

Allocating emissions signatures and enrichment of heavy metals in PM_{2.5} according to the use of alternative raw materials

M. Larión¹, C. Gutierrez-Cañas¹, J. A. Legarreta¹, Vega J.R.¹, Garcia E.², Saioa Astarloa², Guede E.³, Urcelay C.³

¹*University of the Basque Country, Bilbao, Spain;* ²*AlRg S.L., Portugalete, Spain;* ³*Cementos Lemona, Lemoa, Spain.*

1. Background.

The cement industry plays an important role in the utilization of secondary fuels, making in this way a positive contribution to the environmentally compatible utilization of these waste materials. Among other questions it is important to ascertain which residuals can be used, which pollutants are contained as well as their concentration range or, in other words, its quality and its temporal or batch variation, and how is the enrichment of harmful substances in the main process streams and products, clinker or cement.

In this context, a major advantage of the energy recovery from waste in a cement kiln is that the non-combustible ash fraction is recovered as a raw material. In Europe recovery operations in cement plants are in compliance with the provision of both Directive 1996/61/EC –concerning IPPC- and the Directive 2000/76/EC on the incineration of waste. The emission limit values for the cement plants under the “co-incineration” source category define three groups of metals, and also the units and the conversions before they are reported: (Cd + Tl) = 0,05, Hg = 0,05, (Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) = 0,5 . All values in mg/m³, temperature 273 K, pressure 101,3 kPa, 10 % oxygen, dry gas. Fine PM from coincineration sources could be considered as indirectly regulated, through emission limit values for pollutants, such as heavy metals (HMs), that occur in this size range[1].

Exposure to particulate matter is associated with a number of health issues including shortened life expectancy, cardiovascular and lung disease. However, no mechanism has been proposed yet which can fully explain this relationship in terms of the chemical composition of the aerosol [2]. The fraction of metal-rich particulate matter is small and highly variable, and the concentrations of metallic species are generally very low. Spatial and temporal variability of both amounts and physical and chemical properties causes a large uncertainty in aerosol climate forcing calculations [3].

The discussion on PM_{2.5} regulation in ambient air is currently going on. Unlike standards for gaseous compounds, the particle limit values are based on a condensed-phase metric (particulate mass or number) [4,5] without regard to chemical composition. Controlling PM_{2.5} means more

stringent performance requirements on precursors and primary particles emitted from industrial processes. The lower the current value of the mass emission is the harder and more costly to reduce them further.

The particle formation and trace element behaviour during combustion of solid fuels have been studied since almost 20 years [6,7,8,9] and could be considered fairly good described. In clinker processes, there are three central issues: the release into the gas phase –kiln and preheater-, the chemical transformations as function of the local environment, and the subsequent aerosol dynamics. Either from thermodynamic predictions or experimental approaches to combustion systems [6,7,8,9], it is expected that metal-rich particles will occur mostly in the submicron regime of bimodal distributions. Heavy metal emission from combustion sources [10,11,12] is described as originated by the release of metals into the vapor phase, with the particle dynamics of a nucleating, condensing, and coagulating aerosol that may be subsequently formed [20], and with the reactive scavenging of metals. Published data for fine particle and size-resolved HMs have been obtained from combustion and incineration sources, some recent examples are [13,14,15,16,17]. Studies for other pyroprocessing sources are very sparse with the exception of [18,21]

Aerosols are affected by other dynamic processes as they evolve with time and temperature along the preheater and the conditioning tower (Figure 1).

