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Mercury species, mass flows and processes in a cement plant

Tanja Ljubič Mlakar [a,*], Milena Horvat [b], Tomaž Vuk [a], Andrej Stergaršek [b], Jože Kotnik [b], Janja Tratnik [b], Vesna Fajon [b]

[a] Salonit Anhovo, Building Materials, Joint-Stock Co., Anhovo 1, SI-5210 Deskle, Slovenia
[b] Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

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ABSTRACT

The aim of the study was to evaluate the behaviour of mercury in the cement clinker production process. Simultaneous measurements of mercury in all important materials and gas streams were performed in three sampling periods on about 300 solid samples and about 80 samples taken from gas streams. Mercury species in flue gases at characteristic parts of the process were measured as total Hg(t), particulate Hg(p), elemental Hg^0(g) and reactive Hg^{2+}(g) mercury. Based on the results of measurements, mercury mass flows and mass balances of the whole and in certain parts of the process were evaluated. It was shown that the process comprises many mercury cycles which are strongly dependent on the operating conditions and technological specifics. Cycling of mercury causes a significant enrichment of mercury inside the process. In the annual mercury input of about 27 kg, raw materials accounted near by 60% and fuels about 40% (i.e. petrol coke 31%, waste tyres 10% and waste oil 0.4%). The annual emission of mercury represented 40–70% of the inputs, while cement clinker only contained about 10%. The difference between inputs and outputs (11–45%) obtained in the annual mass balance could be assigned to mercury recycling and significant enrichment inside the process, as well as variability between spot measurements. The parts of the process with the highest mercury mass flows and the lowest material/gas flows were identified. Such points represent an opportunity to remove a significant amount of mercury from the process at low material flows and to improve mercury control. Mercury was mainly emitted in gaseous form with 92% (direct mode) or 89% (combined mode) as Hg(g) on average, of which about 2/3 was as Hg^{2+}(g), and about 1/3 as Hg^0(g). Only a small part (the rest) was emitted as particulate Hg(p). Shares of individual mercury species in the last sampling period were 65.7% Hg^{2+}(g), 34.0% Hg^0(g) and 0.3% Hg(p) on average. Ratios between individual mercury forms were found to be related to operating modes. The quantities of Hg(t), Hg(g) and Hg^{2+}(g) emitted were higher when operating with the raw mills off (direct mode). It was seen that the efficiency of Hg removal was strongly related to the dust removal efficiency. Bag filters very efficiently removed all mercury species.

1. Introduction

Mercury is an important element with global relevance that needs to be controlled [1–5]. Mercury emissions from cement plants are significant and they were estimated to be about 5.6% of total mercury emissions from global anthropogenic sources and to about 12.6% in Europe (without Russia) [4,5] based on an emission inventory of cement plants in 2000 [5].

Some studies on the behaviour of mercury in the cement production process have been published [6–17], but the behaviour of mercury inside the production process is still not completely understood. We have not found any paper dealing with detailed measurements of mercury species and flows in the inner parts of the process, as well as with details and partial mass balances of mercury cycling processes. Knowledge about these processes is also very important with regard to possibilities of mercury control and reduction. Some findings about the chemistry and kinetics of other processes could be relevant for cement plants [18–21]. Cement production is far more complex than e.g. coal-fired power plants or incinerators. The raw materials and combustion gases flow in opposite directions and are in direct contact enabling their interaction. Due to the material and gas counter-flow, temperature gradients in the system and filter dust recycling, several internal Hg-cycles are created that make the system even more complex. To control the behaviour of mercury in the process efficiently, it is extremely important to understand exactly the paths of mercury in the system, as well as the extent of mercury cycling. A description of the process is given in Section 2.1.

Mercury is present in different forms within the cement clinker production process. Favourable forms in the emitted gas are Hg^{2+} and Hg(p), which can be more easily removed and they also tend

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[*] Corresponding author. Tel.: +386 5 39 21 510; fax: +386 5 39 737.
E-mail address: tanja.ljubic-mlakar@salonit.si (T.L. Mlakar).

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to be deposited locally or regionally [6,16,22,23]. Mercury from raw materials is transformed to the gaseous form at elevated temperatures between 200 and 700 °C [8,9]. Due to the oxidative atmosphere, mercury is oxidised in the kiln system by homogeneous or heterogeneous reactions, most likely with halogens. $HgCl_2$ is supposed to be a favourable product of Hg^0 oxidation [11,13–15]. There are several possible gaseous (g) and particulate (p) mercury species in the system, e.g. Hg^0(g), $HgCl_2$(g), $HgCl_2$(p), Hg^0(p), Hg^{2+}(p), HgO(p), $HgSO_4$ (p), other halogen compounds, etc. A certain amount of Hg could also be captured in the complex mineralogical structure of clinker in the form of mercury silicate, but the mechanisms and thermodynamic properties are still not known [15].

The main scope of the presented study is: (1) to clarify the processes involving mercury in cement clinker production, (2) to identify mercury species in flue gases in different parts of the process, (3) to identify the parameters which have an important effect on mercury behaviour and emissions, (4) to calculate the mass balances of the whole and parts of the process, (5) to detect cycling processes and points in the process with the highest mercury mass flows and (6) to compare the mercury species removal capacity of two different cleaning systems, namely the FF (bag filter) and ESP (electrostatic precipitator), and thus provide some additional information on reducing mercury emissions.

