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CURRENT TRENDS ON SUSTAINABLE ENERGY, ENGINEERING, MATERIALS AND ENVIRONMENT

# Feasibility study on the utilization of coal mining waste for Portland clinker production

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## Abstract

CMWs (coal mine wastes) as the waste products of coal exploitation or washing plants are a source of pollution that generates waste management problems, especially those that are very old and without a known owner. CMW chemical composition indicates that it contains $SiO_2$-$Al_2O_3$-$Fe_2O_3$ in such percentages that it can be used in the production of Portland cement clinker, which can lead to potential savings in clinker production, not only in raw material but also in fuels if the CMW has a minimum calorific value and has not suffered self-combustion. After characterization of different CMWs from mining sites located in the north of Spain, six types of CMW have been selected and different raw meal formulations have been designed by software, maximizing the substitution rate of CMW and ensuring a correct raw meal chemical parameters. Along with a reference raw meal, all CMW clinkers were sintered, ground with gypsum, and tested determining the setting time, compressive strength, and soundness. The results of the physico-mechanical tests show that the mechanical performance of the CMW cements was consistent with the European requirements for a CEM Type I cement. CMW, especially those with a residual energetic content, can be utilized in clinker raw meal due to its availability in large quantities at low cost with the further significant benefits for waste management and environmental practices in mining and in cement production processes.

**Keywords** Mining waste · Alternative resource · Greenhouse emissions · Sustainable cement · Clinker production

## Introduction

Every day, huge amounts of waste are generated and, considering those produced in the past which remain nowadays without any treatment or reuse, humanity faces an important health and environmental hazard. In that sense, coal mine waste (CMW) causes problems due to the large volumes that must be transported and stored, and by its high economic and environmental cost (altered landscape, stability problems, pollution), especially in areas with a strong mining operations tradition. In those areas, numerous old dumps remain in a state of neglect, with none taking charge of their restoration causing a great environmental, economic, and social burden, which sometimes leads to safety problems (Rodríguez et al. 2011), and health disorders and diseases (Munawer 2017). The EU Waste Framework Directive guides Member States to improve their waste management practices in line with the EU waste hierarchy, supporting the shift towards a resource-efficient, low-carbon economy.

On the other hand, cement sector is an energy and carbon-intensive industry. The cement industry contributes approximately 5% of the global carbon dioxide emissions and it is the second largest $CO_2$ contributor in industry, after power plants. The worldwide production in 2016 was 4.6 billion tons of cement (Cembureau 2018) that required approximately 5 billion tons of resources. The production of cement releases roughly 8% of global $CO_2$ emissions, counting both those generated by carbonate oxidation in the cement clinker production process as fuel combustion emissions (Olivier et al. 2015). Moreover, the economic situation of the cement production sector is deeply affected by the last recession. Action

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lines, both economic and environmental, are required in this industry to increase the competitiveness in the global market through the reduction of manufacturing cost and, at the same time, minimize environmental footprint using methods, processes, and materials more sustainable.

A wide range of options are available to reduce $CO_2$ emissions and save raw materials and energy in the cement sector, as development of alternative processes using waste material. These days, material and energy recovery from waste is a widespread practice in cement plants in most developed countries of the European Union; in some cases, the percentage of energy replaced using waste is very high (Austria 79%, Sweden 69%, and Germany 65% referred to the period from 2015 to 2017), being the EU average 44.4% (CEMA 2018). In 2017, the Spanish cement industry reached an average of material recovery in the cement production process about 4.5% (using 1.4 million tons of waste), and alternative fuels constituted 26.6% of energy substitution (using 798,616 t of waste). These values are lower than the European Union average which stands about 15% for material recovery and 39% for energy (OFICEMEN 2018).

The European Commission has included the cement industry in its Waste-to-Energy Communication that provides guidance to Member States on how to optimize their waste management systems, so that an increase of recovery and valorization in cement plants is expected.

In that sense, the use of CMW provides silicon and aluminum which are required components in the clinker raw meal, so it could replace clay. CMW could act as aluminous corrector in the clinker matrix. Besides, if CMW contains a residual combustion power, it could contribute to save fossil fuel substituting petcoke in clinker production process.

Related with CMW and according to previous studies, the use of CMW has been investigated in different ways: as fine aggregate to produce paving blocks (Santos et al. 2013), in the form of ash, after its activation, in recycled asphalt mixtures (Modarres and Ayar 2014), to stabilize the base and subbase materials for soil stabilization (Kinuthia and Nidzam 2009). Kaminskas and Kubiliute (2010) showed that the use of coal ash into tricalcium silicate raw meal reacted with lime aims to reduce the percentage of $C_3S$ in the sample and raises the proportion of other phases such as $C_2S$ or $C_3A$.

On the other hand, Portland cement is becoming a binding reagent to solidify and stabilize a wide range of wastes, because it reduces toxicity of some contaminants, encapsulates waste particles with an impermeable coating, fixes hazardous constituents by reducing their solubility, and reduces the permeability of the waste form (Yakubu et al. 2018). Thus, a wide range of wastes, especially industrial ones, such as fly ashes, metallic slags, glass, rubber, red mud, and sewage sludge, have showed that their use in clinker process, controlling their proportion in the mix, is possible (Liu and Zhang 2011; Pontikes and Angelopoulos 2013; Alp et al. 2009; Trezza and Scian 2007).

In addition, since 2006 and especially in recent years, a lot of published research works have focused on the use of activated CMW in cement production due to its pozzolanic behavior. Starting from the performance assessment of blended cements formed by 20–30% of activated different Chinese CMW (varying the temperatures from 700 to 1000 °C) (Li et al. 2006), several other studies were carried out, e.g., the use of an activated coal mine waste (ACMW) (650 °C for 2 h) as an addition in the production of blended cements, obtaining that cement produced with up to 20% of ACMW complies with the EU standard (Frías et al. 2012), or the physical–mechanical assessment of a blended cement (up to 20% of ACMW) which showed a slightly accelerated setting times and an increase in compressive strengths at early time, meeting the requirements set out by the EU standard (Vegas et al. 2015). Further, studies of the influence of ACMW in blended cement have been established, e.g., effects on chloride permeability of blended cements in amounts up to 50% CMW resulting in an immobilization of chloride ions and a refinement of the capillary network, decreasing in pore size but increasing electrical resistivity (Caneda-Martínez et al. 2018); durability assessment of blended cement up to 20% ACMW showed that it is not affected by extreme temperatures, showing a similar behavior to a reference mortar under 300 freeze/thaw cycles (García-Giménez et al. 2018); and even, calcium-leaching tests were conducted in ordinary Portland cement (OPC) and in blended cement up to 20% ACMW, and, in the latter, the calcium leaching decreased slightly comparing to the reference, remarking the reduction of $CO_2$ emissions up to 12% (Arribas et al. 2018).

