Zinc oxide nanostructures in EAF steelmaking flue gas: Characterization and modelling for abatement design.

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Introduction

This work has been implemented in a full-scale industrial steelmaking context. The following statements briefly depict the current state-of-the-knowledge of atmospheric pollution control in this sector. The most relevant factors are:

• A new regulatory frame, which has not been encompassed by neither experimental not theoretical knowledge about fine and ultrafine fraction. Mass-based emission limits of trace metals such as zinc have been set up in the frame of European air pollution control policies. However, Zn-rich aerosol occurs significantly within the submicron range, that is in the penetration window of conventional emission control devices. The reference methods for emission compliance are unable to give accurate values of such emissions.

• The emission limit values (operating permits) are frequently based on scattered information from different sources, frequently obtained from heterogeneous measuring systems, and very often just from an assumed average ratio between PM2.5 and PM10, or metals/PMx.

• Air pollution control strategies for EAF steelmaking, as an intrinsic discontinuous process, should be based on a suitable characterization of both raw and emitted aerosol, including a careful assessment of short time-scale variations. Most of conventional reference measurement methods are validated for continuous steady state process.

•Knowledge of process dynamics on the formation of particulate matter is needed as the main factor to specify the requirements for the control devices. Morphology derivation and evolution of ZnO along a duct under a non-constant cooling rate lead to a high variety of morphologies (porous, nanowires-nanorods, flower-like bundles) with different surface properties. A detailed characterization of the aerosol is required to highlight how the cooling history and how the mixing with the coarse inorganic particles from the canopy could be controlled to get an engineered size-distribution upstream of the filter, and to allow for an enhanced control of the size bins which are likely to concentrate zinc-rich condensate matter.

•The development of new process-integrated and flue-gas cleaning measures for reduction of particle emissions a better knowledge of generation mechanisms processes is required.

Process Parameters And Experimental Methods

EAFs use iron scrap, which is substantially an industrial waste, of several grades, and cannot be accurately defined in terms of batch composition as it can contain up to 2%wg of oil, paint and plastics. The common use of galvanized scrap increases the importance of Zn emissions. Fluctuations in scrap quality affect the EAF process control and more knowledge about the effects on emission dynamics of different steel scrap grades are desirable. The control of graphite electrode movements is a critical factor to any EAF control system, affects the actual voltage, the arc intensity, the temperature profile through the scrap pile and, thus, the dynamics of the emission rate and composition. The so-called dedusting system consists of a direct evacuation line – from the furnace itself- and a secondary aspiration –from the meltshop- which ventilate the fugitive emissions coming from the openings of the furnace system. A main canopy is then installed above the EAF collecting also the transient hot gas generated during the charge. of the furnace. The most relevant variables for specifying the direct evacuation line are the furnace off-gas temperature, flow rate and composition. However, the off-gas generation pattern is strongly related to the furnace operation dynamics as well as to blowing practice. Therefore, it is not easy to establish the most suitable air pollution control techniques and operational practices.
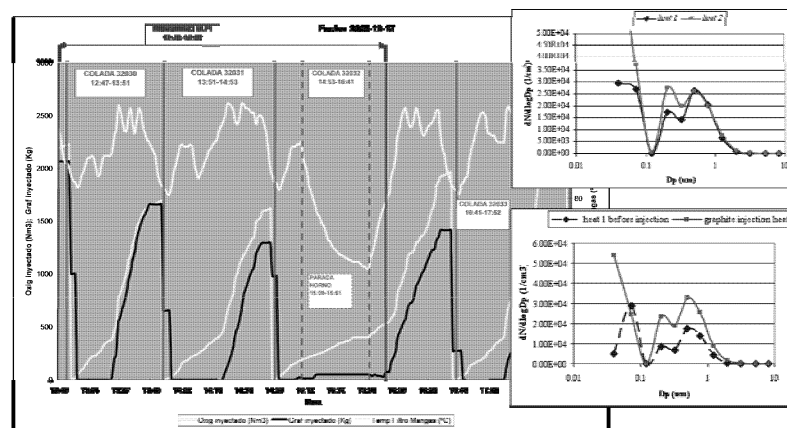

Figure 1. Furnace operation dynamics: graphite injection and size distributions.