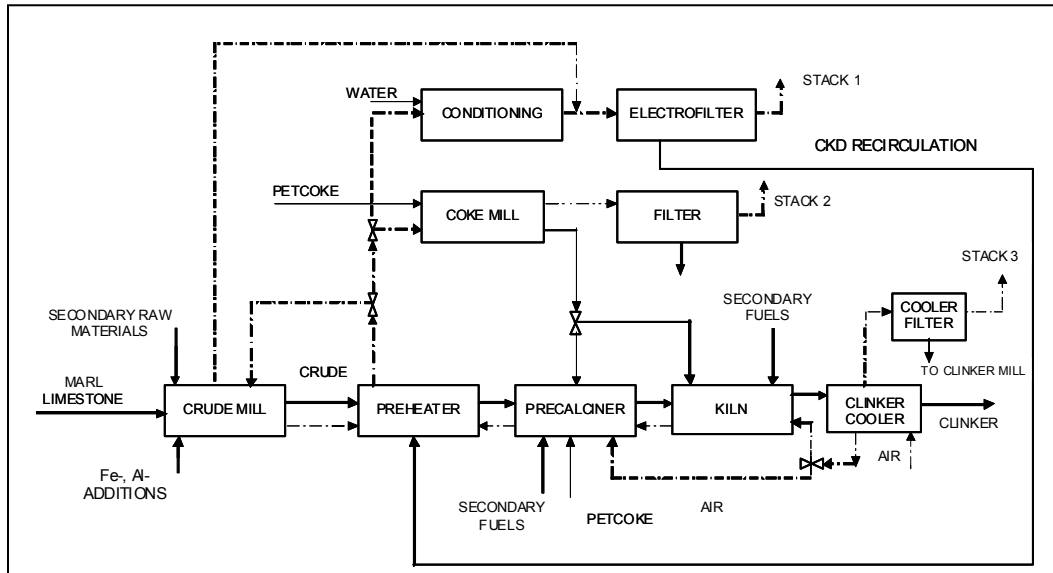
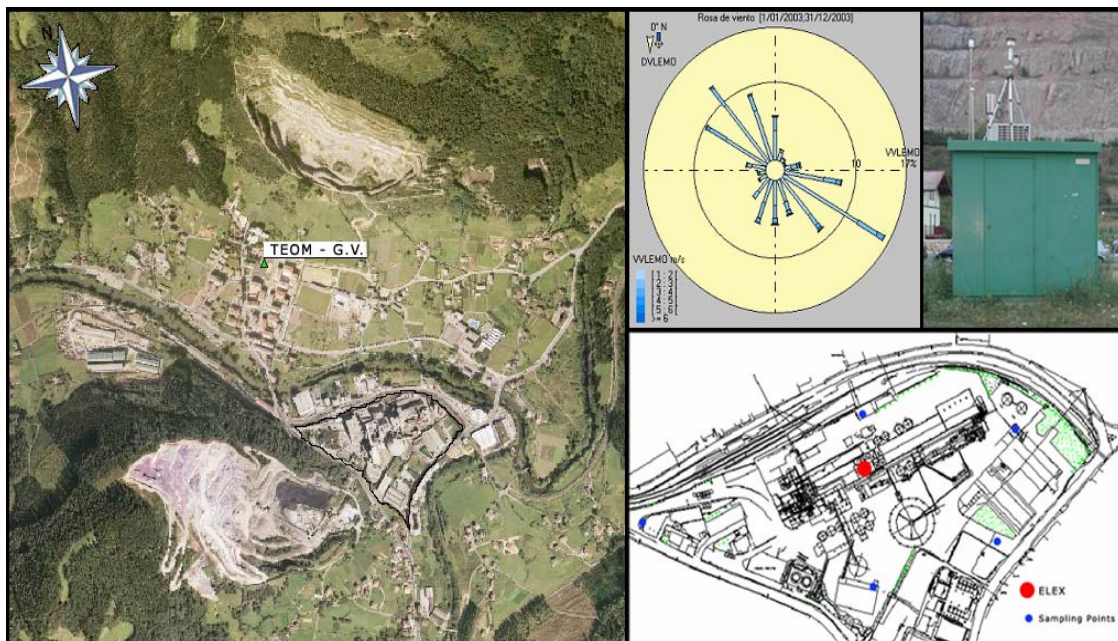


Figure 1 Schematic flow diagram of the clinker production plant. Emission from Stack 1 consist of gases from the kiln, and depending of the mills operation some fraction is a recirculation from the crude mill, or some fraction is directed to the petcoke mill and then evacuated through the Stack 2