Additionally, there are several studies about applications of CMW: in a concrete pavement production by using a mixed cement up to 20% CMW, after its ignition, led to an increase in mechanical properties, especially at 28 and 90 days (Hesami et al. 2016), or in steel bars embedded mortar made with up to 50% ACMW, in which the corrosion rate was tested, observing a delay in chloride content and, therefore, improving corrosion resistance, especially for the 20% CMW cement comparing with an OPC (Caneda-Martínez et al. 2019). In some cases, the potential of enhancing a product is studied, e.g., the improvement of fiber-reinforced cements using blended cements with a 25% ACMW as results comparing with a control fiber-reinforced OPC mortar showed, since a reduction in ~ 60% of pore size and similar strength are achieved (Mejia-Ballesteros et al. 2019).

The main objective of the present study is to go further in` the use of CMW in the cement production, incorporating CMW in the initial raw meal prior to calcination stage, in order to substitute virgin raw material required for the clinker production, and then, asses physico-mechanical behavior to compare the cement made of CMW clinkers with an OPC CEM I

42,5 under EU standards. The novelty of the present study has to be highlighted, since not only a more integral use of natural resources is proposed by reducing non-renewable raw materials but also it contributes to reduce $CO_2$ emissions by reducing the use of fossil fuels. Concerning environmental performance, other advantages are related to improve the mineral resources supply chain, extending the life of current exploitations, and, therefore, reducing the mining environmental effects (noise and dust generation, $CO_2$ emissions, visual impact, space occupation, blasting and required, transport, etc.) (Serjun et al. 2015).

## Materials and methods

### Coal waste sites

Generally, there are no detailed inventories of CMW to date, and tests of the original material discharged cannot be consider for further studies, since, after the deposition, CMW can suffer reactions affecting to organic matter and its mineralization, and even reach self-combustion. These transformations depend on many factors (mineral compositions, organic matter content, moisture content, landfill sha`pe, wind direction, rain, etc.) (Ciesielczuk 2015). In addition, it is usually stored in the same pile or dumps of two different types of CMW: the mine waste originating directly from the exploitation (tailings), or residual material obtained from coal treatment process (bulk coal washing) (Malagón 2013). So, independently of initial tests, CMW which forms the waste piles must be analyzed for research purposes.

This study is focused on coal waste sites located in the north of Spain, in two highly coal-mined areas, Asturias and Palencia, as shown in Fig. 1. Six coal waste sites have been selected to be analyzed: the Camocha, Morgao, and Modesta in Asturias, and Barruelo 1, Barruelo 2, and Vallejo in the north of Palencia, generated in mining and treatment of coal in the past.

The election follows the following criteria: (a) being an obsolete stock, (b) with a lower heating value LHV > 18 KJ/g, and (c) not having suffered self-combustion.

The location of the six potential CMW sites in Asturias and Palencia and their current associated risks from the point of view of safety and each volume are shown in Table 1.

#### Barruelo and Vallejo

Coal waste sites Barruelo 1–2 are located in Barruelo de Santullán, a municipality in the Palencia province of Castile-Leon. A very close coal mine was exploited from 1845 until 2005 when the company Uminsa decided to close its operations there, with its highest production peak in the early decades of the twentieth century.

Barruelo 1 (42°54′17.3″N 4°17′41.2″W) occupies an area of about 60,000 $m^2$ and Barruelo 2 (42°54′09.0″N 4°17′27.5″ W) occupies about 30,000 $m^2$, with an accumulated volume of both around 1,700,000 $m^3$. In Barruelo 1 (B1), three samples were taken at the top of the deposit, and three in the lower eastern part; in Barruelo 2 (B2), three samples were collected from the upper east and three near the river (indicated as B1 and B2, respectively, in Table 2).

About 5 km from Barruelo, near the town called Vallejo de Orbó, the third CMW site is located, called Vallejo (42°53′23.5″N 4°15′26.7″W), which occupies about 408,000 $m^3$. CMW content in Vallejo has been determined by three samples of the top of the deposit and three from the bottom (indicated as VA in Table 2).

