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Characterization of emissions of condensable particulate matter under real operation conditions in cement clinker kilns using complementary experimental techniques

M. Cano^a, T.R. Reina^b, E.Portillo^a, Luz. M. Gallego Fernández^a, B. Navarrete^a*

^a Chemical and Environmental Engineering Department, School of Engineering, University of Seville, C/Camino de los Descubrimientos s/n, 41092 Sevilla, Spain

^b Department of Chemical and Process Engineering, University of Surrey, Guildford GU2 7XH, United Kingdom

ABSTRACT

Historically, the emission of particles from clinker kiln stacks has been one of the main environmental concerns in cement manufacturing processes. Up to now, environmental regulations have only focused on determining and controlling filterable particulate matter (FPM) in industrial emission sources. However, in recent years a growing interest in determining and analysing condensable particulate matter (CPM) has been evidenced due to the significant and established contribution of CPM to total emissions of particulate matter (PM).

In this work, total PM (FPM + CPM) emissions from a clinker kiln in a cement manufacturing process have been characterized. A series of tests were performed to

simultaneously collect FPM and CPM using a sampling train patented by University of Seville. The results showed very low level of emissions compared to regulatory limits. The average FPM and CPM concentrations obtained in the kiln were in the same order of magnitude, at 3.4 mg/Nm^3 and 2.8 mg/Nm^3 , respectively. The CPM analysed was predominantly inorganic and represented 46% of total PM emissions.

In addition, a microscopic morphological analysis was carried out on the samples and confirmed the presence of CPM with a size of less than 2 microns, as well as establishing the principal constituent elements of the same. The main element components were Al, Ca, Fe, Si, C and O. Compounds such as CaCO_3 , alite, ferrite and dolomite were detected with analytical characterization techniques, such as infrared spectroscopy (FTIR) analysis and X-ray diffraction (XRD), providing a better understanding of the sources of contamination within CPM.

Keywords: Condensable particulate matter, Clinker, Emissions, Dilution sampling train, FTIR, XRD

1. INTRODUCTION

One of the greatest global environmental challenges in our industrial developed societies is the improvement of air quality. The number of premature deaths attributable to air pollution is around 4.2 million a year, according to the World Health Organization (WHO). Most of this impact is associated with exposure to high levels of atmospheric particulate material (less than $2.5 \mu\text{m}$, $\text{PM}_{2.5}$)¹. The latest European Environment Agency (EEA) report on “Air quality in Europe”, for 2019, clearly shows that at the EU-28 level there are critical pollutants that exceed the air quality standards set in the various European Directives, or the WHO values to protect human health, among which

is PM_{2.5}. According to the EEA, the industrial sector generates between 10% and 20% of the emissions of this type of particles^{2,3}. Cement industry is one of the industrial sectors that has historically been recognised as an intensive source of particulate matter emissions into the atmosphere.

The main source of particle emissions into the atmosphere in cement production is the clinker kiln. In the kiln, fine particles primarily emitted derive from the physical-chemical reactions involved in the transformation of raw materials and the combustion of fossil fuels, as well as certain waste used as fuel. The combination of this wide range of materials, in conjunction with high-temperature processes (approx. 1500 °C) taking place inside the clinker oven, results in a wide variability in the physical-chemical characteristics of the PM released by the kiln stack. In addition to this, the storage, transport and processing of raw materials and clinker could generate fugitive PM emissions.

Generally speaking, PM emitted from cement industry is made up of both filterable particulate matter (FPM) and condensable particulate matter (CPM). FPM are particles directly emitted from a stack as a solid or liquid at stack conditions and captured on the filter of a sampling train. CPM means that the material is discharged in gaseous form at the flue gas temperature and condensed into a solid or liquid state immediately after discharge into the atmosphere on leaving the stack. CPM is assumed as fine particles of a size smaller than 2.5 µm, which are non-filterable under emission conditions^{4,5}. Up to now, no country in the world has established limits for CPM emissions. However, numerous studies have confirmed the real CPMs are gaseous species emitted from stacks that can condense or contribute to particles, i.e., the conversion of CPM precursors to particles in stack plumes⁶⁻¹¹. Recent studies¹²⁻¹⁵ have established CPM represents between 22% and 96% of total PM emitted, essentially depending on the type

of source of the emissions, the raw material and fuel used, the operating conditions, and the systems employed to eliminate pollutants. This being the case, the total PM values provided were an underestimate if we consider that CPM emissions from different stationary sources have been overlooked.

Different capture methods are currently being proposed to measure CPM, such as those defined in ISO 25597:2013, CTM-039 and the EPA's Method 202. The main difference between these methods is their operating principle: while the sampling trains proposed in ISO 25597:2013 and CTM-039 work by diluting the sample with purified ambient air, which is then collected in a filtering device, the sampling train proposed in Method 202 involves the condensation and retention of the sample in a capture solution. According to the most recent studies¹⁶, Method 202 – even in its latest optimised version – overestimates CPM concentrations, mainly due to the presence of soluble gases (such as SO₂, NH₃ and HCl) that have been partially absorbed by the capture solutions. This was the main reason why the dilution method has been chosen to conduct this study.

Besides the uncertainty regarding the quantity of uncounted CPM, finding out more about the physical-chemical characteristics of the same is another major area of concern for researchers. Physical-chemical characterization of CPM is essential to assess the adverse impacts on the environment and human health, as well as to develop future control technologies. Countless scientific studies have associated fine particulate matter with a range of very significant health problems, such as premature death, an increased number of hospital visits and admissions, worsening of asthmatic episodes, persistent cough, difficulty breathing and pain on breathing, chronic bronchitis, decreased lung function and both work and school absences¹⁷⁻¹⁹. According to the EEA²⁰, there is a lack of knowledge as to which of the contaminants that make up PM_{2.5} cause the

greatest impact, whether these should be regulated separately from PM₁₀, and whether it is necessary to include new pollutants (such as ultra-fine particles or black carbon) in the legislation.

