

## **Biomass-coincineration trials in a cement plant: the role of chlorine content on heavy metals and fine pm emissions**

Gutiérrez-Canas C.<sup>1</sup>, Urcelay C.<sup>2</sup>, Legarreta J.A.<sup>1</sup>, Astarloa S.<sup>3</sup>, Guede E.<sup>2</sup>, Larrion M.<sup>1</sup>  
and Garcia E.<sup>1</sup>

<sup>1</sup>Dpt. Ingeniería Química y del Medio Ambiente. Escuela Superior de Ingenieros. UPV.  
48013. Bilbao. Spain. [crisrina.gutierrezcanas@ehu.es](mailto:crisrina.gutierrezcanas@ehu.es)

<sup>2</sup>Cementos Lemona S.A., B. Arraibi s/n. 48040 LEMOA-Spain.

<sup>3</sup>AIRg S.L., María Díaz de Haro 68, Bajo, Pab. 4, Portugalete, 48920-E, Spain

Approximately 60% of the CO<sub>2</sub> release from clinker pyroprocessing originates in limestone calcination, being the remaining related to fuel combustion. Biomass alternative fuels, such as wood wastes or sewage sludge, are currently considered effectively climate-neutral. Thus, this could enable a means to reduce global emissions without hindering the calcination capacity.

On the other hand, a major advantage of the energy recovery in a kiln is that the non-combustible ash fraction is effectively recovered. High combustion temperatures, long residence times, high turbulence and alkaline conditions allow the complete conversion of even the most stable organic compounds. The kiln size provides a high thermal inertia resulting in very slow temperature changes. Thus, transient conditions due either to process malfunctions or feed changes do not lead to a significant conversion loss (safe use of alternative fuels).

Recovery operations in cement plants are in compliance with both Directive 1996/61/EC –also known as IPPC– and the Directive 2000/76/EC. However (1), the state-of the art emission factors for heavy metals as taken from EMEP/CORINAIR (1999), consists of data for 5 plants, from 1992 or before.

Concern about trace pollutant formation and emissions continues to be a driving force for research in combustion and pyroprocessing. Previous experience with some biomass fuels has revealed problems, closely linked to their composition and related both to operational malfunctions (deposits, corrosion) and to the emission of heavy metals. This is due to the enhanced formation of submicron aerosol particles, by condensation of volatilized material, mainly alkali salts, which may precipitate in the installation. Previous findings indicate that the control of volatile metals mostly present in the filter penetration window depends on their species(2,3,4). Thallium forms very volatile halides leading to build a closed loop that could become unstable depending on the temperature. Less volatile and insoluble lead species are partially present in the clinker, because of the gas-phase reaction pathways and the capture or chemical reaction with pre-existing particles.

An understanding about how these mechanisms compete and how can be shifted to yield an aerosol size distribution of suitable filtration properties is needed to allow a safe use of biomass fuels (maximum substitution rate, blending criteria).

## **METHODS**

Two years ago a trial burn plan was designed on this basis for a 2200 t clinker/day-long dry kiln- burning petcoke and coincinerating used tyres, bone meal and waste plastics.. Testing campaigns correspond approximately to same thermal efficiency periods for the kiln. Operational parameters were carefully filed. Data gathered during each period include continuous emission monitoring data as well as specific results for the size-segregated metals emission and the analysis of each feed stream (among others heating value, metals and alkaline halides) and some intermediate ones (also including morphological and elemental analysis).

The values of process parameters and gas composition were collected continuously. The experimental campaign was designed to cover all the representative process operation regimes and all the fuel mixtures before and after the air pollution control unit. Database consist of more than 60 valid experiments.