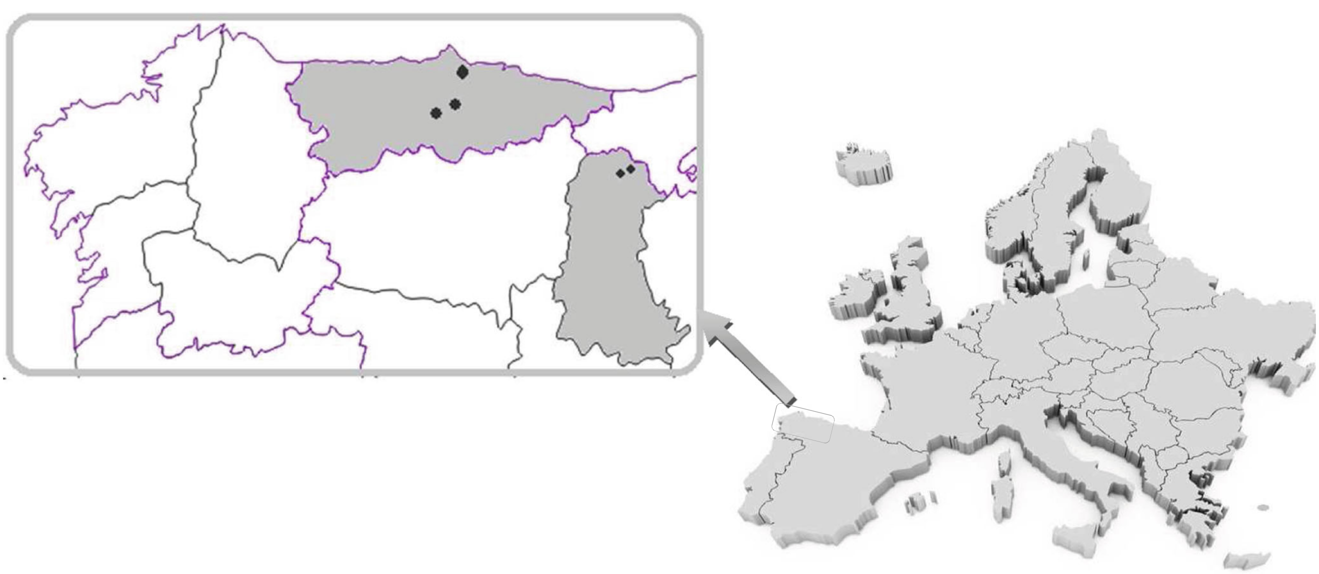

**Fig. 1** Geographical location of coal waste deposits characterized in the north of Spain

**Table 1** CMW sites' volume and H&S risks

| Mine waste | Location | Estimated volume ($m^3$) | Associated risks |
|---|---|---|---|
| Barruelo 1 (B1) Barruelo 2 (B2) | Barruelo de Santullán (Palencia) | 1,700,000 $m^3$ | Visual impact, risk of landslide, proximity to village |
| Vallejo (VA) | Vallejo de Orbó (Palencia) | 408,000 $m^3$ | Visual impact, proximity to village |
| La Camocha (LC) | San Martín Huerces, Gijón (Asturias) | 1,300,000 $m^3$ | Visual impact, risk of landslide in upper slopes |
| Morgao (MR) | Mieres (Asturias) | 3,000,000 $m^3$ | Small slides caused by surface run-off, problems with water and vegetation |
| Modesta (MD) | Langreo (Asturias) | 1,500,000 $m^3$ | Visual impact, risk of landslide, proximity to village |

## La Camocha

Camocha Mine was located at 6 km South of Gijón, a municipality in Asturias, and it was active from early last century until the end of 2008. CMW was deposited throughout years, constituting a settling dump and a huge pile (43°29′16.3″N 5°40′04.0″W).

It occupies an area of about 56,200 $m^2$ on a flat ground, and the cumulative volume is 1,300,000 $m^3$. According to studies, the northern dump was about 2.1 million tons and the southern was approaching 0.5 million tons.

The dump, with a form of truncated cone and an overall height of approximately 40 m, is divided into three banks, heights ranging between 7 and 20 m, and two berms with a width varying between 5 and 15 m. The slopes have an inclination of about 35 or 40°, and in some places, there are some cracks. It presents some slippage risk in the upper slope, where it shows the above signs of cracking. It is unrestored, causing a significant visual impact in the area. The deposit is very close to the city of Gijon and to several urban roads and could have industrial interest.

According to the literature, fine tailings were accumulated in this dump having relative calorific value, e.g., those deposited in 1996 had a lower calorific value (LCV) of 1.832 kcal/kg (Fernández 2001).

**Table 2** Chemical composition of CMW

| % | B1 | B2 | VA | LC | MR | MD |
|---|---|---|---|---|---|---|
| $SiO_2$ | 55.71 | 56.03 | 35.46 | 41.09 | 44.04 | 46.83 |
| $Al_2O_3$ | 17.3 | 22.7 | 27.18 | 24.94 | 24.01 | 18.23 |
| $Fe_2O_3$ | 6.11 | 5.02 | 4.34 | 8.95 | 4.8 | 17.69 |
| CaO | 0.55 | 0.24 | 0.13 | 0.01 | 0.09 | 0.01 |
| MgO | 1.12 | 0.97 | 0.01 | 0.4 | 0.74 | 0.92 |
| $K_2O$ | 3.78 | 3.4 | 0.12 | 3.04 | 3.3 | 2.44 |
| $Na_2O$ | 0.22 | 0.24 | 0.01 | 0.02 | 0.7 | W.D. |
| $SO_3$ | 1.34 | 0.61 | 0.49 | 1.29 | 0.33 | 0.11 |
| $TiO_2$ | 0.98 | 0.81 | 1.56 | 0.68 | 0.35 | 0.61 |
| LOI | 12.04 | 10.43 | 30.21 | 19.46 | 22.8 | 13.26 |

*W.D.*, without detection

For sampling, three samples were taken at the top of the heap northern and three in the southern bottom (indicated as LC in Table 2).

## Morgao

The dump of Morgao (43°15′42.8″N 5°46′15.4″W) is located near to the city of Mieres, close to Batán coal washing plant, in Morgao valley. Coal waste was deposited there from 1961 to 1972. This dump has a height of 70 m and an area of approximately 90,000 $m^2$. It is formed by two berms with a slope of about 60° and an intermediate berm over 200-m wide at its center. Its estimated volume is about 3,000,000 $m^3$.

The coal washing waste was the only material dumped in it, so it is very homogeneous. Later, the lower part of the dump was re-vegetated. In 1997, a large quantity of cider apple trees was planted in the upper part of the dump, but later, probably due to landslide phenomena, part of the CMW has been exposed.

In that case, two samples were taken at the upper part, two in the intermediate berm, and two more in the lower part (indicated as MR in Table 2).

## Modesta

The dump of Modesta (43°17′19.8″N 5°40′39.6″W) is located in Langreo, a city of Asturias. Coal waste from Modesta coal washing plant was deposited in it about 20 years, until 2007. It is partially replanted, although the sterile deposited in the upper part emerges along a large area. It consists of two slopes with an inclination close to 40° and a total height of 40 m. It contains an estimated volume of 1,500,000 m3 coal tailings.

Although the area affected has been extensively revegetated, the visual impact of this dump is medium and presents risk of landslides that could affect its surroundings.

In this site, three samples were taken in the central eastern part and three in the lower western part (indicated as MD in Table 2).

## Characterization methods

Several techniques were used to characterize chemical, physical, and mineralogical CMW samples and CMW clinkers. Chemical composition was determined by X-ray fluorescence analyzer (FRX PHILIPS PW2404-2540). Mineral phases of the samples were analyzed by X-ray diffraction (XRD) using random parts of the samples in powder (D8-FOCUS, Bruker AXS). Fine content was determined by laser ray-diffraction (Mastersizer 2000, Malvern). Free lime content in the CMW clinkers (unreacted CaO) was determined by the ethylene glycol method. The compressive strength of mortar prisms (40 mm × 40 mm × 160 mm) was determined at the ages of 2, 7, and 28 days according to European Standard EN 196-1. Consistency and setting times of mortar pastes were determined using a Vicat apparatus according to the European Standard EN 196-3, and Le Chatelier method was used to determine expansions of the pastes.

## CMW samples

Chemical composition of CMW is given in Table 2. According to the general CMW compositions, a priori, its use is feasible for the clinker raw meal production. Ordinary Portland cement clinker belongs to the system $CaO$-$SiO_2$-$Al_2O_3$-$Fe_2O_3$, being CaO the majority component, decreasing the rest in the order $SiO_2$-$Al_2O_3$-$Fe_2O_3$. This indicates that the raw meal components should be predominantly calcareous, with successive smaller quantities of siliceous, aluminous, and ferruginous constituents.

CMW chemical analysis also showed that the CMW contained impurities such as heavy metals including Cu, Co, Zn, and Pb with potentially hazardous character (Fig. 2).

Besides, all the selected CMWs have a residual calorific value, increasing the potential of fossil fuel savings; Table 3 shows the lower heating average value of each CMW site.