Concerning the analysis methods, there is not currently an established technique allowing to ascertain the composition of CPM with sufficient accuracy. The literature consulted²¹⁻²³ indicates that PM_{2.5} can be made up of different chemical elements, including inorganic and organic components such as carbonaceous material, traces of metals, sulphates and nitrates, and volatile organic compound (VOC). It is vitally important to characterize the CPM coming from each source of emissions given that the composition of the same will depend largely on the raw material, the fuel used and the operating conditions. In our previous study²⁴, we analysed the CPM from a cement production process and found elements such as Hg, Cl, Al, K and Ca as major components of CPM. Since this work there have been very few studies performed at cement production facilities to determine and characterise condensable particles under real operation conditions.

Under these premises, this study deals with the detailed analysis of CPM and FPM emissions in the stack of a clinker kiln used in a Portland cement production process collected under real operation conditions. Our approach allows establishing a comparison with the results obtained from stationary sources of emissions. The organic and inorganic fractions of CPM have been determined, and its microscopic morphology has been analysed. Likewise, the chemical composition of samples has been thoroughly characterised using non-destructive techniques which are innovative in this field. All the determinations were carried out using a dilution sampling system patented by the Chemical and Environmental Engineering Department of the University of Seville.

2. EXPERIMENTAL PLAN.

Facility. The experimental measurements were carried out at a 4000 t/d capacity cement production plant located in Spain, specifically at the stack of the clinker kiln. The clinker production procedure is a dry process with a horizontal rotary kiln system and a cyclones preheater. The raw materials consumed for the production of clinker are marl, sandstone and mixed materials, while, besides clinker, the production of cement also uses gypsum and other additions (fly ash, blast furnace slag, limestone, pozzolan). The fuel used in the clinkering process is petroleum coke.

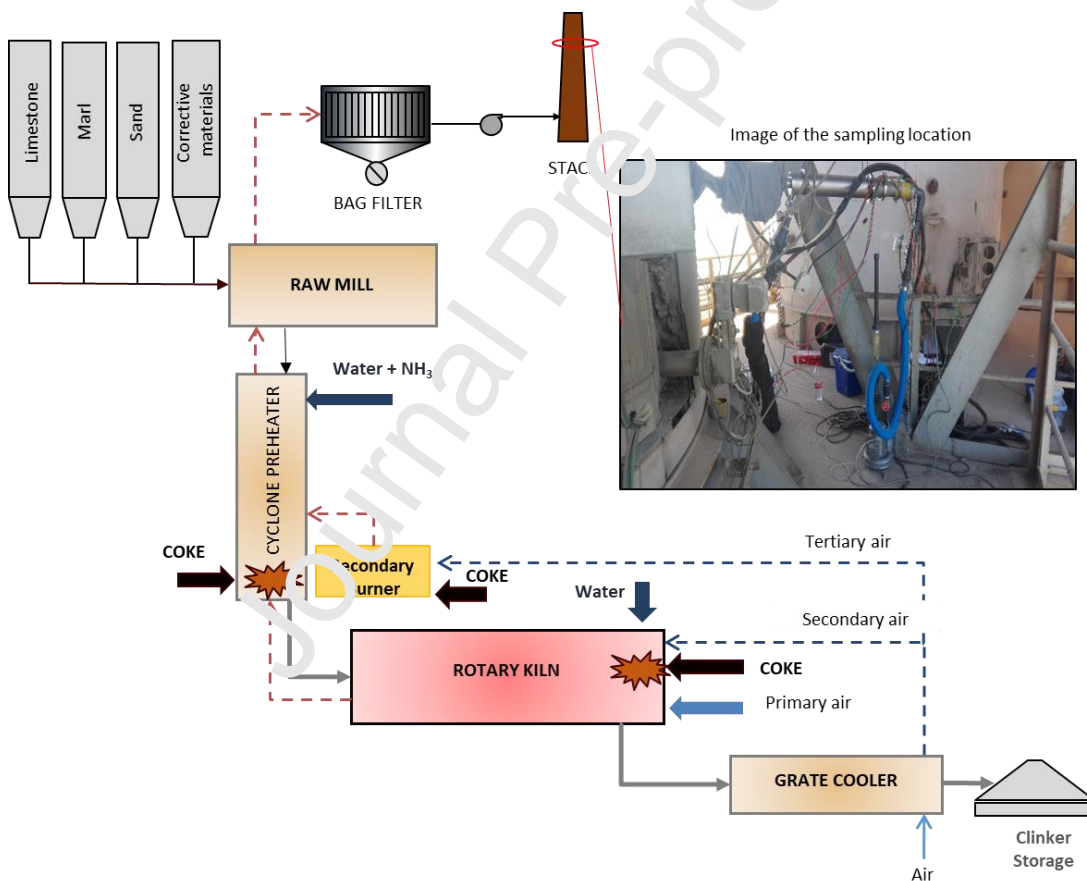


Figure 1. Process diagram of the Clinker production plant-sampling location.

The flue gases leave the clinker kiln and reach the cyclones preheater tower, after which they go through the raw mill to heat the raw material and are then treated in a bag filter (BF) before being expelled into the atmosphere, as shown in Figure 1.

Particle measurements were performed specifically at the two sampling points located on the clinker kiln stack. The stack is a vertical pipe with a circular cross section and a diameter of 3.7 m. The height of the emissions outlet is approximately 80 m. Flue gases from the clinker kiln and the heat exchange circuits for raw materials (tower and raw mill) go through the stack after being treated in a bag filter. The sampling point has a fixed platform with 4 sampling outlets. Each sampling outlet has an internal diameter of about 150 mm and they are fully suitable for sampling gases and particles. The location of the sampling outlet complies with current regulation regarding the adequacy of sampling points (Order of 18 October 1976, on the prevention and correction of atmospheric pollution of and industrial origin).