2. Methods, measurement and analysis

To ascertain the source profile (size-resolved chemical and morphological-distributions) and the corresponding profile in the surroundings of the plant, simultaneous measurements were carried out. The results here presented have been collected along an intensive campaign (six months) in and around a cement plant (continuous process, 2000 t clinker day⁻¹), located in a narrow valley with a complex pattern of sources: natural aerosol, heavy-duty traffic, urban and other minor industrial sources as can be seen in Figure 2. Previous work: on emission measurement showed a rather high variability of size distribution, depending on process dynamics, and up to 70% mass emission as PM_{2.5} fraction.

Figure 2. Cement plant layout



The operation records and continuous monitoring parameters of the clinker plant were filed, likewise the continuous emission monitoring values. All the reported measurements were done at full load of the kiln that represents over the 78% of the operational hours in a year.

The stack sampling used [24] is similar to other studies looking for the same or analogous results [3,6,11-15], although differences on specific features of the process or on the equipment are reported. These measurements illustrated the capacity of this procedure to follow up the temporal evolution of the size distributions, to establish their relationship with process or operating conditions and their potential to be used in specific situations as a surrogate for trace pollutants.

The set of process streams is the following: crude, clinker, CKD –as shorthand for the collected dust in the ESP- and precalcined material

(about 950 °C). The main components of the clinker were analyzed by XRF following the operation routine. Trace metal concentrations were analyzed by AAS and ICP/AES. Sample treatment and analysis of heavy metals were conducted according to VDI3868 [25]. Some analyses were carried out in the Institut fuer Chemische Technik, TU Karlsruhe in a high resolution ICP/MS, for traceability and comparison purposes. Special provisions, described in [26] were taken to the proper digestion of silicate-rich samples, that is, those of crude and emission. The concentrations are reported either in ppm wt% and enrichment factor, as defined in [26, 27], that is the ratio of the concentration of a given metal in a given stream to the concentration of the metal in the crude stream.

Previous evidence about the partitioning of several metals in water-soluble and insoluble fractions for CKD [4, 28] was confirmed by analysis of size-separated samples for trace metals, both water soluble- and insoluble fraction. Additional evidence, although partial, was obtained from thermodynamic equilibrium data, such as in [27] from the comparison among the Gibbs energies of formation for several metallic species as pure components. A multicomponent approach has been made by means of MTDATA a Gibbs free energy minimization model Version 4.74 [29] to identify the most probable species along the process.

The total mass concentration was measured with isokinetic sampling trains [30,31] for periods about 1 to 2 hours according to standards for the measurement below 50 mg/m³ standard conditions. The particle mass size distribution, integrated over a sampling period from 1 up to 2 hours- was determined by cascade impactors (Dekati PM10; Kalman and Mark III). The impactors were preheated located in the stack as train heads.

3. Results and discussion

The concentrations of HMs are summarized in Table 1, and the range of relative mass percentages to the PM10 for different process dynamics in Table 2. In Figure 3 the mean chemical signature in terms of enrichment factors can be seen. Note that the CKD and the emission have very different profiles of relative chemical abundances of HMs. In some cases, the dust collected in the APCDs was proposed as an indicator for source apportionment purposes. This assumption is not valid in this case.

Table 1a and 1b. Heavy metal concentration (µg/g) in process streams and in emission

Table 1a. Concentrations (µg/g) for Cr, Ni, Pb, Tl and V

Process streams and emission					
	Cr	Ni	Pb	Tl	V
Crude	21.6-30.2	18.7-19.5	18-23.4	45-53.6	37.2-55.4
Clinker	45.2-49.8	49.3-57	32.6-37.7	<0.2	343-362.4
Cyclone IV	33.7-39.1	10.7-13	494-525.3	5.0-7.2	243.5-270