Experimental combines two temporal scales. Near real-time size distribution was measured using a TOF spectrometer -APS3321 (TSI Inc)- together with a SMPS - WSP1000 (MSP Corp.) or an ELPI (Dekati, Ltd)- along extended periods covering successive heats to characterize the aerosol dynamics in terms of both aerodynamic and mobility particle size. Time-integrated samples, such as ELPI sustrates as well as conventional cascade impactors provided samples for chemical and morphological analysis. Figure 1 shows the evolution along successive heats as well as the typical size distributions (integrated over 10s). Figure 2 shows the temporal evolution of the number

concentration along several heats seggregated in size channels. The most relevant size bin is identified between 0.3 and 0.5 μm.
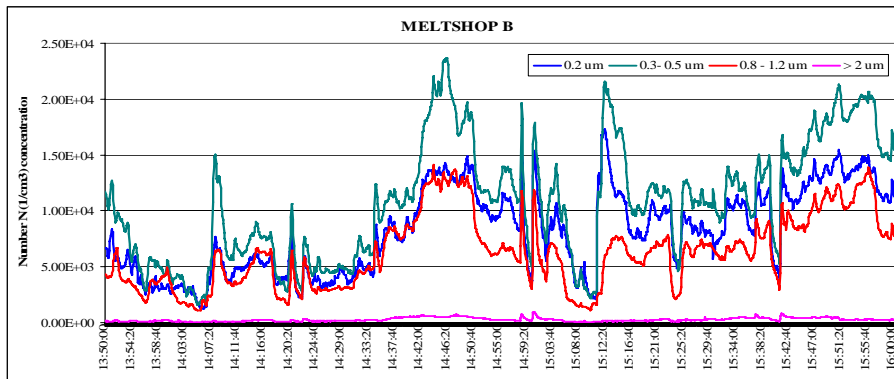

Figure 2 Number concentration dynamics: high-grade steel, low-quality scrap.

Zinc Aerosol Characterization And Modeling

The objectives of this work require a detailed calculation of the physical properties of aggregated/agglomerated aerosol particles. The physics of highly dispersed aerosols consisting of single submicron particles has been studies extensively during the past few decades (Filippov et al, 2000; DeCarlo et al, 2004; van Gulijk et al, 2004; among others). Zinc aerosol formation, speciation and growth is strongly linked to the furnace dynamics (charging, melting; O_2 refining and liquid steel casting) and cooling rate. There are several particle-leading pathways depending on the cooling history and the oxygen availability (Zn/ZnO). Therefore, a broad range of coalescence times is possible during particle formation and growth.

Zinc oxide aerosols occur frequently as consisting of aggregates of some tens to some hundreds of small spherules. The geometry is often statistically described as fractal-like aggregates, of fractal dimension ranging from 1.6 up to 2.3.
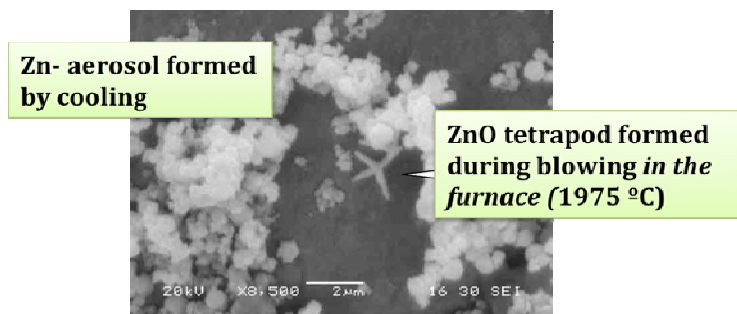

Figure 3 Coexistence of non- and chemically driven Zn-rich particle patterns

There is still very little theoretical information about the transport behavior of such particles, because of the likely strong interaction among particles with high surface energy. Some observations relevant the requirements of the control device reveal that

chemically- and non-chemically growth patterns lead to a pretty broad range of size and morphology of Zn-rich particles. The theoretical basis concerning the size of primary particle versus the cooling history states that at high temperatures, the individual particles grow continuously because coalescence of the particles occurs on contact, resulting in aggregates/agglomerates of large individual particles. For low temperatures, coagulation leads to agglomerates with a high specific surface area since particle fusion takes place slowly. The characteristic time scales that define the final particle structure are: (1) Collision time, (2) Residence time, and (3) Fusion time as defined by Friedlander as " the time necessary for complete coalescence of two individual particles after being brought into contact". The mechanisms responsible for particle fusion are viscous flow for liquid systems, solid state diffusion for solids. For both models the change in surface free energy is the major driving force. Depending on the cooling rate the size of primary particle may vary substantially (Koch & Friedlander). Coalescence time is a strong function of the temperature.
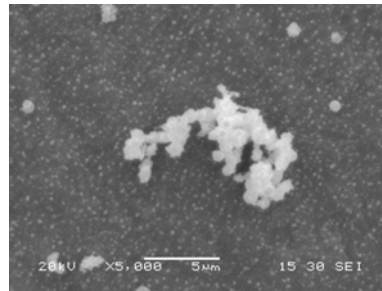

Figure 4 Fractal-like Zn-rich soft agglomerates grown at medium temperatures

Half-life of particles as limited by coagulation can be calculated. Given that each collision leads to attachment and coagulation, following (Preining, 1992). For concentrations in the order of 1 g m^{-3} of primary particles of about 1 nm, the resulting half-life is in the order of 1 μs, whereas for particles of 10 nm the half-life is still as short as about 1 ms. Therefore, the coagulation under the conditions prevailing in the flue gas duct is estimated as almost instantaneous. The production rate of primary particles is very sensitive to the supersaturation ratio and, thus, to the cooling rate. Under the prevailing conditions along the cooled duct immediately downstream of the EAF, the generation rate of primary particles is so large that their coagulation must be very fast. This means that it is not possible to separate the formation of metallic aerosol in the range of nm from the coagulation of these nuclei.