Plan of measures. A campaign of five different sample-takings were performed to determine the CPM and FPM concentrations. Table 1 shows the duration of the samplings performed as well as the characterization of the gas stream found during sample-taking. This characterization is vital for establishing the starting conditions of the isokinetic sampling required to determine FPM concentrations. Table 1 shows the average value of different parameters measured over flue gas exhausted from clinker kiln. On the one hand, these parameters are the velocity (V), temperature (T), flow rate (FR), and humidity (w), which are measured according to EPA Methods 2 and 4^{25,26}. On the other hand, the CO₂, SO₂, NO_x, CO, O₂ concentration, expressed in percentage of the volume of this stream, is another measured parameters through the Testo 350 automatic analyser.

The values obtained are typical concentrations and are consistent with the values obtained at other cement production plants^{27,28}.

A 47 mm quartz microfiber particle filter was used in all the sample-takings, placed on the end of the isokinetic probe, in a heated box, to determine the concentration of primary filterable particles (US EPA Method 5²⁹). A filter with a diameter of 70 mm, made of the same material, was used in a CPM filter holder, to determine the concentration of primary condensable particles (CTM-039³⁰, ISO 25597:2013³¹).

In addition to the CPM captured in the filter, different parts of the sampling train were rinsed after each sample-taking in accordance with standard CTM-039 in order to collect any possible CPM left on the same.

Table 1. Characterization of the gas stream from the stack of a clinker kiln.

| Parameters | Duration (min) | Gas V (m/s) | Gas flow rate | Gas T (°C) | Static P (mmca) | Humidity (w) (%) |
|-------------------------|-------------------|----------------|------------------------------|-----------------|--------------------|---------------------|
| | | | (FR) (Nm ³ /h) | | | |
| Average value (± SD) | 218 (± 27) | 16.58 (± 0.4) | 373,944 (± 7,050) | 171.20 (± 7) | -22 (± 2) | 10.22 (± 1) |
| Compositional analyses | | | | | | |
| Parameters | CO ₂ | O ₂ | SO ₂ | NO _x | CO | |
| | (% v/v) | (% v/v) | (ppmv) | (ppmv) | (ppmv) | |
| Average value (± SD) | 19.04 (± 2) | 10.04 (± 1) | 5.00 (± 10) | 501.40 (± 67) | 187.40 (± 87) | |

It is important to highlight that, although the research was performed at an industrial facility, meaning that the availability and operation of the kiln were always subject to the plant's production conditions, it was possible to meet the objectives of the tests and obtain satisfactory results.

Sampling Equipment and Methods. The sampling system used to perform the in-situ measurements is depicted in Figure 2. The intellectual property PCT/ES2016/000115 for this advanced analysis device belong to the Department of Chemical and Environmental Engineering at the Higher School of Engineering of the University of Seville³². Descriptive details of the system can also be found in previous studies performed elsewhere^{12,24}.

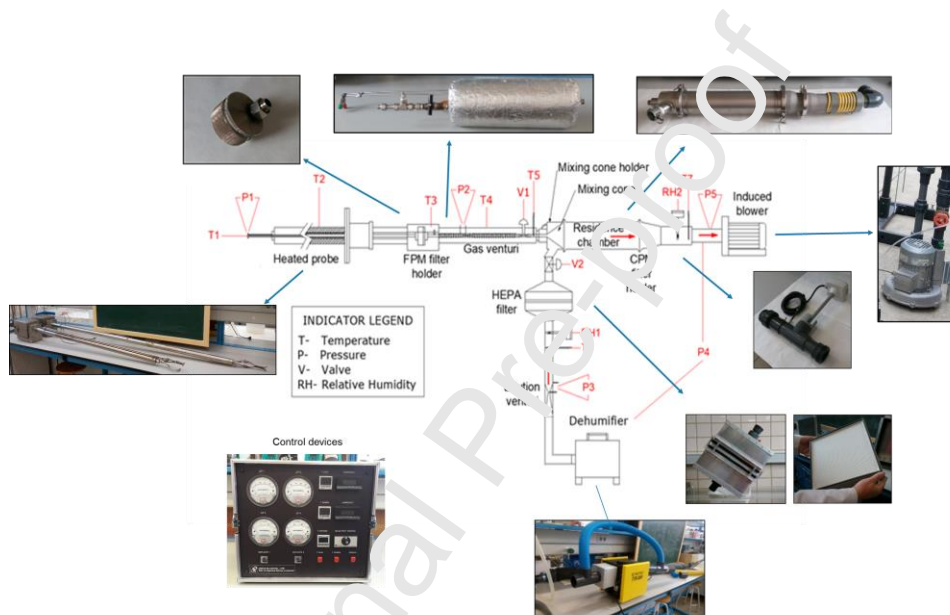


Figure 2. Dilution-based sampling system used to determine FPM and CPM. Patented. PCT/ES2016/000115, WO 2017068208 A1.

The system extracts approximately 6 l/min of flue gases containing particles from the stack of the clinker kiln using a 1.5 m isokinetic probe heated to 5°C over the temperature of the gases. The FPM is collected in a filter housed in a heated box placed at the end of the probe. After this, the flue gases, free of FPM, are mixed with dehumidified and filtered ambient air in the residence chamber with an air/gas dilution ratio (DR) of 10. The CPM formed under controlled humidity and temperature conditions is then collected in a filter (CPM).

To obtain the CPM concentration, the gas velocity was measured using a pitot tube during the sampling, while isokinetic regime was achieved by adjusting the size of the sampling nozzle for each test.

Analytical procedure and quality assurance. The analytical techniques used to characterise the samples mainly consisted of a combination of different physicochemical methods, some of which are non-destructive and innovative in this field. These techniques include a gravimetric analysis of all samples to quantify CPM and FPM emissions, the use of scanning electron microscopy (SEM) for a morphological analysis of the CPM and analysis coupled an energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and infrared spectroscopy (ATR-FTIR) to determine chemical composition.