CKD	26.3-28.2	19.7-21	91.2-96.3	317-332.5	71-82.9
Emission*	35-67	51-79	257-386	254-314	85-97
Range of size-resolved HM concentrations					
>10 μ m	42.9-46.7	9.7-10.3	50.2-61.7	92-97.8	45.1-48.7
2.5<d _{ae} <10	19.8-22.7	9.2-12.2	31.1-40.6	54.4-59.2	28.8-29.6
1<d _{ae} <2.5	31.8-38.7	18-20.1	64.3-70.2	112-145	44.4-46.3
d _{ae} <1	101-123	27.8-31	80.1-84.3	174-199	82.2-87.8

Table 1b. Concentrations (μ g/g) for Sb, As, Cd, Co and Cu

Process streams and emission					
	Sb	As	Cd	Co	Cu
Crude	1.1-2.5	5.6-8.2	<0.5	2.5-4	7.5-11.2
Clinker	1.3-3-6	14.5-17.8	<0.5	7.6-9.9	19.7-25.8
Cyclone IV	<1	8.4-10.9	9.8-14.5	5.3-6.3	10.8-12.2
CKD	<1	8.4-9.7	1.2-4.3	2.6-3.1	10.8-14.5
Emission*	8-25	72-112	2-13	8-15	82-126
Range of size-resolved HM concentrations					
>10 μ m	<0.5-1,6	3.1-4.8	1.-1.2	1.2-1.4	19.8-24.6
2.5<d _{ae} <10	<0.5-4.5	2-3.2	0.60-0.9	1-1.5	6.7-7.8
1<d _{ae} <2.5	1.0-2.3	9.2-11.6	0.8-1.3	2.9-4.6	20.9-23.5
d _{ae} <1	1.53	9..2-11.3	0.9-1.6	5.3-7.2	49.6-53.5

* Collected on a single thimble. Not as sum of impactor stages.

The total mass concentration ranges from 20 to 40 mg/Nm³, depending on direct or coupled operation. Intensive ESP rapping periods, as corrective action for high Δ V across the layer due to humidity changes, sticky behavior of the deposit layers or other causes, the time integrated concentration increases up to 60 mg/Nm³. During the normal operation transient periods, such as change from direct to coupled operation, short measurements indicates than up to 80 mg/Nm³ are emitted. These values are not affected by the feed pattern.

Table 2 Range of relative mass percentages to the PM10

	2.5<d _{ae} <10 μ m	1<d _{ae} <2.5 μ m	d _{ae} <1 μ m
Direct operation	20	60	20
Coupled operation	40-60	20-30	<20-30
Emission factors [16]	39% total, 46.5% PM10	* d _{ae} <2.5 μ m, 45% total, 53%PM10	

The mass distribution using in-stack impactors is strongly affected by the operation regime, as shown in Table 2. Samples were taken along the stable period for each operational regime. The differences with published emission factors [41] are remarkable, since PM10 emission data currently quoted in most of the national inventories are sourced from the operators' estimates, based either on these factors or even assuming all the particulate matter as PM10.

Figure 3 represents the enrichment factors for the metals designated in the 2000/76 Directive. It is observed how the group Cd+Tl is directly related to the ESP performance. With the exception of the antimony, all the metals were concentrated on samples of $d_{ae} < 2.5 \mu\text{m}$. The contact with unburned solid material along the preheater allow scavenging, and the temperature profile lead to the build up of some condensation-vaporization loops in the upper stages of the preheater and the ESP.

Figure 3 Enrichment factors: Mean chemical signature.