Under the prevailing conditions of Zn aerosol formation in steelmaking, a critical factor to explain the particle behavior is surface functionalities. When the Knudsen number indicate either transition or free molecular regime, and when the adsorption energy is greater than about 0.1 eV molecule, the particle will carry adsorbed molecules, which in turn may change the particle properties. Preitning depicts this situation as follows: "The particle is surrounded in its immediate vicinity by a cloud whose molecules are continuously changing within nanoseconds based on the residence time of molecules near the particle. So it **c**an said that this cloud belongs to the particle". From

measurements of Kelvin-equivalent diameter, it can be concluded that small particles behave differently than bulk chemical. Other trace aerosol components may change the coalescence time substantially. (Koch and Friedlander. 1990; Artelt et al, 2006)

The most frequent chemically-driven nanostructures of Zn aerosol are tetrapods and nanorods. Uniform zinc oxide tetrapod-like particles (as in Figure 3) are produced in bulk quantity by early oxidation inside the furnace as high-quality nanocrystals of legs length about 2–3 μm and edge size of centering nucleus about 70–150 nm. Isolated nanorods (see Figure 5) and nanorod assemblies are observed. The formation of these high-density ZnO nanorods of single crystalline wurtzite hexagonal structure is assumed to follow a a vapor–solid mechanism (Buckle et al, 1980: Liu et al, 2006). The observed isolated nanorods have a diameter of 150–250nm while their lengths are quite variable. Morphological studies indicated that the as-grown bundles in the range of several microns of equivalent diameter are flower-shaped containing several hundreds of nanorods.
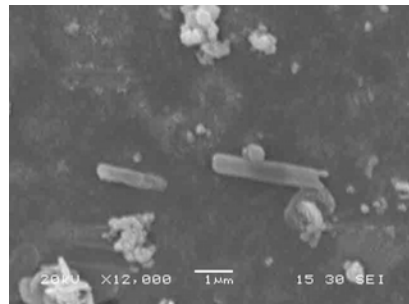

Figure 5 Isolated ZnO nanorods of single crystalline wurtzite hexagonal structure

Finally, it has been observed (see Figure 6) how the interaction with coarse inorganic sorbents carried by the secondary aspiration from from the canopy leads to an efficient scavenging of the metallic aerosol, becoming filterable as adsorbed because of the shift of the size bin concentrating metallic aerosol components.
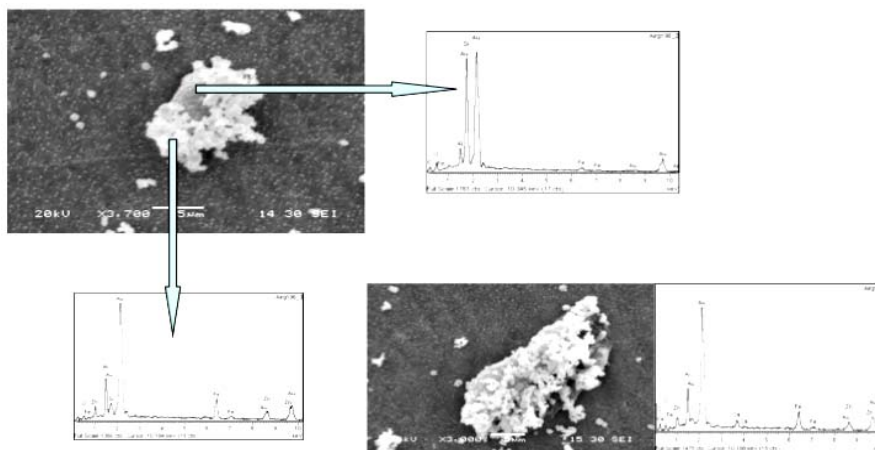

Figure 6 Scavenging of Zn-rich particles onto coarse slag fragments.

Synthesis

Size-resolved emissions and zinc-rich fractions have been identified for different process conditions, as well as the most relevant operation parameters. The distribution of the Zn-aerosol entering to the filtration unit could significantly vary under slightly differences on process operation. The control of T-t history along the process line, as well as the injection of specific inorganic sorbents have been identified as the most promising measures to prevent this emissions.

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