To carry out these characterization techniques, samples were previously treated and prepared. Spent filters were divided into 3 parts and each of these was identified and weighed. The first portion of the filter was used to analyse the morphology of the CPM, verifying their presence in the filters, as well as its quantity and particle size. The technique used was scanning electron microscopy (SEM) JEOL JSM-7100F, coupled with the Energy Dispersive X-ray Spectroscopy (EDX) analyser (Oxford Link, Oxford, UK), which allowed us to obtain images of the CPM and a semi-quantitative analysis of the composition of the particles deposited in the filters. Prior to undergoing analysis, the samples were treated with a gold covering using a Sputtering metallizer and the images were processed using Image J software.

The second portion of the filter was used to apply the XRD and FTIR analysis, with the objective of establishing the chemical composition of the CPM. A BRUKER Alpha II spectrometer was used to perform Fourier-transform infrared spectroscopy of

attenuated total reflectance of samples (ATR-FTIR). In addition, the crystalline structure of the samples was characterized through X-ray diffraction (XRD) analysis using the X'Pert Pro PANalytical device. X'PertHighscore software was used to interpret the results.

The third portion of the filter, together with the rinsed fractions from the different parts of the sampling system, were used to determine the total mass of inorganic and organic matter. The analytical procedure was conducted in the laboratory according to EPA Method 202. To achieve this, the filter portion was placed in a glass vial with 10 ml of Milli Q water and put in an ultrasonicator for 15 min. This operation was repeated twice. Subsequently, hexane (10 ml) was added to the filter vial to extract the organic elements and, then it was ultrasound for 15 min. Subsequently, hexane (10 ml) was added to the filter vial to extract the organic elements and, then it was ultrasound for 15 min. The operation was repeated twice and the content was poured through a 250 ml decanting funnel with an additional 20 ml of hexane to separate the solution into two phases. The inorganic aqueous solution went out at the bottom, whereas the hexane solution (organic) went out at the top part. Consecutively, the solutions were evaporated to determine the mass of organic and inorganic components of the filter. Finally, the inorganic and organic mass from 1/3 of the filter were weighed with the analytical balance.

The total CPM and FPM concentrations were calculated based on the difference in the weights of the filter and its corresponding rinses, both after and before being used in the test sampling, and the volume of gases sampled.

3. RESULTS AND DISCUSSION

Distribution of mass concentration of FPM and CPM. Proportion of inorganic and organic fractions in CPM. Table 2 summarised the results obtained for CPM and FPM in the samplings performed during the testing campaign at the cement production plant. Mass of CPM captured in the filter, mass of CPM from washing the different parts of the sampling train, and total volume of gas from the sampling process are shown. In addition, we are presenting the dilution ratio (air/gas ratio) used, as well as the temperature at which CPM is collected. The CPM and FPM concentrations for each sampling, expressed in mg/m^3 (standard) are also presented. Finally, this research estimated emission factor, namely EF, as another evaluation index to evaluate the amount of FPM and CPM produced. EF was defined as a representative value to relate the amount of pollutant emitted to the atmosphere with an activity associated with the emission of the pollutant. According to Feng et al.³³, this index was calculated using Equation (1):

$$EF_i = \frac{C_i \cdot Q_N}{B \cdot 10^3} \quad (1)$$

In this equation, EF_i is the CPM emission factor or FPM emission factor, g/t; C_i is the CPM emission concentration or FPM emission concentration, mg/Nm^3 ; Q_N is the gas flow rate, Nm^3/h ; and B is the fuel consumption rate, t/h.

Table 2. CPM and FPM Concentrations in the stack of the clinker kiln.

| Parameters | Test no. | | | | |
|------------------------------------|----------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 |
| CPM filter (mg) | 6.5 | 5.6 | 2.9 | 2.1 | 2.2 |
| CPM rinse (mg) | 2.3 | 2.9 | 3.4 | 2.0 | 2.6 |
| V_m ($\text{m}^3(\text{std})$) | 1.313 | 3.105 | 2.933 | 3.075 | 3.788 |

| | | | | | |
|---|-------|-------|-------|-------|-------|
| DR | 10 | 10 | 10 | 10 | 10 |
| T_{mix} (°C) | 27 | 25 | 24 | 21 | 21 |
| C_{CPM} (mg/m³ (std)) | 6.7 | 2.7 | 2.1 | 1.3 | 1.3 |
| C_{FPM} (mg/m³ (std)) | 7.1 | 3.6 | 2.3 | 2.0 | 2.0 |
| EF_{CPM} (g/t) | 326.5 | 133.7 | 104.6 | 65.9 | 66.21 |
| EF_{FPM} (g/t) | 345.9 | 178.3 | 114.5 | 101.4 | 101.9 |

The CPM emissions are influenced by the type of fuel used, the combustion process, the operating conditions and the pollutant abatement systems^{8,12}. Specifically, in this process, the average CPM emissions could reach values of 2.8 mg/m³ (std), while FPM emissions were at 3.4 mg/m³ (std). In this study, the FPM and CPM concentrations increased upon raising the gas mixture temperature. According to H-H Yang et al.⁸, a low gas stream temperature reduces CPM formation. The ratio of CPM/FPM concentrations was approximately 0.8 for the tests performed.

The concentration of CPM obtained represents 46% of the total PM emitted (CPM+FPM). Comparing this value with the results obtained by M.Cano et al.²⁴ in a similar clinker plant, a slightly lower value was obtained in this case. The difference might be mainly due to the influence of the particle elimination device used and the fuel employed. The elimination of FPM was less efficient when a bag filter (BF) is used than when hybrid filters are used³⁴, indicating that the quantity of FPM would increase, thereby decreasing the percentage of CPM. This assessment was also supported by the emission factor values. As can be seen in Table 2, FPM emission factors were higher than the quantity associated with CPM, showing an average value emitted of 170 g/t and 140g/t, respectively.

Figure 3 shows the distribution of FPM and CPM masses across total PM emitted by clinker plants, compared with the results of other studies with different sources of emissions. The value represented for clinker plants was the mean between the results

obtained in this study and the results obtained by M. Cano et al.²⁴ in a clinker plant with particle abatement using a hybrid filter. The graph below showed that the results obtained in this study were similar to those reported by other authors^{12,13} for brick plants, arc furnace, incinerator and coal fired boilers.