**Table 3** LHV of each CMW

| kJ/g | B1 | B2 | VA | LC | MR | MD |
|---|---|---|---|---|---|---|
| LHV | 27.21 | 26.5 | 21.35 | 32.24 | 18.42 | 25.37 |

## Design of dosages of raw meal clinker

Knowing the chemical composition of CMW from each site, six different types of CMW clinker raw meals were prepared and compared with a reference one.

The design procedure is based on obtaining an optimal lime saturation factor (LSF, maximum amount of lime which can be hydraulically combined with $SiO_2$, $Al_2O_3$, and $Fe_2O_3$), a silica modulus (ratio of silica to the flux considers iron oxide plus alumina) in a determined range, and a suitable alumina modulus (ratio of iron oxide and alumina), which ensure later a correct distribution of

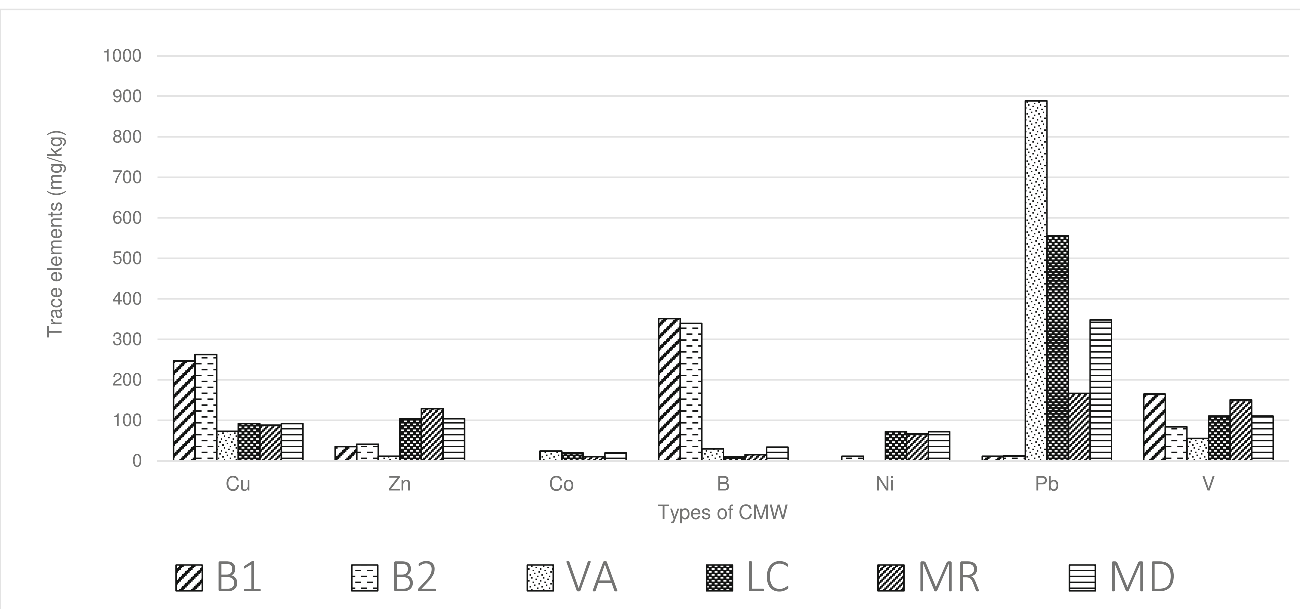


**Fig. 2** Trace elements of CMW in mh/kg

clinker minerals (alite, belite, tricalcium aluminate, and ferroaluminate), and, also provides the clinker with enough burnability. The reference clinker composition was established from a real mix and the rest of the combinations were designed, maximizing the CMW incorporation, to meet the following hypothesis:

Lime saturation factor = 95%

$2.0 < \text{silica modulus} < 3.0$

$1.9 < \text{alumina modulus} < 3.2$

Relation $CaO/SiO_2$ in the clinker $\geq 2$

Limestone, shale, and silica sand, as well as reference raw meal clinker, were collected individually from a cement plant in Cantabria, Cementos Alfa, and their chemical compositions are given in Table 4.

CMW clinkers' design was calculated with Excel Solver tool using the GRG Nonlinear solving method to determine the optimal solution among those that meet the required conditions listed above. Table 5 summarizes the composition of the different CMW clinker raw meals calculated, and the composition of the reference clinker raw meal.

To prepare the different raw meals, CMW and raw materials were dried at 105 °C to constant weight to eliminate the water present and, after that, were quantitatively weighed in the proportion shown in Table 5, and finally were ground in a Bond ball mill to simulate the real preparation conditions, obtaining a granulometry characterized by more than 75% particles passed through the 90-μ sieve.

The clinker raw meals were pelletized and placed into a furnace at 500 °C, scaling up the temperature in a range of 15 °C/min up to 1450 °C. After the sintering process, clinkers were cooled by air in a dryer to avoid $C_3S$ decomposition and $\gamma$-$C_2S$ formation from $\beta$-$C_2S$, due to $\beta$-$C_2S$ reacts slowly with water and $\gamma$-$C_2S$ is almost inert (Wang et al. 2015).

CMW clinkers and the reference were analyzed by XRF, and free CaO was determined using the ethylene glycol method.

**Table 4** Chemical analysis of traditional materials for clinker production and the reference raw meal

| % | Limestone | Shale | Silica sand | Raw meal clinker reference |
|---|---|---|---|---|
| $SiO_2$ | 2.14 | 14.46 | 95.01 | 14.13 |
| $Al_2O_3$ | 0.77 | 4.42 | 2.04 | 3.86 |
| $Fe_2O_3$ | 0.32 | 1.53 | 0.25 | 1.33 |
| CaO | 53.1 | 41.87 | 0.33 | 42.73 |
| MgO | 0.42 | 1.22 | 0.18 | 1.09 |
| $Na_2O$ | 0.1 | 0.08 | 0.01 | 0.08 |
| $K_2O$ | 0.08 | 0.72 | 0.04 | 0.62 |
| $SO_3$ | 0.00 | 1.19 | 0.10 | 1.00 |
| LOI | 42.59 | 33.1 | 2.03 | 34.60 |

*W.D.*, without detection

**Table 5** Raw meal composition for clinker production without CMW (REF) and with CMW (RM)

| % | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 |
|---|---|---|---|---|---|---|---|
| Limestone | 14.23 | 41.77 | 46.99 | 12.83 | 56.99 | 28.76 | 44.50 |
| Shale | 84.00 | 49.03 | 42.99 | 83.92 | 29.87 | 64.83 | 45.67 |
| Silica sand | 1.77 | 3.13 | 4.08 | 0.00 | 6.35 | 2.37 | 4.40 |
| B1 | | 6.07 | | | | | |
| B2 | | | 5.95 | | | | |
| VA | | | | 3.25 | | | |
| LC | | | | | 6.79 | | |
| MR | | | | | | 4.04 | |
| MD | | | | | | | 5.42 |

## Results and discussion

### CMW materials

In a first analysis, it can be seen that the predominant compounds are $SiO_2$ and $Al_2O_3$ in all cases, whose sum can determine two groups within the different CMWs. The first group would be formed by samples B1, B2, and VA with an average value of 75% in the sum of $SiO_2$ and $Al_2O_3$ (range between 73 and 79; see Fig. 3), and a second group covering LC, MOR, and MOD with a mean value of the same parameter of 66% (range between 65 and 68). This is due to the different host rocks in which the deposits are that determine the greater or lesser presence of clay minerals.