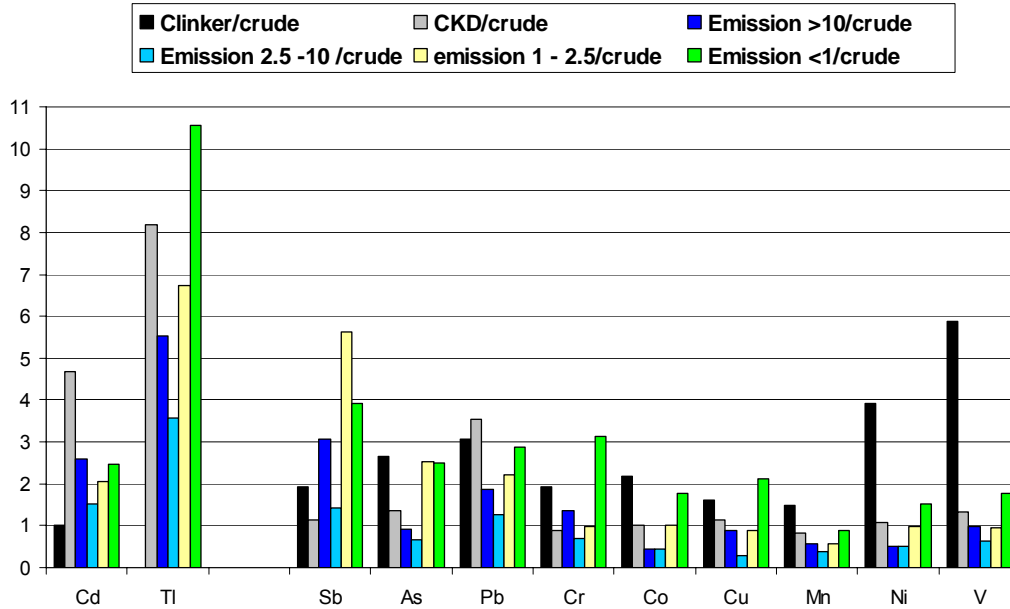
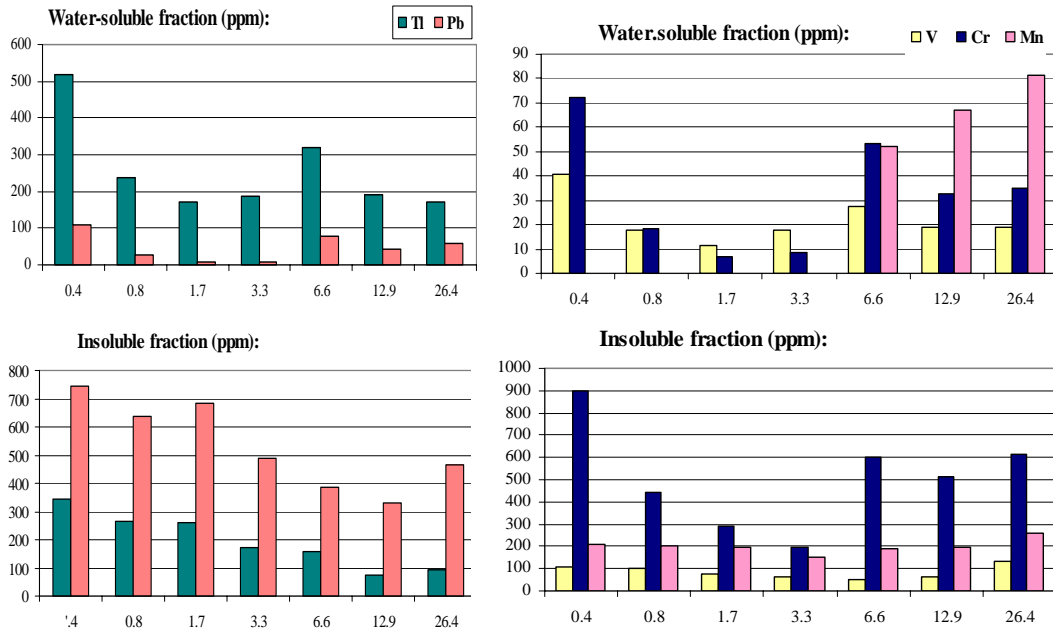


Figure 4 summarize the different behavior of metallic elements, from both elemental analysis of water-soluble and insoluble fraction for CKD. Results for the semivolatile metals Tl and Pb, and for the non-volatile metals V, Cr and Mn are presented. All the elements are more concentrated in the lower size ranges, in the insoluble fraction, and present different split patterns. A noticeable exception is the thallium, since it is concentrated in the soluble fraction, presenting a clear bimodal distribution. Water-soluble lead is less concentrated than thallium but the maxima occur in the same size bins.