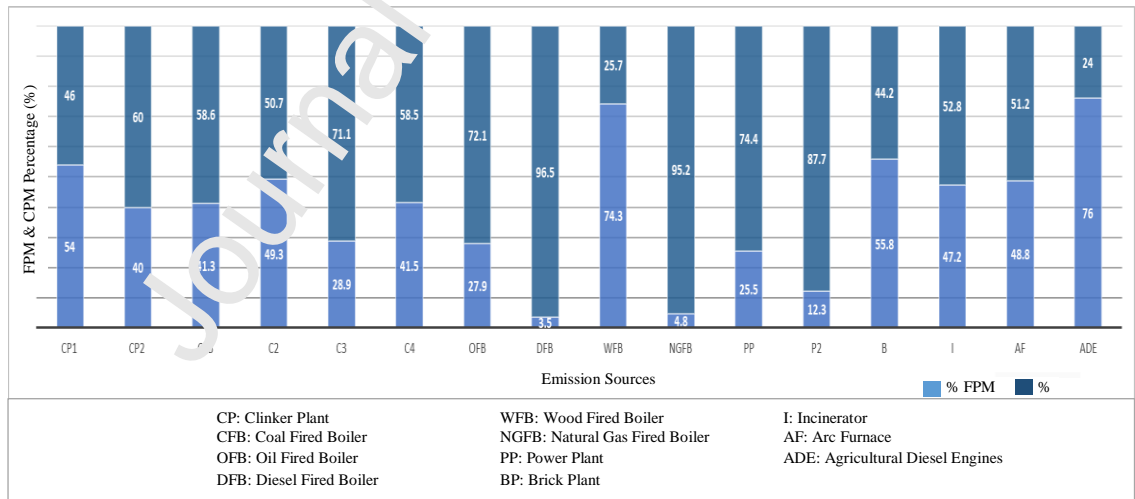


Figure 3. Distribution of FPM and CPM masses in different combustion processes.

On the other hand, Table 3 shows a comparative study with other literatures where the relationship between FPM and CPM emission to atmosphere with the raw material

used during the combustion process from different emission sources was evaluated.

EF_{FPM} and EF_{CPM} and ratio of EF_{CPM} / EF_{FPM} were used as parameter comparative included in this study.

Table 3. Emission factor comparison from different stationary sources.

| Source | Fuel | FE_{FPM} (g/tn) | FE_{CPM} (g/t) | Ratio (FE_{CPM}/FE_{FPM}) | Ref |
|-------------------|----------------------------------|-------------------|------------------|-------------------------------|---------------|
| CP | Coke | 170 | 140 | 0.82 | Current Study |
| CP | Coke | 292 | 467 | 1.6 | 24 |
| CP | Bituminous Coal & Waste Tires | 20 | 211 | 10.6 | 35 |
| DFB | Diesel | 507 | 1572 | 3.1 | 12 |
| PP | Bituminous Coal | 7 | 65 | 9.3 | 35 |
| PP | Lignite Coal | 93 | 2400 | 25.8 | |
| PP | Bituminous Coal | 139 | 1250 | 8.9 | 33 |
| PP | Anthracite Coal | 87 | 1300 | 14.9 | |
| PP | Bituminous Coal | 7 | 65 | 9.3 | 6 |
| PP | Coal | 4 | 106 | 26.5 | 36 |
| PP | Coal | 19 | 280 | 14.7 | |
| CP: Clinker Plant | | PP: Power Plant | | DFB: Diesel Fired Boiler | |

In general terms, the particulate matter emission depends on the raw material and type of fuel used in the clinker process production. In this sense, the use of coke as a fuel in the clinker plant has shown the lowest results for both FPM and CPM emission value, and hence, an average ratio EF_{FPM}/EF_{CPM} close to 1 around the cement plants compared in Table 3. According to these results, the second fuel responsible of the particulate matter emissions was the diesel, which showed an EF_{FPM}/EF_{CPM} ratio of 3.1. Finally, the coal was the fuel with the highest FPM and CPM emission values, regardless of the stationary source where it has been used. Comparing the type of coal used, the results showed that lignite coal presents the highest ratio (close to 26), whereas the sub-bituminous and anthracite coal showed values between 9 and 15.

Figure 4 shows the distribution of the total inorganic and organic fractions of CPM from the extraction, for both the filter and the CPM rinses, for all the samplings performed.

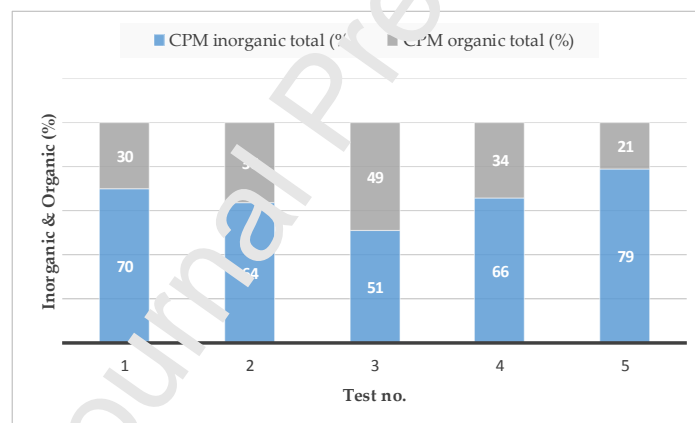


Figure 4. Distribution of inorganic and organic fractions in CPM.

The average inorganic and organic fractions of CPM were 66% and 33%, respectively. These results showed that the CPM from cement production plants mainly have an inorganic composition. According to other studies, the CPM from combustion processes in stationary sources was principally inorganic^{4,13,37,38}. Corio and Sherwell³⁷ investigated the organic and inorganic fractions of CPM in coal-fired boilers, demonstrating that 77% of total CPM was of an inorganic origin. In just one of the

boilers analysed it was found that the organic fraction of CPM was 57%. His-Hsien Yang, et al.¹⁵ concluded that for coal-fired boilers, 63.4% of the total CPM was the inorganic fraction, which was a very similar result to that obtained in this study, for cement production plants fuelled with petroleum coke.