2. Experimental

2.1. Description of the case study

The study was performed in the cement production plant of Salonit Anhovo Joint-Stock Co., a middle-sized production unit, situated in the western part of Slovenia, with a current cement production of about 900,000 t per year. A simplified scheme of the cement clinker production process is presented in Fig. 1. The cement plant uses a dry production process with a five-stage suspension cyclone preheater and a satellite clinker cooler. Fuels enter the process via the main burner and at the bottom of the preheater. The temperature of the main burner flame is app. 1800–2000 °C, while the gas temperature at the bottom of the preheater reaches 1000–1100 °C. Raw materials are ground in the raw materials mill, stored in the raw meal silo and then dispensed into the kiln through the heat exchanger, where it is heated up to 900 °C in a counter-flow with flue gas from the kiln. Cement clinker is formed in the temperature range of 1000–1450 °C and is then released from the kiln through the satellite clinker cooler. 10% of the air enters the kiln directly through the burner, while the main stream of combustion air enters the kiln through the clinker cooler and is thus preheated by the hot clinker. This so-called secondary air reaches a temperature of between 900 and 1000 °C. Waste gases from the preheater are partly used for raw materials drying in two raw meal production lines (two ball raw mills). At this point it should be mentioned that the different operation modes have important effects on mercury behaviour in the system. In the direct mode (D) the raw mill is not in operation and the stream of flue gas flows directly into the cleaning device. In the combined mode (C), the raw mill is operating and part of the flue gas flows through the mill. The gas stream is then led into two cooling towers, where it is cooled by a water spray. Finally, the gases enter two dust filters and are released to the outside air through the stack [16,17].

2.2. The measuring concept

The selected measuring methodology enabled us to obtain information about mercury behaviour in different parts of the process. Sampling of materials was performed according to the procedures listed in Table 1. Samples were taken from the process periodically and simultaneously measurements of mercury species in flue gases were performed. Mercury was measured during different operating regimes. Flue gases were measured at the three characteristic sites M1, M2 (inner sites) and M3 (emission) presented in Fig. 1. The site M3 was located just before the stack, the inner site M1 was located in the gas flow after the exit of flue gases from the heat exchanger and before the ventilators, while the site M2 was immediately after the raw meal mill. For the purpose of the study the additional measuring sites M1 and M2 were arranged in accordance with requirements for isokinetic measurements. All of the measurements were performed on one of the two production lines. Data from the process and mandatory emission measurements (Table 3) were used additionally for better interpretation of the results. Elemental gaseous mercury was measured in the air near the entrance of the kiln (M_{air}) with an RA-915 + Zeeman Mercury Analyzer in the second sampling period.

To check the ranges of mercury concentrations, initial samples of materials from the process and a set of pure individual components (raw materials) from the quarry were analysed. After that measurements of materials and flue gases in different parts of the process were performed in three sampling periods, consisting of several measuring sets in different operational modes: INITIAL PERIOD: 12. -13.1.2005 (direct mode, ESP); FIRST: **20.7.2005** (combined, ESP); SECOND: **14.2.2006 AM**, **15.2.2006 AM** (direct, ESP), **14.2.2006 PM**, 15.2.2006 PM (combined, ESP), THIRD: **5.12.2006** (combined, FF), **6.12.2006** (direct, FF). Materials from the process were sampled in all sampling periods, while measurements of gaseous Hg species were performed in the periods given in bold-type. Initially the electrostatic precipitator (ESP) was used to remove dust particles from the exhaust gas and the temperature in the filter was about 100–120 °C (the average dust emission was about 10–20 mg/Nm^3). In 2006 the ESP was replaced by a modern bag filter (FF), which operates at 120–140 °C with an average dust emission of about 2 mg/Nm^3.

2.3. Sampling and analytical methods

2.3.1. Sampling of mercury species in the flue gas

Gaseous Hg species in flue gases were determined by the MESA method [24,25]. The MESA sampling system for gas phase Hg species employs a series of heated, solid phase absorbent traps. The flue gas is drawn through a heated quartz tube followed by a series of two KCl/soda lime traps and two iodated carbon traps. Oxidised Hg species (Hg^{2+}, MeHg) are absorbed by the KCl/soda lime sorbent, while Hg^0 passes through and is collected by the iodated carbon sorbent.

2.3.2. Sampling of solid particles in the flue gas

Solid particles from the flue gas were sampled by the manual gravimetric method for determination of the concentration and mass flow in the stack (performed by RACI, d.o.o.). The method is appropriate for concentrations between 0.005 and 10 g/m^3. The measuring uncertainty is greater than 10% with concentrations below 0.05 g/m^3. In the third sampling period sampling was performed by the manual gravimetric method according to EN 13284-1:2002 standard (Institute for Health Protection, Institute for Environmental Protection, Maribor). The method is appropriate for dust concentrations between 0.0005 and 5 g/m^3 with a declared measuring uncertainty below 30%.

2.3.3. Sampling of solid materials

Heterogeneous samples (e.g. raw mixtures, limestone, etc.) were taken in large quantities, e.g. 100–200 kg and prepared by the homogenization, crushing and quartering method (according to EN 932-1:2006 procedure). 100 g of each final sample was