Figure 4.



The thermodynamic feasibility of soluble species requires a description of the gas-phase chemistry because it establishes the speciation of the metals. As can be seen in Figure 5, Tl and Pb condensed species are likely to occur in the preheater, whereas other metals such as V or Cr are expected to condense inside the kiln. Thallium forms very volatile halides leading to build a closed loop that could become unstable depending on the process temperatures. 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. In this case, lead chloride along the preheater is not easily adsorbed captured by silica-rich particles in comparison to lead oxide thermodynamically probable under kiln conditions.

Although a more precise interpretation would require kinetic data, these findings indicate that the control of volatile metals mostly present in the penetration window requires an assessment of the fractional efficiency. Further work is needed about the practical issues of sampling at intermediate stages of the preheater in order to verify this description

Figure 5.

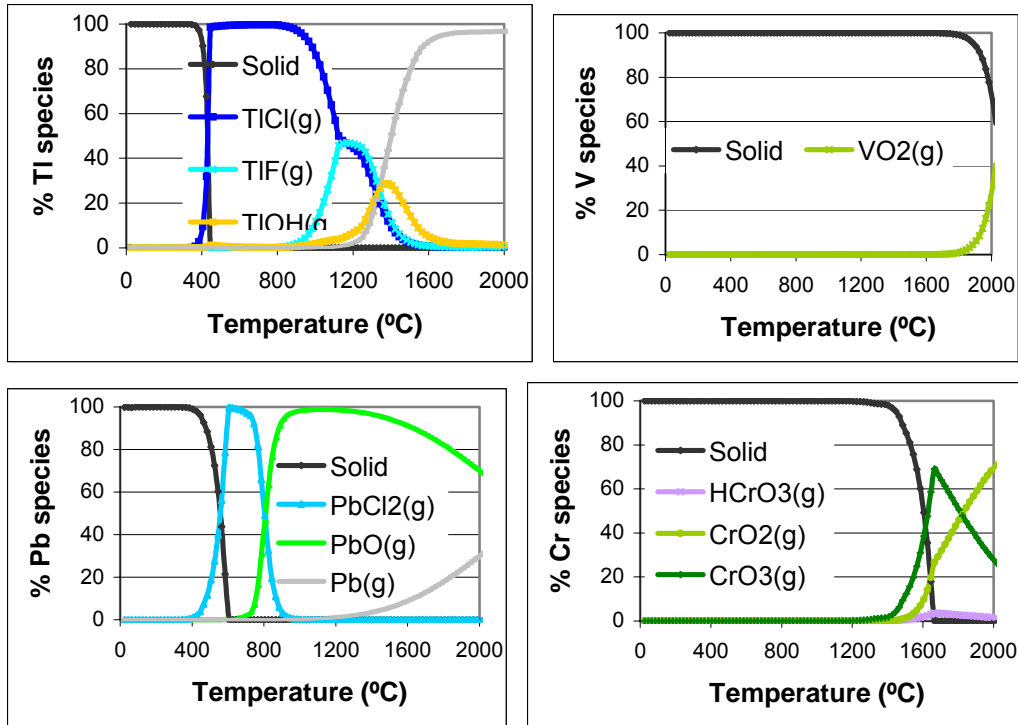
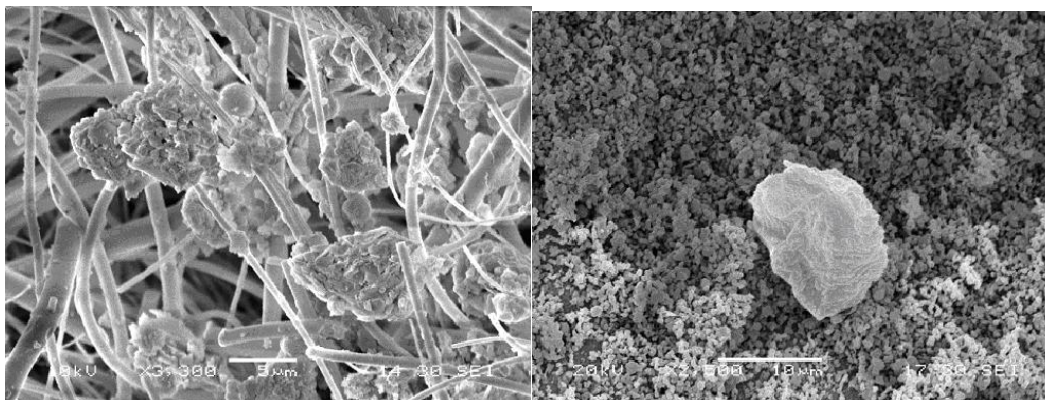
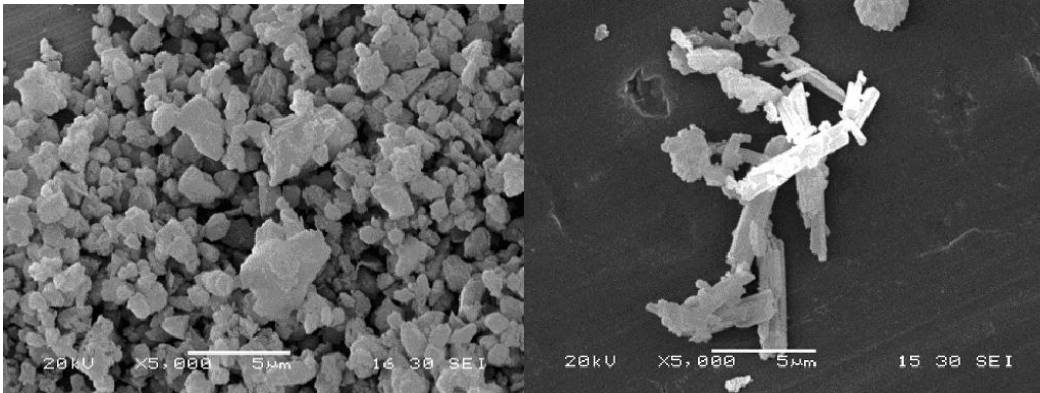