Chemical characterization. Table 4 shows the results of chemical composition analysis carried out using EDX technology for samples collected from quartz microfiber filters.

Table 4. Energy-Dispersive X-Ray Spectroscopy (EDX) Testing Results for CPM Samples.

| Element | BLANK | | CPM-1 | | CPM-2 | | CPM-3 | | CPM-4 | | CPM-5 | |
|---------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|
| | wt% | at% | wt% | at% | wt% | at% | wt% | at% | wt% | at% | wt% | at% |
| C | | | 2.7 | 5.1 | 4.8 | 8.0 | 4.9 | 8.4 | 4.3 | 7.0 | 6.7 | 10.9 |
| O | 48.9 | 62.6 | 30.2 | 43.2 | 46.3 | 57.8 | 41.5 | 53.2 | 50.0 | 61.7 | 45.8 | 56.0 |
| Al | | | 2.5 | 2.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.3 | 0.2 | 0.3 | 0.2 |
| Si | 51.1 | 37.4 | 56.9 | 46.3 | 46.4 | 33.0 | 49.4 | 36.2 | 41.4 | 29.1 | 46.7 | 32.6 |
| Ca | | | 3.3 | 1.9 | 1.8 | 0.9 | 4.0 | 2.0 | 3.6 | 1.8 | 0.4 | 0.2 |
| Fe | | | 1.3 | 0.5 | 0.3 | 0.1 | | | 0.3 | 0.1 | | |
| Ni | | | 0.5 | 0.2 | | | | | | | | |
| In | | | 2.5 | 0.5 | | | | | | | | |

Given that particles were attached to the filter during the scanning electron microscopy (SEM) sample, some filter components were present in the energy spectrum

of PM. Presence of Si and O are present in the background value, which was ascribed to the quartz fibre filters used in this study. The main components of CPM were Al, Ca, Fe, Si, C, and O. Al, Ca, Fe and other metal elements were mainly generated during the combustion process in these types of process or because of the possible formation of species during the heating of the raw material by direct contact with the flue gas in the crude mill. According to previous studies on coal-fired boilers, metallic elements such as Al, Ca and Fe were also identified as being part of the inorganic fraction of CPM, although SO_4^{2-} was the main component, independent of source type or fuel burned^{7,39,40}. In this study, only traces of S were found in the gas stream, so that S was not detected in the CPM analysis. In and Ni were detected only in CPM-1 sample, probably due to spectral interference or sample contamination.

Figure 5 shows SEM and elemental EDS mapping analysis of a quartz microfiber filter after sampling. As can be seen, elements like Si and O from the quartz in the filter were distributed across the entire image due to being present in all the microfiber, while elements like Ca atoms, shown in red, were concentrated exclusively on the condensable particle itself. Hence, Ca was clearly identified in these images as one of the main components of the analysed CPM from cement manufacturing. Elements such as C and Al were mainly concentrated –on the CPM particles as intended from the high colour intensity in the mapping image although these elements were also dispersed across the filter microfibers.

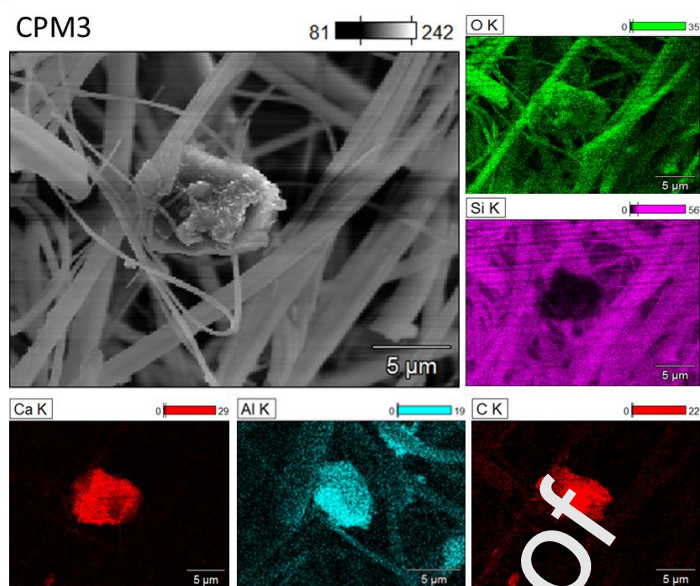


Figure 5. SEM with elemental EDX mapping analysis of filter after sampling.

Given the limitations of the EDX analysis in terms of field of vision and exclusive focus on a given section of the filter, further studies by means of FTIR and XRD were conducted to extract further information on the chemical nature of CPM.

Figure 6 displays the results obtained from a blank sample (the bare filter) and three of the collected samples (CPM-1, CPM-3 and CPM-5) to FTIR and XRD analysis.