As shown in Table 2, the CMW samples contain $SiO_2$ (41–56%), $Al_2O_3$ (17–27%), and $Fe_2O_3$ (4–17%) since host rocks of coal deposits contain quartzite, sandstone, slate, or carbonaceous materials and carbonates, respectively (Areces et al. 1994). The CMW samples studied could act as a replacement for siliceous material and could provide fluxes to the mixture in clinker matrix. Besides, thanks to the fact that CMW content residual power's use could save traditional fuels and $CO_2$ emissions.

### Calculated raw meal dosages

Due to the fact that parameters to find dosage solutions are expressions that relate the CMW main compounds (since both the LSF and the silica and alumina modulus consider the oxides that enter the calculation which are $SiO_2$, $Al_2O_3$, $Fe_2O_3$, and CaO), the formulations follow a pattern shown in Fig. 4. As can be seen, the only two dosages that bear similarity are those made with B1 (RM1) and B2 (RM2) due to both of them came from the same mining exploitation. The use of VA (RM3) and MR (RM5) samples is limited in the final solutions, to 3.25% and 4.04%,

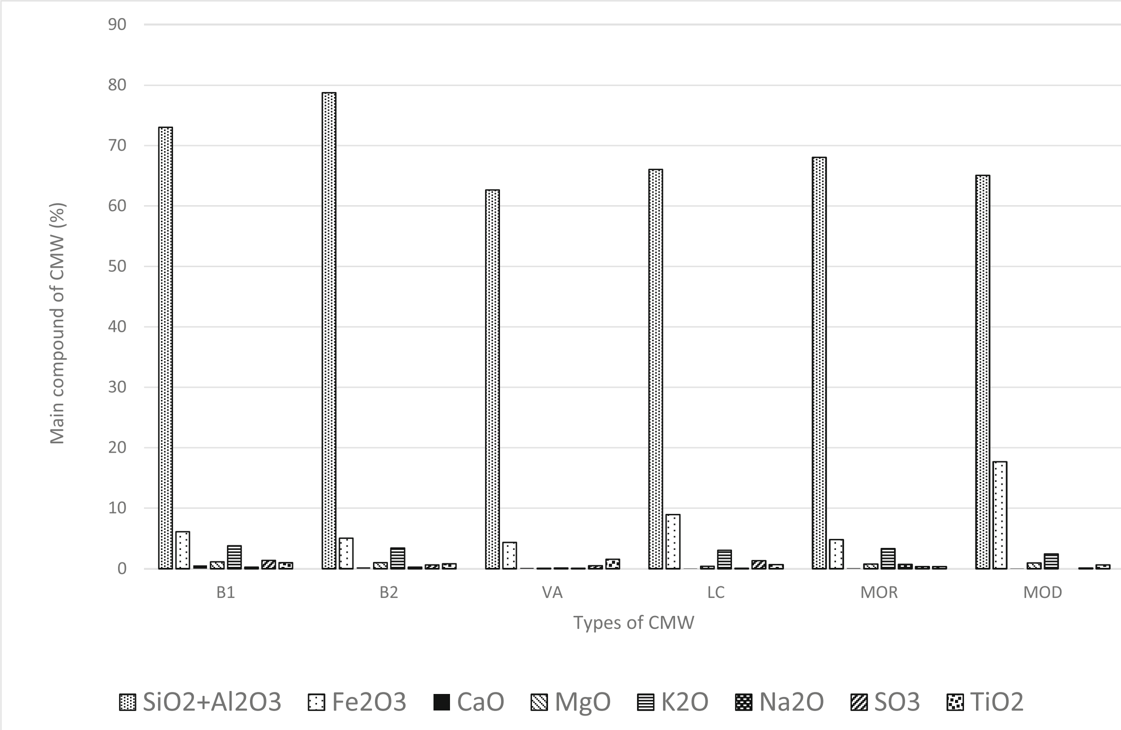


**Fig. 3** Main compound of CMW , highlighting the SiO2 and Al2O3

respectively, due to their high loss of ignition values, which indicates a high carbonate content in both materials.

## Clinker chemical composition

Regarding reference clinker and the CMW clinkers, differences in their chemical composition are analyzed. As it can be seen in Table 6, the amount of CaO and $SiO_2$ is very similar, although $SiO_2$ varies from 21.03 to 22.18 (mean 22%, standard deviation ± 0.44) versus 21.62% in the reference clinker, due to the more siliceous nature of the CMW with respect to the substituted raw materials.

The content of $Al_2O_3$ and $Fe_2O_3$ is higher in CMW clinkers than that in the reference, although, in fact, the formulations calculated with the CMW samples greatly reduce the shale/limestone ratio (from 84/14 of the reference to 52/38 of the CMW clinkers) and, therefore, the contribution of $Al_2O_3$ and $Fe_2O_3$ in the CMW clinkers that