Samples of material from ESP and bag filter hoppers, crude mill, petcoke mill, clinker and other intermediate solid substreams were collected corresponding to the aerosol measurement periods. Their size distribution was measured with a PSD3603 (TSI Inc.). The fractional efficiency was determined from the inlet and emission stream size distribution. The mass concentration was determined with isokinetic sampling trains (EN13284). The particle mass size distribution was determined by means of cascade impactors (Dekati PM10; Kalman and Mark III) which allow for further analysis; an example of the relative mass histograms of emission under different operational conditions are shown in Figure 1. Neither significant interstage losses nor bounce-off effects were observed. Other main error sources -particle bounce-off and particle size changes inside the impactor during sampling due to vapour -condensate phase conversion, were avoided. Sampling temperatures were well above the acid dew point. The temperature set-points for both the hot- and cold- section of the sampling train were continuously recorded and were used as a discriminating criterium for the run validity. In all the cases, prior to aerosol analyzer, the flue gas was diluted with a 2-stage (hot and cold) ejector diluters (Dekati Ltd.).

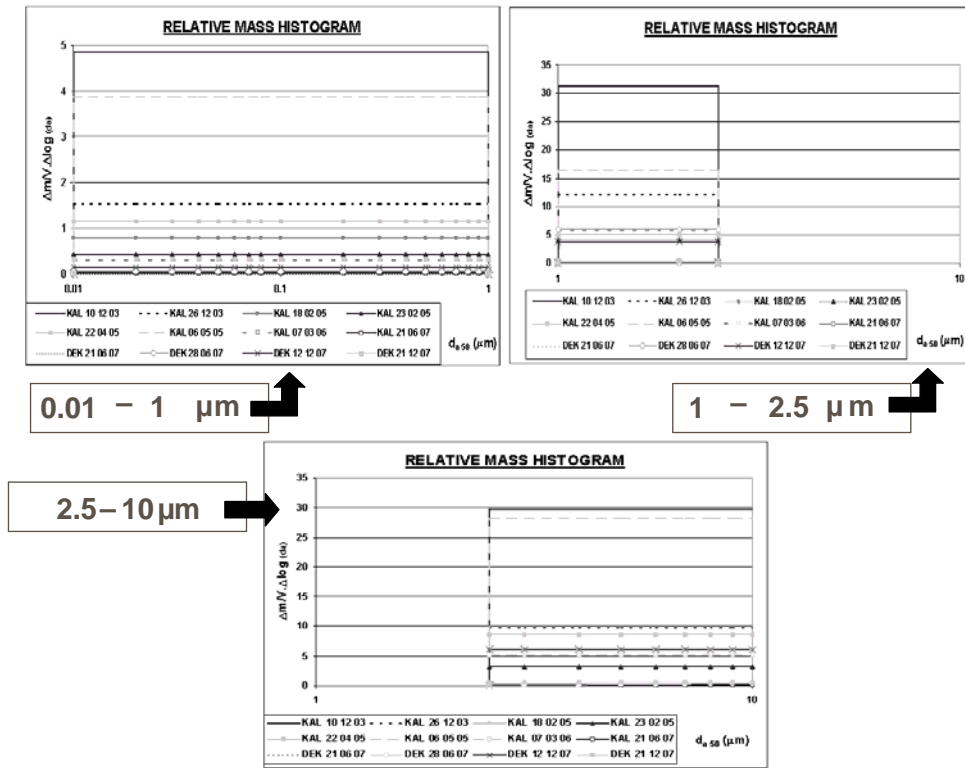


Figure 1. Relative emission mass histogram under different feed patterns.

The number size distribution was determined with an ELPI, allowing for emission dynamics assessment and further analysis of integrated samples along intervals ranging from 1 to 2 hours. Substrate (Al foils) stability tests were conducted. Gravimetric errors arising from substrate instability were estimated below  $7 \cdot 10^{-6}\text{g}$ . Losses due to particle bounce were only observed in the channel 2 of the ELPI (corresponding to a nominal cut diameter of  $0.0722 \cdot 10^{-6}\text{m}$ ).