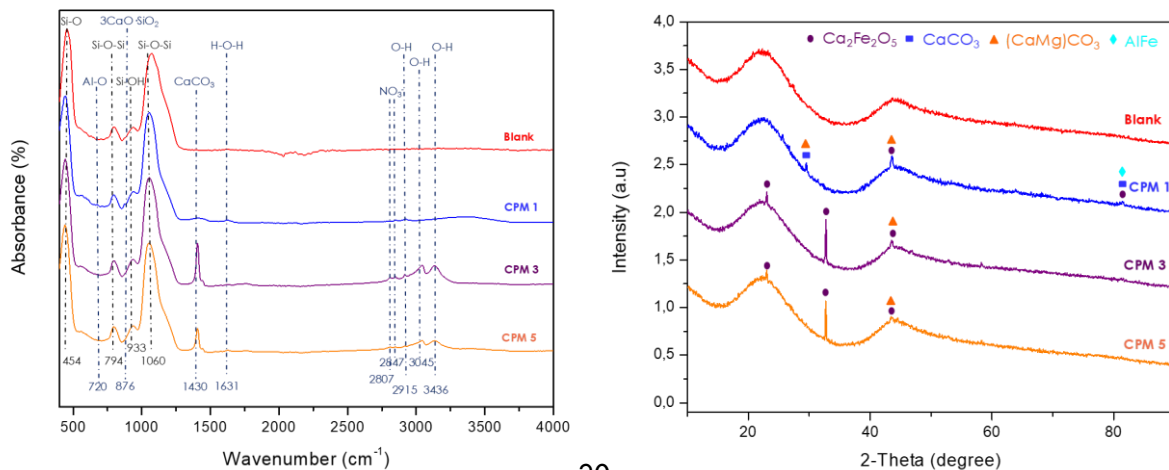
The infrared spectra obtained for both the blank and the samples had a broad band between 1000 cm^{-1} and 1300 cm^{-1} . This band was a strong peak, associated with the stretching vibration of Si-O-Si. Meanwhile, the peaks detected at 454 cm^{-1} and 933 cm^{-1} were associated with Si-O bending vibrations with no bridging Si-OH bonds, and the stretching vibration of Si, respectively^{41,42}. All the peaks detected in the blank corresponded to Si compounds from the quartz of the filter and were present in all the studied samples in good agreement with the SEM-EDX data. However, for the CPM-1, CPM-3 and CPM-5 samples new IR bands were detected evidencing the presence other compounds. In particular bands ascribed to 3CaOSiO_2 , CaCO_3 , Al-O and H-O-H, were

detected indicating the presence of mixed Ca/Si oxides and/or silicates, calcium carbonates, water and aluminium oxides in the CPM.

More precisely, the FTIR spectra of the samples had broad OH stretching vibration bands of 2900-3500 cm^{-1} and H-O-H bending vibration bands of about 1631 cm^{-1} present in water^{43,44}. Also, as in the study by Husillos Rodriguez⁴³, the silicate Si-O stretching vibration zone showed a peak at 876 cm^{-1} , which is typical of tricalcium silicate or alite ($3\text{CaO}\cdot\text{SiO}_2$), a typical compound found in Portland cement clinkers at a percentage of 40-60%. Another small signal appeared at 720 cm^{-1} in one of the samples analysed, which denoted Al-O in the ferrite and the tricalcium aluminate or celite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), which are also compounds found in the clinker, although in a smaller proportion (7-10%).

Two of the samples also presented a very strong peak at 1430 cm^{-1} , suggestive of possible C-O bands from the CaCO_3 ⁴⁵. The CaCO_3 detected in the CPM analysed probably comes from limestone, a basic raw material in clinker production in a cement plant.

Finally, bands can be observed at 2807 and 2847 cm^{-1} originating from NO_3^- from the combination of N=O and NO_2 ⁴⁴, nitrogen oxides present in the composition of a gas stream in the stack of a clinker kiln.



(a)

(b)

Figure 6. a) FTIR spectra and b) XRD patterns of the field blank and CPMs samples.

As for XRD analysis results, it should be pointed out that different crystalline compounds were detected. All the samples present the typical XRD reflections of SiO₂. These were indeed two broad diffraction peaks indicating a certain degree of amorphous nature of the SiO₂ domains within the filter. Very interestingly, the CPM samples revealed some peaks that were not present in the blank, thereby confirming the existence of compounds like calcite (CaCO₃) and dolomite (Ca Mg)CO₃, a raw material and a mineral additive typically found in Portland cement⁴⁶. Along with calcium containing species our XRD data revealed the presence of some Al and Fe containing compounds in good agreement with the FTIR and SEM-EDX analysis.

Morphological characterization. The morphology of the particles was analysed using the Scanning Electron Microscopy (SEM) technique. This technology made it possible to determine the existence of CPM, its geometric shape and its size.

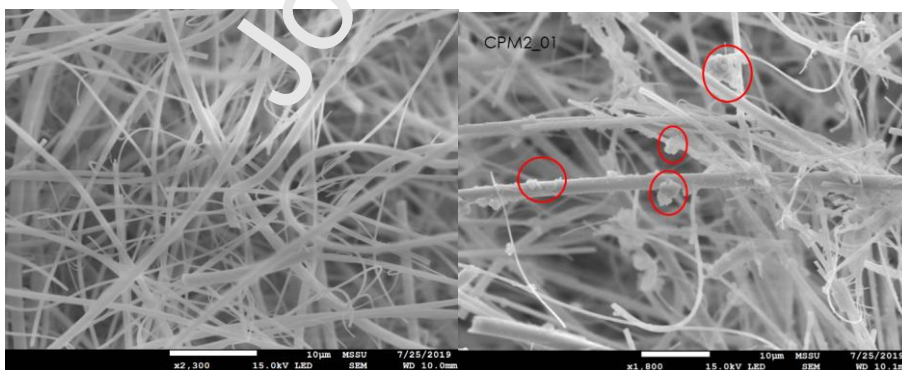


Figure 7. Quartz microfiber filter before and after the sampling

Figure 7 shows the image captured by the SEM of a flat 70 mm quartz microfiber filter after sampling. On the left-hand side of Figure 8, the fibrillar structure of the blank is detailed, while on the right-hand side the presence of CPM attached to the fibres comprising the filter is shown. The particles presented an agglomerate irregular shape, which somehow reflects its heterogeneous nature.