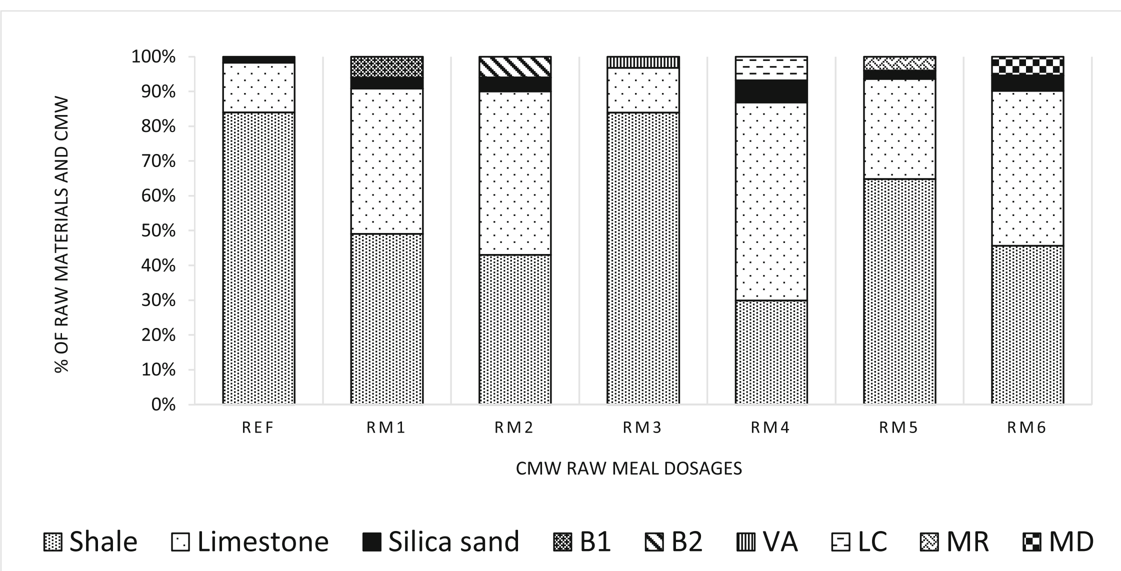


**Fig. 4** raw meal dosages of the reference clinker and calculated CMW clinker

**Table 6** Chemical composition of CMW clinkers and the reference one

| % | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 | Mean | SD |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 21.62 | 22.15 | 22.05 | 22.07 | 22.18 | 21.03 | 22.09 | 21.93 | ± 0.44 |
| $Al_2O_3$ | 6.12 | 5.67 | 5.75 | 7.38 | 5.95 | 6.48 | 5.80 | 6.17 | ± 0.66 |
| $Fe_2O_3$ | 1.92 | 2.03 | 1.99 | 2.11 | 1.81 | 2.10 | 2.87 | 2.15 | ± 0.37 |
| CaO | 65.90 | 66.87 | 66.16 | 64.70 | 66.75 | 66.61 | 66.01 | 66.18 | ± 0.80 |
| $SO_3$ | 0.54 | 0.43 | 0.61 | 0.35 | 0.33 | 0.41 | 0.36 | 0.42 | ± 0.10 |
| MgO | 1.73 | 1.30 | 1.38 | 1.62 | 0.99 | 1.19 | 1.09 | 1.26 | ± 0.22 |
| $Na_2O$ | 0.13 | 0.14 | 0.14 | 0.10 | 0.11 | 0.16 | 0.09 | 0.12 | ± 0.03 |
| $K_2O$ | 1.03 | 0.95 | 0.89 | 0.78 | 0.62 | 0.88 | 0.59 | 0.79 | ± 0.15 |
| LOI | 0.19 | 0.23 | 0.39 | 0.42 | 0.37 | 0.43 | 0.49 | 0.39 | ± 0.09 |
| CaO free | 2.03 | 2.66 | 1.90 | 2.01 | 2.30 | 2.25 | 2.10 | 2.20 | ± 0.27 |
| $Na_2O$equ | 0.81 | 0.77 | 0.73 | 0.61 | 0.52 | 0.74 | 0.48 | 0.64 | ± 0.12 |

come from the shale is reduced in contrast with what occurs in the clinker reference. This rise is due to the higher $Al_2O_3$ and $Fe_2O_3$ content in CMW samples compared with the traditional shale, although in comparison with respect to the reference clinker, the ascent of $Al_2O_3$ is attenuated by its great presence in the traditional shale. In that case, $Al_2O_3$ varies from 5.67 to 7.38 (6.17% + − 0.66) versus 6.12% in the reference. $Fe_2O_3$ content varies from 1.81 to 2.87 (2.15% + − 0.37) versus 1.92% in the reference. RM6 shows the highest data of $Fe_2O_3$, but despite this, it is well-balanced burnt with a CaO-free of 2.10.

Regarding the free lime content slightly higher in CMW clinkers than in the reference due to its more content of CaO, in all the samples, CaO-free percentage represents a well-burnt clinker, although in RM1, the CaO-free is quite high, showing an unsatisfactory burning or a poor cooling rate which could have raised the free lime content (Neville and Brooks 2010).

Regarding the $Na_2O$ equivalent ($Na_2O + 0.658*K_2O$), the alkali content is lower in the CMW clinkers than that in the reference one. The presence of alkalis helps to the formation of belite, but its presence in the final cement could lead to problems related to the alkali–silica reaction in its use together with some aggregates, forming gels in the presence of moisture, producing expansion, and reducing strength and durability (Gadea et al. 2010), so, in this sense, there is an improvement in the properties of the clinker and, therefore, of the final cement. The alkali equivalent content varies from 0.48 to 0.77 in the CMW clinkers (0.64% + − 0.12) versus 0.81% in the reference.

MgO content has a clear influence in the final cement performance, due to that a high percentage in the cement could generate expansion due to the hydration of periclase. The content of MgO in the CMW clinkers is lower than that in the reference, and all of them are less than 0.9%, so there is no risk related to the periclase formation.

## Mineralogical phases' distribution

Mineralogical composition estimation trough Bogue's formulas was calculated. Table 7 shows the results.

Analyzing the CMW clinkers by comparing with the reference, it is observed that three of them have a distribution of the main mineralogical phases very similar to the reference (RM1, RM2, and RM4). In the case of RM1 and RM2, it is notorious that both come from the same deposit, although in the case of the RM1, calcination has not been completed, since free lime is the highest of all the samples (2.66%). In general, $C_2S$ rises comparing with the reference, and $C_3S$ and the $C_4AF$ rise too, but slightly. $C_3A$ decreases due to the decrease in the calculated formulation of the percentage of shale containing alumina. Besides, in the case of $C_3A$, it is necessary to consider that the incorporation of alumina to the silicate phases is directly proportional to the amount of $SO_3$ which depends on the type of fuel used in calcination, leading to a $C_3A$ decrease, so that the content of $C_3A$ could be lower than that calculated by the Bogue formulas (Horkoss et al. 2010).

Analyzing clinker by clinker, it is observed that the biggest difference is in the RM4, since the $C_3S$ decreases by 17%, and the $C_2S$ increases by 14% with respect to the reference, so the resistance behavior of this formulation is expected to be different from the rest. RM5 behaves in the

**Table 7** Potential mineral composition of CMW clinkers and the reference one

| % | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 | Mean | SD |
|---|---|---|---|---|---|---|---|---|---|
| C3S | 60.06 | 62.85 | 60.24 | 43.02 | 60.57 | 64.76 | 57.73 | 58.20 | 7.81 |
| $C_2S$ | 16.76 | 16.18 | 17.86 | 30.90 | 17.99 | 11.52 | 19.87 | 19.06 | 6.46 |
| $C_3A$ | 12.97 | 11.59 | 11.87 | 15.99 | 12.70 | 13.62 | 10.51 | 12.71 | 1.92 |
| $C_4AF$ | 5.84 | 6.18 | 6.06 | 6.42 | 5.51 | 6.39 | 8.73 | 6.55 | 1.12 |

opposite direction, increasing the $C_3S$ by approximately 5% and decreasing $C_2S$ by the same amount with respect to the reference.