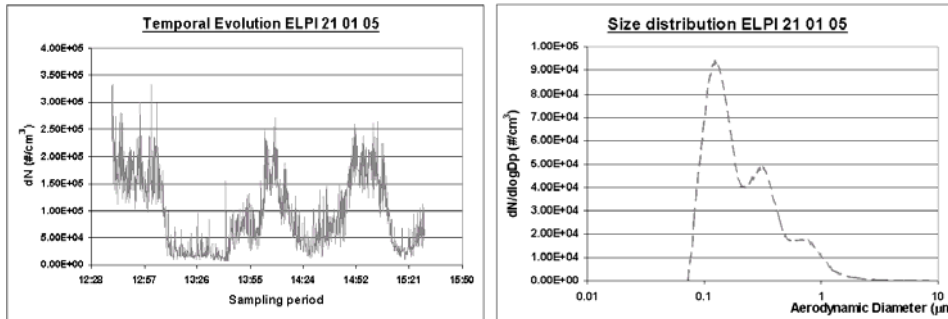


Figure 2 Total number concentration evolution (left) over a period of changing operation conditions. Number size distribution (right) under direct operation, i.e. flue gas coming exclusively for the pyroprocessing line.

The Figure 2 shows an example of changing nature of emissions depending on the operational conditions, by means of the total number concentration over time as measured by the ELPI. A typical number size distribution of the equivalent aerodynamic diameter, using alternative fuels and secondary raw materials is also shown in the Figure 2. The sampling and collection system employed in this work generated a profile with three distinct regions. The smallest cutoff diameter impactor stages collect an ultrafine vaporization mode centered at 0.137  $\mu\text{m}$  which could be described as a young aerosol generated by fresh particles nucleating either in the probe or shortly before sampling. Thus, the presence of more volatile metals should be significant on this size fraction.

Slightly larger impactor stages collect submicron particles showing a second mode at 0.330  $\mu\text{m}$ . The presence of this submicron particle size region from pulverized coal combustion has been explored in detail by previous researchers, assessing the presence of major refractory elements (Fe, Si, and Ca). The fractionation of larger particles to submicron-sized particles may also contribute particles to the submicron size fraction, although this contribution has been established as highly fuel dependent. For coal combustion, the submicron size region is typically only 1-7% of the total fly ash mass but has a very high particle number density (6). In the case of Figure 2, for a mean value of  $9.42 \cdot 10^{-4} \text{ \# cm}^{-3}$  (after dilution with dry, clean air at a flow rate factor of 73), the percentage of particles smaller than 1  $\mu\text{m}$  is about 97.1%, whereas the value for particles <0.5  $\mu\text{m}$  is 89.6%.

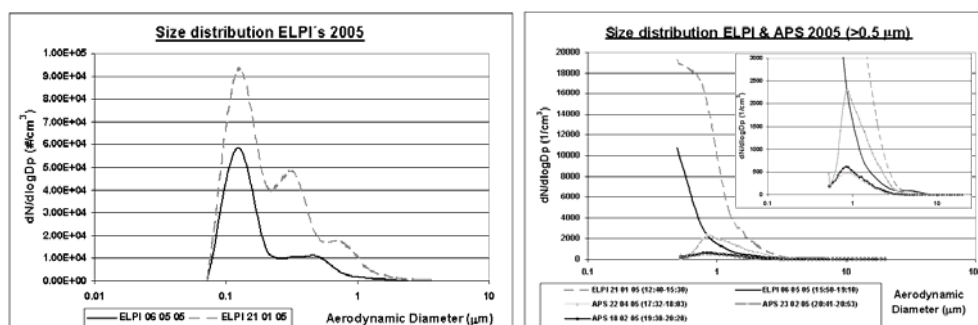


Figure 3 Number size distributions depending on the feed pattern (left) display different modes in the near-micron size range. The size distribution in the supermicron range (right) is highly dependent on the fuel/raw materials composition.

SEM images of the collected particles on the first stages –supermicron range- of the ELPI impactor are shown in Figure 4. Near-micron sized particles are commonly observed to have submicron particles fused to the surface of larger, irregularly shaped particles (4). Larger particles are hardly described by an equivalent aerodynamic diameter.