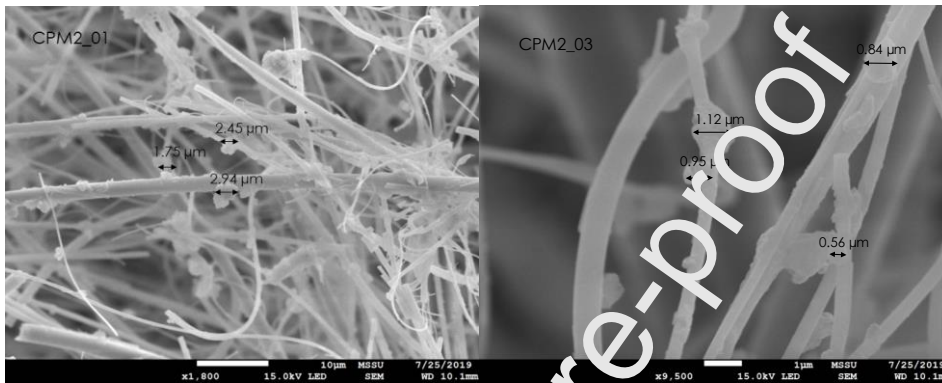


Figure 8. Average sizes and superficial appearance of the CPM.

Figure 8 shows the appearance of some of these particles in greater detail. As can be seen in the image and insets, these particles were very small clusters (*ca.* 1-2 μm) presenting an irregular and rough superficial appearance, similar to those obtained in a previous study performed on another cement production process²⁴.

4. CONCLUSIONS

This study presented an original contribution dealing with the particles emitted by a clinker kiln in a cement production process, captured using a dilution sampling system under real operation conditions. The kiln's emissions were assessed through a campaign of 5 sampling tests lasting about 3 hours each. The operating conditions in place were stable throughout the testing, ensuring that the results of the different parameters

obtained were homogeneous and reproducible. The concentrations of FPM and CPM were established, the distribution of both was studied and the physical-chemical characteristics of the CPM was analysed.

The filters were analysed using a combination of complementary techniques that provided an overall understanding of the elemental and chemical composition of the CPM. The gravimetric analysis revealed that CPM contents are slightly lower than FPM. Concretely, the average concentrations obtained for FPM and CPM were 3.4 mg/Nm³ and 2.8 mg/Nm³, respectively. Total PM concentrations in this kind of processes are substantially low, compared with the emissions limits established (20 mg/Nm³) in this sector. Nonetheless, it is important to highlight the significant contribution of CPM to total PM emissions, which is not currently being recorded in any industrial process. The CPM fraction represented 46% of the total PM emitted by the kiln. In other words, the values for fine particles emitted by the cement production process could almost double the values currently being recorded.

The CPM from this type of process is mainly composed by inorganic species. The chemical analysis of the CPM using the FTIR reveals the presence of alite (3CaOSiO_2), calcium carbonate (CaCO_3), ferrite and tricalcium aluminate or celite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), as compounds within the CPM. Such compounds are usually found in Portland cement clinkers, whether originating in the raw material or in the products of the combustion reactions.


The XRD analysis detected the crystalline species present in the CPM. It mainly confirms the existence of CaCO_3 in the crystalline phase and the presence of $(\text{CaMg})\text{CO}_3$ (dolomite), a typical additive used in cement.

Finally, the microscopic morphological analysis performed using SEM/EXD identified that the average size of the CPM was under 2 microns, with an irregular and rough superficial appearance, being composed mainly of Ca, Al, Fe, C, Si, O, In and Ni. Overall our work shed some lights on the nature (quantity and composition) of CPM within the cement manufacturing sector, providing new insights for the development of new flue gas pollution control techniques which can eventually improve the air quality and benefit the environment.

- **AUTHOR INFORMATION**

- **Corresponding Author.**

- *E-mail address: mcano@us.es

- ORCID:  0000-0002-6157-9517

- Phone Number: +34 954481397

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▪ **ABBREVIATIONS**

ATR-FTIR, infrared spectroscopy; BF, bag filters; VOC, volatile organic compound; CPM, condensable particulate matter; CTM, Conditional Test Method; DR, dilution ratio; EEA, European Environment Agency; EPA, United States Environmental Protection Agency; FPM, filterable particulate matter; ISO, International Organization for Standardization; PM, particulate matter; SEM-EDX, scanning electron microscopy with energy-dispersive X-ray spectroscopy; WHO, World Health Organization; XRD, x-ray diffraction.

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CRedit authorship contribution statement

M.cano: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing—original draft. **T. R. Reina:** Resources, Formal analysis, Data curation, Writing - Review & Editing, Validation, Supervision, Funding acquisition. **E. Portillo:** Investigation, Formal analysis, Data curation, Visualization, Validation, Writing - Review & Editing. **Luz. M. Gallego Fernández:** Investigation, Formal analysis, Data curation, Validation, Writing - Review & Editing. **B. Navarrete:** Formal analysis, Data curation, Validation, Writing - Review & Editing, Project administration, Funding acquisition.

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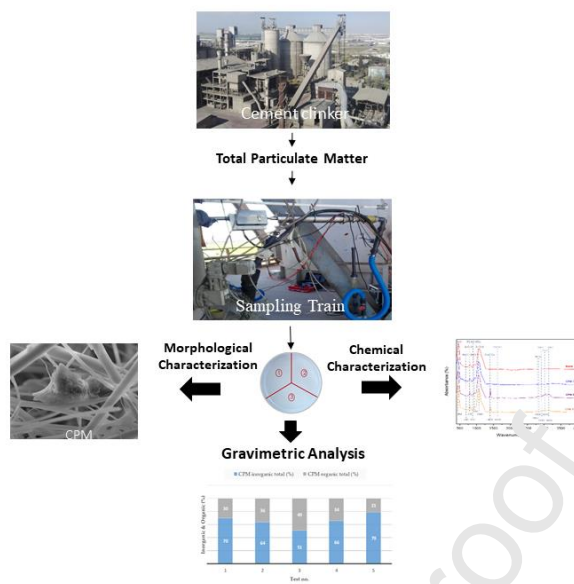
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Graphical abstract



HIGHLIGHTS

- Understanding the physical-chemical nature of CPM from a clinker.
- Multi-technique analytic approach including SEM-EDX, FITR and XRD.
- The CPM was predominantly inorganic and represented 46 % of total PM emissions.
- CaCO_3 , alite, ferrite and dolomite were detected in the composition of the CPM.

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