 t. In an analysis of industrial waste samples, however, Pipilikaki et al. (2005) concluded that no more than 30 wt% of the fuel could be replaced by tires because the excess Zn would otherwise pose problems during cement manufacture.

Puertas and Blanco-Varela (2004) studied industrially manufactured clinkers using both conventional and alternative fuels (meat meal, used tires and mixes of the two). The replacement ratio was not over 10 wt% of the traditional fuel. The clinkers obtained when shredded tires were used as fuel had higher Zn and Mn contents, but no significant differences between the clinker produced and the conventional product were observed in terms of mineralogical composition, size, shape or majority phase distribution.

The present study explored the feasibility of using activated carbon as an alternative fuel to replace oil coke in portland clinker furnaces. This involved determining its composition, calorific value, and ash and heavy metal content. Since the ash generated by the use of activated carbon is taken up by the clinker, the possible effect of such uptake on clinkerization or the properties of the clinker obtained had also to be ascertained.

2. Experimental

2.1. Materials

The materials used in this study included spent activated carbon from a DWTP and a reference oil coke. The prime materials used to prepare the cement raw meal were limestone, clay, sandstone and laboratory grade Fe_2O_3. The composition of the prime materials is given in Table 1. The total chlorine content determined as recommended in Spanish and European standard UNE-EN 196-2 (2006) (not shown in Table 1) was found to be <0.001% in all the materials.

Carbon and oil coke ash were both obtained by ramping the temperature to a peak of 815 °C (as described in Spanish standard UNE 32004 (1984)).

2.2. Raw meal preparation and firing

When spent activated carbon burns, the inorganic fraction, which is converted to ash, is taken up into the cement clinker. The burnability of two types of meal was consequently compared to study the effect of activated carbon ash uptake. One, the reference raw meal, was made with industrial prime materials (limestone, 82.32 wt%; clay, 16.14 wt%; sandstone, 0.6 wt%; and Fe_2O_3 0.94 wt%) and the other, the ash raw meal, with all the same materials except clay, which was replaced by activated carbon ash (limestone, 81.36 wt%; carbon ash, 10.93 wt%; sand, 6.30 wt%; Fe_2O_3, 1.38 wt%). The Fe_2O_3 used in both cases was a laboratory reagent. The reference and ash raw meals had the same:

- chemical composition;
- silica modulus (Ms: $SiO_2/(Al_2O_3 + Fe_2O_3)$) = 2.30;
- lime saturation factor (LSF: $CaO/(2.8SiO_2 + 1.18Al_2O_3 + 0.65 Fe_2O_3)$) = 0.98; and
- flux modulus (Mf: Al_2O_3/Fe_2O_3) = 1.50.

Before the materials were mixed, the limestone was milled to <125 μm, the clay to <63 μm and the sand to <45 μm. The carbon ash was not ground, i.e., it was used without altering the original particle size distribution.

Approximately 4 g of raw meal were pressed into a 2-cm diameter cylindrical tablet which was then heated at 1400, 1450 or 1500 °C for 30 min, after which the tablets were removed from the furnace and air-cooled. The burnability of the ash raw meal was studied on samples fired at 1400 and 1500 °C, while the sample treated at 1450 °C was used to study the effect of ash on the mineralogy and microstructure of the clinker phases formed.

2.3. Ash cement hydration and calorimetry

Ash-based cement was obtained by grinding a mix of 95 wt% of clinker fired at 1450 °C and 5 wt% of gypsum in a laboratory mill to a particle size of under 45 μm and subsequently mixing 3 g of the dry materials with 1.2 g of water. Hydration was detained with acetone after 7 days.

The heat of hydration generated by ash cement at T = 25 °C was monitored on a TA Instruments THAM AIR conduction calorimeter.

The thermal behavior of the 7-day ash cement paste was studied on a TA Instruments SATQ600 differential thermal and thermogravimetric analyzer, heating the samples at 10 °C/min. to a maximum temperature of 1050 °C in N_2 and air.

2.4. Materials and product characterization

The carbon, hydrogen and nitrogen contents in the activated carbon and the oil coke used as a reference and the total sulfur (in the activated carbon, oil coke and ashes of both) were determined in Leco kilns. Moisture was found by measuring weight loss in a drying oven at 105 °C and the calorific value as per international standard ISO 1928 (1995) (Table 2). The total chlorine content was 0.0015 ppm.

Carbon ash mineralogy was determined on a Bruker D8 Advance X-ray diffractometer, fitted with a high voltage; 3-kW generator and a (1.54 Å CuKα) copper anode X-ray tube normally operating at 40 kV and 50 mA. This instrument was coupled to a Lynxeye

Table 1
Chemical analysis of the raw materials (XRF) (wt%) and ICP (ppm). **1**: clay; **2**: limestone; **3**: sand; **4**: Fe_2O_3.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LOI*
1	52.00	15.10	6.02	4.01	4.95	2.60	0.58	4.55	0.73	0.10	0.15	9.2
2	5.60	1.30	0.58	51.10	0.58	0.00	<0.01	0.23	0.07	0.01	0.10	40.5
3	89.40	3.90	0.61	2.06	0.03	0.00	0.07	1.79	0.04	<0.01	0.03	2.1
4	0.00	0.00	96.00	0.00	0.00	0.42	0.00	0.00	0.00	0.32	0.45	0.5

LOI*: loss on ignition at 1000 °C.