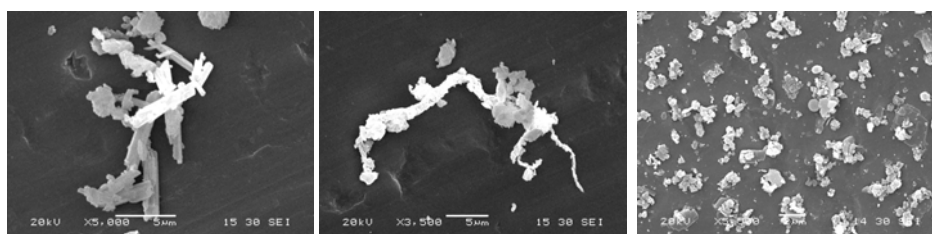


Figure 4 Morphology of coarser (left, center) and near-micron (right) particles.

Near real-time PM measurements were conducted by means of two types of aerosol analyzers. The first train combines a SMPS with light scattering detector (WSP1000; MSP Corp.) and a TOF spectrometer (APS3321; TSI Inc.). The other one is based on an ELPI (Dekati Oy) featuring the near real-time size distribution measurement and collection of a time-integrated aerodynamic-separated sample; which provides the means to correlate the analysis results with the size distributions, either under stable and transient conditions. The emission dynamic was also described by means of an APS3321 (TSI Inc) and a WSP1000 (MSP Corp.), over extended sampling periods covering all the successive operating regimes. In this last case, the aerosol analyzers could be considered as the core of a near real-time monitoring system allowing for the use of size distribution as the main indicator of trace pollutants behaviour. This mode

requires the application of data gathered through extractive sampling and analysis runs using impactors. Ongoing research is focused on the improvement of reliability of continuous measurements and the integration with process monitoring system.

Trace metal concentrations were analyzed by AAS, ICP/AES and ICP/MS. The fuel mix appears to influence trace metal partitioning routes and the composition of fine particulate matter in the exhaust.

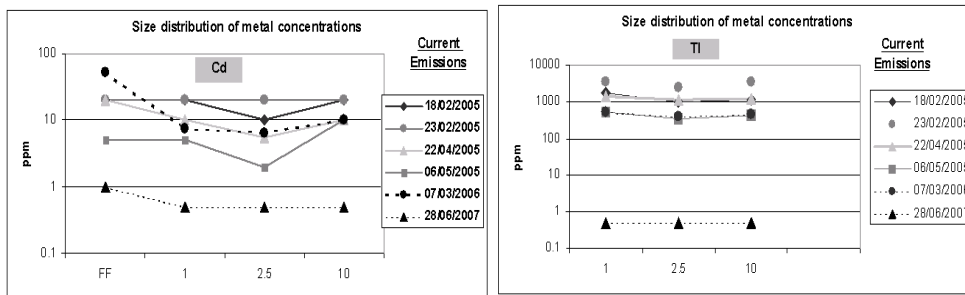


Figure 5 Volatile metals distribution over four impaction cuts. FF denotes aerodynamic equivalent diameter  $<1\mu\text{m}$ ; 1 the fraction from 1 to  $2.5\mu\text{m}$ , 2.5, the fraction from 2.5 to  $10\mu\text{m}$ ; and 10, the coarser fraction. All the concentrations are expressed in ppm wt.

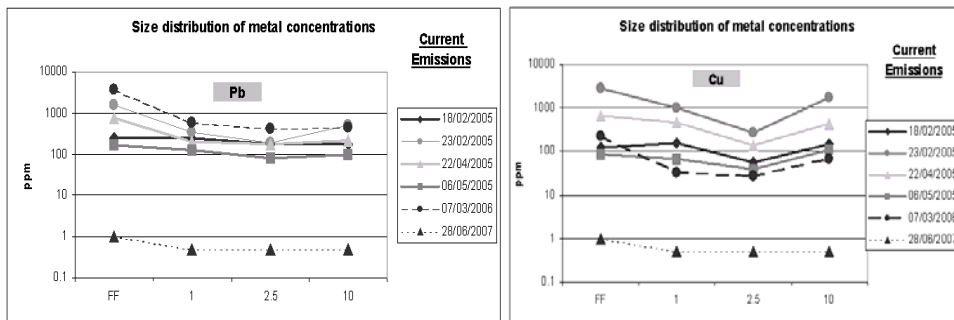


Figure 6 Lead and copper as an example of semivolatile metals. The convention used is the same as in Figure 4.