## Physical and mechanical tests for the CMW cements

All the clinkers were grounded in a ball mill within industrial gypsum (98%, *w/w*; $Ca_2SO_4 \cdot 2H_2O$), to adjust the total soluble $SO_3$ content to the EN requirements (≤ 4% for a standard CEM I-42,5 R) according to EN 197-1 Cement - part 1: composition, specifications, and compliance criteria for common-use cements (UNE EN 197-1 2011) and EN 197-2 Cement - part 2: conformity assessment (UNE EN 197-2 2014), as Table 8 shows.

Particle size distributions were analyzed by a laser scattering analyzer (Cilas: Model 1064). All of the particles of each cement passed through a 90-μm sieve, and about 90% of them passed through 64 μm as well, as shown in Table 9. Specific surface values ranged from 366 to 400 $m^2/kg$.

The fineness of CMW cements has been determined, and the results are shown in Table 9.

The water demand for a normal consistency is shown in Table 10, together with setting times and soundness, all of them tested in accordance with EN 196-3. Methods of testing cement - part 3: determination of setting times and soundness (UNE-EN 196-3 2017). The water content at normal consistency has the same pattern than the reference cement, except for RM6; in this case, it must be taken into account that an increase in water content will enhance the amount of capillary porosities decreasing the strength of cement paste and extending the setting time.

EN requirement only regulates the minimum value of the initial setting time, and all of the cements meet the criteria (< 50 min for a standard CEM I-42.5 R), although dispersion is observed in the results, despite having added an appropriate amount of gypsum in each CMW cements depending on the content of $C_3S$ and $SO_3$ in clinker. Besides the $C_3S$, in the initial setting time, the fineness of cement must be considered, since the finer the cement particles are, the larger total surface area is, and the bigger area contacting with water is. Thus, the setting will be quick, as well as the hardening (Gambhir and Jamwal 2014), but as it said above, fineness is correct of all CMW cements. The delay observed in some cases (RM4, RM6, and especially in RM3) might be related with the presence of heavy metals (Haibin and Zhenling 2010), such as lead or copper. In that sense, the RM3 has a high Pb content due to it is formed by Vallejo CMW (3.25 *w/w* of VA) which presents a high concentration of Pb (880 ppm) and, in the case of RM4 which is formed by La Camocha CMW (6.79 *w/w* of LC), it presents the highest concentration of Pb (540 ppm). Some researches about the effect of the presence of lead on the hydration of cement show that both the additions in the form of soluble compound ($PbNO_3$) or insoluble oxide (PbO) considerably retard the hydration of the pastes, the initial setting time increases with the consequent loss of initial resistance, but the compressive strength at 28 and 90 days is similar or superior (Bhatty 2011; Fernández Olmo et al. 2001).

Besides, in the case of RM3, its potential $C_3S$ is the lowest of all (43%) which also promotes an extended initial setting time.

In general, CMW clinkers have higher soundness values than the reference clinker, which can be produced either by free lime or by free magnesia. In this study, this fact is not attributable to the MgO content due to its limited presence in CMW clinkers (Table 6), but correlates with the free CaO content. It should be noted in the case of the RM1, in which the soundness is very near to the limit value required in EN 197-1 (≤10 mm), RM1 shows a high soundness value (9 mm) due to a very high CaO-free content which could indicate a poor cooling process after its calcination. During storage, this value may decrease because a part of the reactive lime is changed into calcium hydroxide and carbonate (Neville and Brooks 2010; Bye 2011).

Compressive strength tests were performed at the ages of 2, 7, and 28 days on mortar prisms (three prisms for each test) with dimensions of 40 mm × 40 mm × 160 mm,

**Table 8** $SO_3$ content in CMW cements and reference one

| | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 |
|---|---|---|---|---|---|---|---|
| $SO_3$ content (%) | 3.64 | 3.66 | 3.67 | 2.96 | 3.54 | 3.29 | 3.58 |

**Table 9** Particle size distribution, density, and fineness of CMW cements and the reference one

| | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 |
|---|---|---|---|---|---|---|---|
| > 90 μm | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| > 64 μm | 11.4 | 9.8 | 10.1 | 11.0 | 11.6 | 10.5 | 9.8 |
| Density ($kg/m^3$) | 3.14 | 3.15 | 3.13 | 3.20 | 3.11 | 3.19 | 3.12 |
| Blaine ($m^2/kg$) | 391.2 | 400.5 | 391.0 | 400.1 | 388.5 | 366.0 | 386.3 |

**Table 10** Water demand for a normal consistency, setting times, and soundness in CMW cements and reference one

| | REF | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 |
|---|---|---|---|---|---|---|---|
| Water demand (%) | 25.5 | 25.8 | 27.8 | 27.4 | 26.1 | 27.5 | 30.1 |
| Setting time | | | | | | | |
| Initial (min) | 135 | 140 | 145 | 190 | 165 | 125 | 155 |
| Final (min) | 180 | 185 | 195 | 255 | 215 | 170 | 195 |
| Soundness (mm) | 1.9 | 9.0 | 1.3 | 2.7 | 4.8 | 3.2 | 1.5 |

