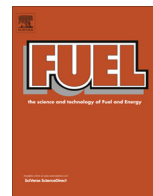




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Short communication

Spent limestone sorbent from calcium looping cycle as a raw material for the cement industry



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ABSTRACT

It has been found that a spent limestone sorbent, coming from a pilot-scale calcium looping fluidized bed (CaL-FB) plant and purged after 60 cycles of calcination and carbonation, can be successfully employed in the Portland cement clinker manufacture in place of natural limestone. Laboratory measurements showed that the burnability index for a clinker-generating raw mixture consisting of commercial clay and the exhausted sorbent was better than that of a reference mixture containing the same clay and fresh limestone. The results of the burnability test were confirmed by (i) the mineralogical composition data on the synthetic clinkers obtained from both raw mixtures at 1500 °C and (ii) the hydration rate of the related Portland cements, evaluated by means of X-ray diffraction analysis and simultaneous differential thermal-thermogravimetric analysis, respectively. Preliminary and novel results reported in this communication show that the utilization of the spent limestone sorbent as a raw material for making cement can have a very favorable effect not only on the economics of the CaL-FB process, but also on the cement manufacture in terms of (i) reduced generation of carbon dioxide and pollutants, (ii) saving of raw materials and fuel, (iii) decreased flow rate of gaseous emissions.

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1. Introduction

Carbon capture and storage technologies have the potential to almost completely eliminate CO₂ emissions from power plants and other industries [1]. Calcium looping (CaL) cycle is one of the most promising post-combustion CO₂ removal methods [1–3]. The process involves the use of two interconnected fluidized bed (FB) reactors: (1) the carbonator, where CO₂ present in an industrial flue gas is captured by CaO particles at about 650 °C; (2) the calciner, where (i) CaCO₃ produced in the carbonator is heated up at about 900–950 °C (through oxyfuel combustion) and decomposed to CaO for the next carbonation stage, and (ii) a CO₂-rich gaseous stream ready for further processing and final storage is generated. The use of a dual interconnected FB system is required to ensure both a good gas–solid contact and an easy transport of solid sorbent streams from one reactor to the other. Following repeated cycles of calcination and carbonation, sorbent particles undergo thermal sintering/deactivation [4,5] and must be purged (typically, from the calciner) and replaced with fresh limestone. The CaL technology has been under investigation for several years [1–8], and the economics of the process can be improved using the

spent sorbent (rich in CaO) as a raw material for making cement, so potentially decarbonising both power generation industry and cement manufacture process [9–13]. Using a non-carbonated source of lime can result in a number of remarkable advantages for the cement industry. Apart from CO₂ saving (about 60% of the total carbon dioxide emission from a cement kiln is due to limestone calcination), a strong decrease of the kiln thermal input can be obtained inasmuch as most of the energy requirement is represented by the heat of CaCO₃ decomposition. This, in turn, will decrease the fuel-related kiln CO₂ emissions. A considerable reduction of both fuel-raw materials specific consumption and gaseous stream-pollutants flow rate can be therefore achieved [14,15]. In a recent paper [3], several synthetic Portland clinkers were produced by heating mixtures of (i) commercial silica sand, (ii) analytical reagent aluminium and iron oxides, and (iii) CaO sources resulting from a final calcination step after looping cycles in a lab-scale reactor with and without simultaneous *in situ* fuel combustion. The concentration values of alite (the most important Portland cement clinker phase) in the synthetic clinkers were lower than those usually occurring in commercial clinkers; as a matter of fact, depending on the number of cycles, they were 23–41% and 43–50% lower, for clinkers generated by CaO sources obtained with and without *in situ* fuel combustion, respectively. Furthermore, it has been

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found that the conversion degree toward alite for the former series of synthetic clinkers increased with the increase of the number of cycles. This communication aims at giving a further contribution along this research path, within the framework of a broader research activity focusing on the reuse of wastes coming from FB processes in the field of construction materials [16–18]. The adopted approach differed from the previous works due to the use of spent limestone sorbent from pilot-scale CaL cycles and commercial clay. Both materials were utilized as components of a clinker-generating raw mixture (*M*) submitted to a burnability test [15,16], using as reference term the binary mixture (*RM*) composed by fresh limestone and the same clay as above.

2. Experimental

The CaL experiments were carried out in a 10 kW_{th} dual interconnected FB facility (electrically heated), described in detail elsewhere [19,20], using as a sorbent for CO₂ capture a commercial limestone, originating from south Germany [5]. This sorbent was also employed as a calcareous component of the *RM* mixture for the synthesis of Portland cement clinker. The CaL tests were aimed at generating spent sorbent, with a circulating FB (71 mm-ID, 12.4 m-height) operating as a carbonator (630 °C, fluidizing gas containing 14% CO₂ to simulate a typical combustion flue gas) and a bubbling FB (150 mm-ID, 3.5 m-height) acting as a calciner (905–920 °C, fluidizing gas containing up to 65% CO₂, to simulate oxyfuel calcination with CO₂ recycle). Exhausted sorbent was retrieved after 60 calcination/carbonation cycles (10 h-continuous operation); it was used as a substitute for limestone in the *M* mixture. In both *M* and *RM* mixtures, commercial clay (generally employed for Portland clinker manufacture) was utilized as a second constituent. The chemical composition, in terms of major oxides, of the three materials was determined by X-ray fluorescence (XRF) analysis (Bruker Explorer S4 apparatus) and is indicated in Table 1 together with the loss on ignition (LOI) values. Inspection of data in Table 1 clearly shows that the raw limestone was nearly pure CaCO₃, while the spent sorbent was essentially consisting of CaO. On the other hand, the clay mostly contained oxides of Si, Al, Ca and Fe. Commercial natural gypsum, containing about 80% of CaSO₄·2H₂O by mass, was used for Portland cement laboratory preparations submitted to hydration tests.