Cofiring of wood wastes with petcoke slightly increases the ultrafine/submicron particle emission compared to firing coal alone. This effect is most likely due to an interaction between species derived from biomass (chlorine and possibly alkali metals) and those from petcoke (sulfur and/or chlorine) and, thus is to be expected a strong correlation with the chlorine content from the secondary raw materials and alternative fuels. However, this point has not the same relevance in clinker pyroprocessing than in biomass cofiring boilers, because of the process requirements, that is for clinker production the chlorine content is limited to a 0.02% in the raw meal, and  $<1\%$  in any waste material to be used.

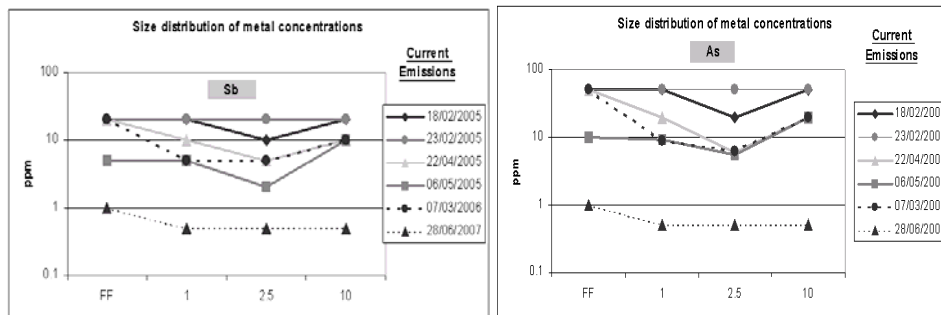


Figure 7 Antimony and arsenic as an example of semivolatile metals. The convention used is the same as in Figure 4.

Vapor-to-solid phase partitioning and scavenging of some semivolatile metals, such as copper and lead displayed in Figure 6 as well as arsenic and antimony in Figure 7, is controlled by surface reaction with active surface sites during biomass combustion with petcoke in the precalciner, allowing the metals to be reactively scavenged by calcium from marl and limestone. The concentration of individual heavy metals has a strong dependence on size fraction. A substantial portion of these semivolatile trace elements is expected to volatilize in the vicinity of burning fuel particles and then partition back to the solid phase through surface reaction in the precalciner, the kiln and, in some extent, along the preheater. The reaction of volatilized trace elements with sites on supermicron particles could explain the presence of these metals in the coarser range.

Source signature is determined by feed and fuel nature and flows, by operating practices, by particle control devices performance and finally by the effect of secondary particles (from NO<sub>x</sub>, SO<sub>x</sub>, and alkalis). More data are needed and open questions about currently available source profiles for stationary sources include: to identify the chemical species that differentiate among sources, to identify the chemical species that can reflect an adequate feed pattern –to be used as tracers and as basis for waste materials acceptance criteria-, to overcome the lack of standardisation or equivalences among methods and measuring devices; to reflect the source operation and dynamics and to report the variability, inaccuracy and uncertainty of chemical abundance measurements.

The central questions in terms of an industrial perspective are, therefore, whether the clinker production process can be efficiently monitored, in order to ensure the simultaneous compliance of regulatory requirements and product quality constraints. - Insight on this point can be acquired neither by the use of conventional emission factors, nor by extrapolation of data from other conversion processes, nor by modelling-, whether the incentives for waste treatment are realistic, or coherent with emission limits and product quality, whether cement industry contributes to a life cycle of other products processes in an operation compatible with environmental requirements, and

whether the need for innovative design, operation and management tools, incorporating sustainability criteria, could be implemented.

The dependence of emissions upon process dynamics is not efficiently measured by conventional on-line PM monitors. Evidence should be acquired by intensive sampling. The use of cascade impactors as sample pre-separators has been proven useful for analytical purposes, despite the limitations to achieve a mass size function distribution for complex particulate matter due to the differences of physical diameters on the same aerodynamic stage.

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