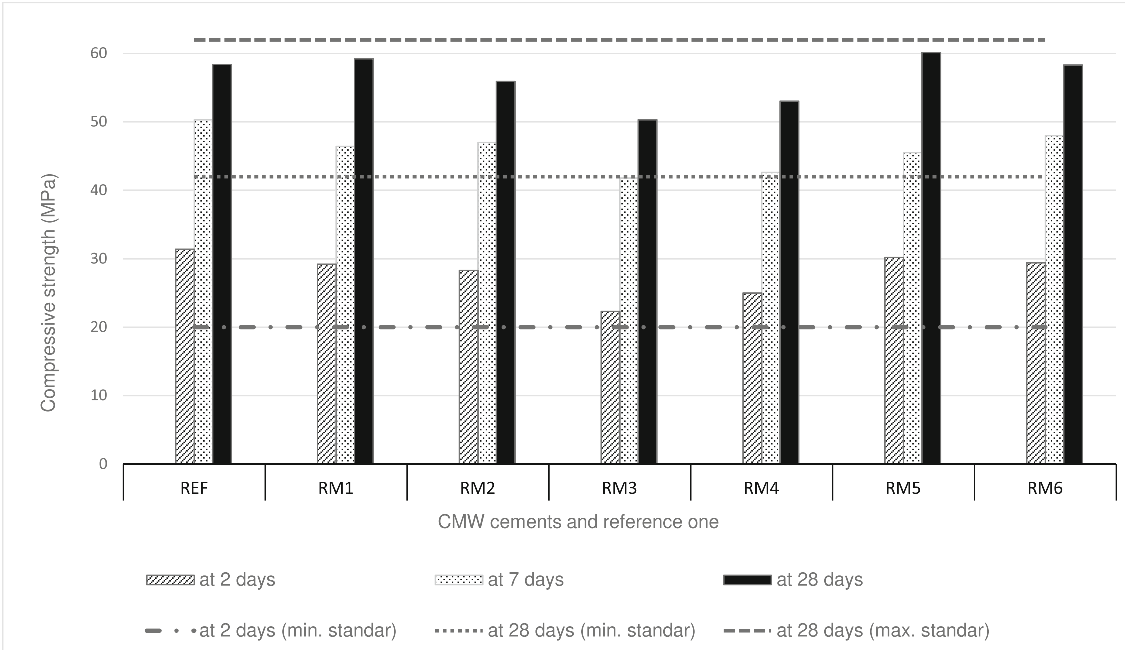


**Fig. 5** Compressive strength results ate the ages of 2, 7, and 28 days

according to European Standard EN 196-1 (UNE EN 196-1 2018). These tests were performed in triplicate, and the mean values are presented in the results (Fig. 5).

In general, at all reaction times, compressive strenght for CMW cements is lower than that for the reference one, especially at short ages, but all of them comply with the values in the EN standards for a CEM-I-42,5 R. RM1 and RM2, which are formed by a CMW of similar origin (B1 and B2) and have a similar substitution ratio (~ 6%), present a lower compression in initial ages, more pronounced at the age of 2 days, but that decreases as 28-day age approaches, to match the reference. This difference may be due to the greater presence of copper in these CMW clinkers, since, according to the XRF of the CMW, both materials had Cu concentrations of 229 and 260, respectively. Cu is almost completely incorporated into the clinker (Ract et al. 2003). And it is mainly concentrated in the phase of $C_4AF_3$, $C_3S$, and $C_3A$ (Hornain 1971).

The presence of copper delays the hydration process during the first days, producing a decrease in the initial compression resistance (Bhatty 1995). In both samples, the threshold limit is exceeded, from which the formation of $C_3S$ is reduced (Gineys et al. 2011), which may explain the decrease in compression in the initial ages, although it is not consistent with the Bogue calculations.

RM3 and RM4 are characterized by a large reduction in compression values at short ages (− 14 and − 9% with respect to the reference). In the case of RM3, it is related to a lower presence of $C_3S$ and a greater presence of $C_2S$, which reduces the initial resistance, but increases the final resistance, as can be seen in the results at 90 days. In the RM3 case, it presents a high content in alumina which leads to a starting raw meal composition different from the others (see Table 5), being limestone percentage lower (13%) and shale proportion higher (84%) than the other raw meal compositions. And other reason that could explain this decrease in both samples is the content of heavy metals in the CMW.

The samples RM3, RM4, and RM6 present high Pb content of 889, 555, and 360 mg/kg, respectively, and although the percentages of use of CMW are low, they provide a high presence of Pb in the stream of final material entering the kiln.

Although lead compounds are volatile, the incorporation of a high percentage of this element in the clinker has been documented. In this way, if there is 0.05% PbO in the raw meal, a 100% incorporation to the clinker is assured, and it is 50% incorporated for contents higher than 0.5% weight in PbO (Barros et al. 2004).

In this sense, setting time and compressive strenght results of RM3, RM4, and RM6 are consistent with the research on the effect of the presence of lead on the

**Table 11** Percentage of fuel saving due to CMW residual HVV

| | RM1 | RM2 | RM3 | RM4 | RM5 | RM6 |
|---|---|---|---|---|---|---|
| % CMW in raw meal | 6.07 | 5.95 | 3.25 | 6.79 | 4.04 | 5.42 |
| MJ/t ck from CMW | 1.65 | 1.58 | 0.69 | 2.19 | 0.74 | 1.38 |
| Minor factor | 50% | | | | | |
| Total fuel consumption (MJ/t ck) | 3.76 | | | | | |
| CMW fuel contribution (%) | 22.0 | 21.0 | 9.2 | 29.1 | 9.9 | 18.3 |

hydration of cement, which shows that the PbO retards the setting time, but does not affect the compressive strenght of cementitious products at long sample ages (Fernández Olmo et al. 2001; Bhatty and West 1993).

Despite this, all the 28-day compressive strenght of CMW cements complies with the current European standard for a CEM I 42,5 R (≥ 42.5 MPa).

### Fuel saving for CMW residual HVV

Considering the residual calorific power of the CMW (see Table 3), the residual power (in MJ) is calculated based on the CMW amount that each dosages incorporates, representing it as a percentage of the unit energy consumption per ton of clinker. For this calculation, it has been assumed that only 50% of the calorific value of the CMWs will be used. As can be seen in Table 11, savings on fossil fuel can reach up to 29% (range from 9 to 29%).

## Conclusions

Conclusions resulting from the experimental results of the CMW clinkers are as follows:

1. After analyzing the different coal mine wastes, it can be concluded that the common chemical feature of the CMW is its silico-aluminous nature, which allows its use in cement clinker.
2. The calculation method, previously and by software, of the maximum percentage of substitution of CMW, considering both the chemical composition of the CMW itself and the rest of raw materials, ensures correct parameters of the raw meal clinker prior to calcination.
3. It is proved that the presence of a high Pb content in CMW (> 3% in the raw meal clinker) produces a very pronounced compression decrease in short ages and a lengthening of the initial setting time. Likewise, the presence of Cu in CMW (> 1.5% in the raw meal clinker) is related to a decrease in compression values at initial ages but does not alter any other characteristics.
4. All CMW clinkers are tested according to the European standard, and, considering their physical and chemical properties and mechanical performance, comply the requirements for a CEM Type I cement with a compressive strength of 42.5 MPa.
5. Besides, material coming from CMW contains a certain residual power, which leads to save fossil fuels in the kiln combustion up to 29%, with aproximately 6% of rate sustitution and a residual calorific power of 2.19 MJ/t (which is the case of RM4).
6. By way of summary, the use of a controlled percentage of CMW in Portland clinker production is technically feasible. However, further inventory and characterization of CMW deposits over Europe is needed, especially for its trace elements' determination.

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