Figure 5. Thermodynamic estimate of the gas phase species occurrence. It is shown the fractional contribution of each probable species to the total of the metal as function of the temperature.

In Figure 6, four results from SEM are presented. From left to right and top to bottom SEMs from the following stage of ELPI are presented. Stage 1, 6, 8 and 11. In stage 1 the most fine particles are present, combining homogeneous and heterogeneous forms. In stage 6 and 8, mostly homogeneous distributions are presented, but with a coarse particle in stage 6. In stage 11 particles with a quite different morphology are presented.





Ongoing research is focused on the improvement of reliability of continuous measurements and the integration with process monitoring system. An effective control will require particles of a desired size distribution. This population is the results of the competition of several chemical and physical mechanisms [43], which could vary along the process depending on the changeable environment conditions. Therefore, a condition to improve the control of these emissions is to understand how these mechanisms compete and then how can be shifted the result to yield particles of suitable properties for APCDs.

4. Conclusions

Decreasing total particle emissions does not necessarily decrease fine particle emissions. There are no direct emission limit values for fine particles, but it is possible in the future as a consequence of PM_{2.5} air quality standards. The size stratification of selected trace metals in the clinker dust aerosol, as in other aerosols arising from high-T processes, implies that an efficient control of heavy metals emissions must be based on fractional efficiency criteria.

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_x, SO_x, and alkalis). More data are needed 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-.

Because of the complex transformations occurring under diverse local conditions (meteorological, influence of other sources, among others) it is difficult to establish the actual contribution of fine particle emitters. The performance assessment of the determination of the size-resolved composition before aging and the dilution sampling trains require more experimental data.

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