The burnability of a raw mix for Portland cement manufacture can be defined as the ability of calcium oxide, derived from limestone calcination, to react in the kiln with silicon, aluminium and iron oxides contained in the argillaceous material to give the clinker. According to a fixed heating cycle, burnability is evaluated by either (i) the amount of unreacted calcium oxide (free lime) present after a given treatment duration or (ii) the burning time needed to reduce the free lime content to some specific value [14]. The test adopted in this investigation [15], aimed at obtaining a burnability index (*BI*) for both *M* and *RM* mixtures, was based on the following thermal treatment: (a) first step at 105 °C for 120 min; (b) second step at 600 °C for 30 min; (c) third step at the final temperature

Table 1

Chemical composition of raw limestone, spent limestone sorbent and clay, % by mass.

	Raw limestone	Spent limestone sorbent	Clay
CaO	56.0	94.1	10.4
SiO ₂	0.3	0.5	54.1
Al ₂ O ₃	0.1	0.2	11.5
Fe ₂ O ₃	0.1	0.1	4.5
Others	0.3	0.9	6.4
LOI at 950 °C	43.5	4.5	13.0

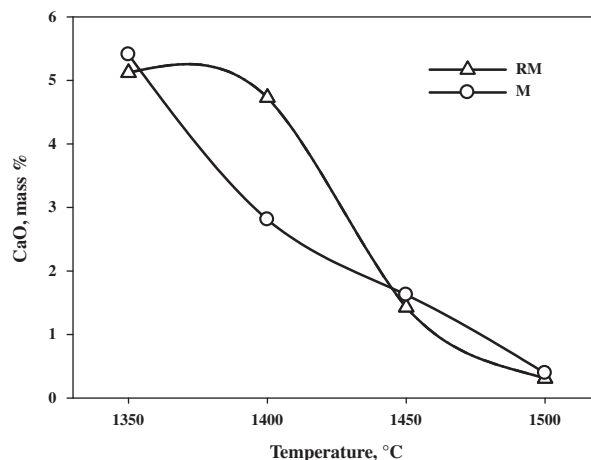


Fig. 1. Free lime concentration values in the synthetic clinkers obtained from *M* and *RM* mixtures vs. final temperature of each thermal cycle of burnability test (average values based on three measurements for each sample, standard deviation in the range 0.122–0.181).

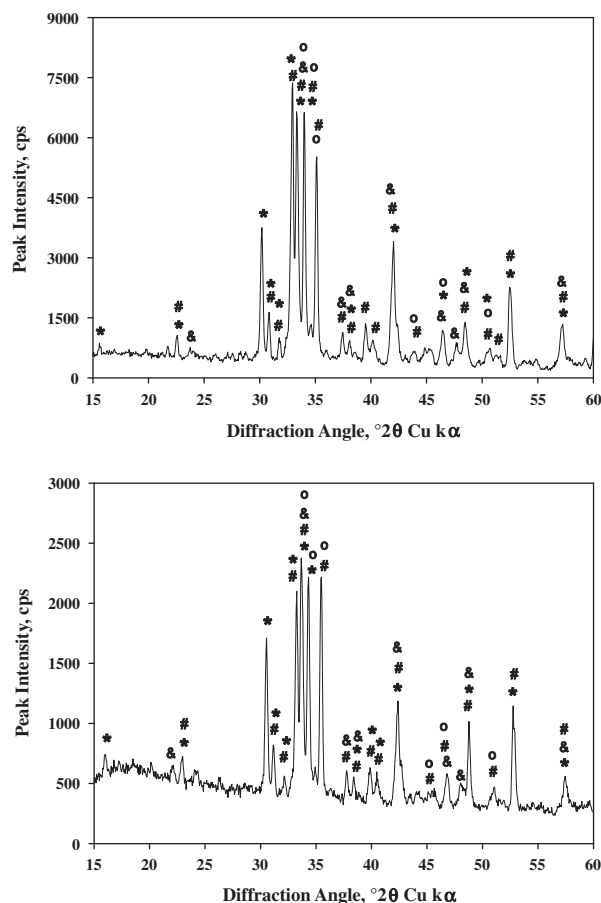


Fig. 2. XRD patterns for *M*-1500 (top) and *RM*-1500 (bottom) clinkers (* = 3CaO·SiO₂, # = 2CaO·SiO₂, & = 3CaO·Al₂O₃, o = 4CaO·Al₂O₃·Fe₂O₃).

(1350, 1400, 1450 or 1500 °C) for 15 min. *BI* is given by the following formula:

$$BI = 3.73 \cdot (A + B + 2C + 3D)/(A - D)^{1/4} \quad (1)$$

where *A*, *B*, *C* and *D* are the free lime contents (% by mass) in the products burnt at 1350, 1400, 1450 and 1500 °C, respectively. *A*

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