DISTRIBUTION OF HEAVY METALS IN BLAST FURNACE IN- AND OUPUTS WITH RESPECT TO THE UTILISATION OF WASTE PLASTICS

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Abstract

One way for recycling of waste plastics is the utilization as an alternative reducing agent within the blast furnace process. There they are substituting commonly used reducing agents such as coke and heavy oil, for example. However, the utilisation of waste plastics as an alternative reducing agent is also associated with an additional input of heavy metals in the blast furnace process. Some heavy metals, such as Zn and Pb, are proven to negatively influence the process. Therefore, the amount and concentration of heavy metals, such as Pb, Zn, Cr, Ni, Hg and Cd, in the different input and output flows of the blast furnace process were investigated in detail. In particular the different input flows were analysed in order to evaluate the additional input of heavy metals due to the utilisation of waste plastics. For these investigations measurement data, including concentration and mass or volume measurements, respectively, for a period of five years were evaluated. The results of the analyses indicate that the additional input of heavy metals from waste plastics into the blast furnace is for the most elements (Zn, Pb, Cr, Ni) of minor significance. The distribution of the heavy metals in the process outputs is partly varying considerably for the different years. However, distribution patterns for the observed heavy metals were identifiable.

Keywords: blast furnace, heavy metals, waste plastics

1. INTRODUCTION

Heavy metals, such as for example lead, zinc, mercury or cadmium, are inserted into the blast furnace process either through “geogenic” materials such as iron ores, coke and heavy oil or through alternative reducing agents such as for example waste plastics. Waste plastics can be used as an alternative reducing agent to substitute e.g. heavy oil or crude tar. So far, numerous investigations have been carried out to describe the influences on the process due to the utilisation of waste plastics (e.g. [1], [2], [3], [4], [5], [6]). However, the utilization of waste plastics also represents an additional input of different heavy metals, whereby the elements zinc and lead are proven to be harmful for the process stability.

Zinc, for example, enters the process mainly in form as an oxide or as a sulphide. Especially ZnO is reduced in the lower zones of the blast furnace process. The resulting zinc is immediately vaporized due to the relatively low sublimation point of about 907 °C. The zinc vapor rises with the gas to the upper zone of the furnace where it is re-oxidized. On the way to the upper part of the blast furnace zinc vapor can condense on the charge materials with which it descents. In the lower part of the furnace (at higher temperatures) zinc is vaporized again. This causes the formation of an inner zinc circulation. A part of the zinc vapor also seeps through the bricks joints into the lining. There it condenses around the cooling plated. This leads to an accumulation of Zn which finally results in an impairment of the burden decent. The other part of the zinc is leaving the process through the top gas [7], [8], [9], [10].

Lead enters the blast furnace process mainly within the composition of sulfur compounds or oxides. Lead is not soluble in iron. Moreover it has a higher density compared to iron and accumulates, therefore, under the hot metal. There it can seep through the refractory linings and destroy them [7], [11].

The distribution of cadmium in the blast furnace and its satellite processes is only described by Prater [12]. In his study he reported that cadmium is mainly found in the blast furnace gas washing water solids. For other output flows like hot metal, slag or gas washing effluents the cadmium concentration was below the analytical detection limit.

One way to evaluate the distribution of heavy metals in the blast furnace outputs is to conduct material flow analysis (MFA). MFA is based the conservation of mass. It offers the possibility to deal with huge amount of measurement data such as mass flow- and volume flow measurements as well as concentration measurements. Moreover, measurement uncertainties can be considered. The method allows also the determination of so-called “transfer coefficients”. These describe the partitioning of a substance within a process, and its transfer into a specific output. Thus, transfer coefficients can be used to determine the concentrations of heterogeneous input or output flows. For example, from the results of the output flow measurement the composition of the input flows can be derived utilizing transfer coefficients and vice versa. Additionally, the measurement reliability could be increased and the measurement uncertainty decreased, if sampling and measurements can be carried out at homogenous material flows [13]. This was successfully demonstrated with indirect waste analysis campaigns conducted at waste-to-energy plants [14].

The aim of this study was to evaluate whether the injection of waste plastics represents a significant additional input to the total insertion of heavy metals. Additionally the distribution patterns of the heavy metals were investigated. Therefore, the method of material flow analysis (MFA) was used.

2. MATERIALS AND METHODS

Input and output flows of a blast furnace process were analysed with respect to their quantity and quality to conduct a MFA for selected heavy metals (Hg, Cd, Zn, Ni, Pb and Cr). Routinely measured data, which have to be collected to fulfil quality reasons as well as regulatory requirements, were evaluated over a total period of 5 years.

The following input and output flows were considered: iron ores, coke, heavy oil, waste plastics, process water, hot metal, slag, sludge, top gas dust, cleaned top gas and casthouse dust (see **Fig. 1**).

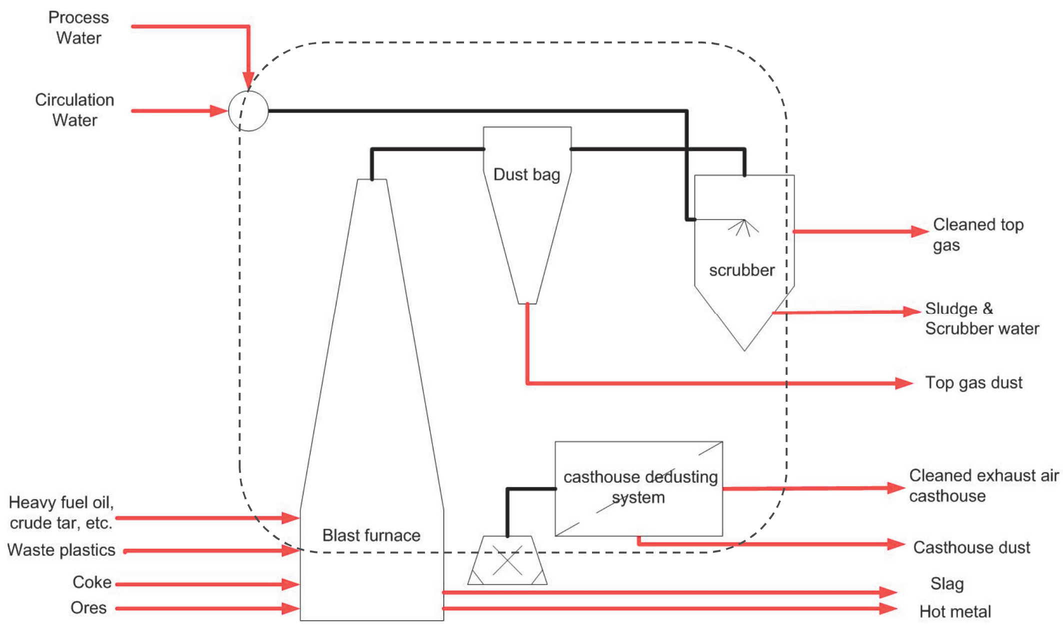

Fig. 1 Scheme of the blast furnace and top gas cleaning system for the MFA model: Flows for which measurement data (mass/volume flow and content of heavy metals) are available are indicated in red

Quantitative and qualitative data (mass/volume flows and heavy metal concentrations) of these flows were available at different temporal resolution and for different degrees of uncertainty. The uncertainty was dependent on the utilized measurement method, the magnitude of the heavy metal concentration and the heterogeneity of the material.

Based on these measurement values annual means were calculated and subsequently used to determine annual flows for the investigated heavy metals. Thereto, the MFA software STAN [15] was used. This software allows considering data uncertainties of material flows by using error propagation and data reconciliation. The latter applies only if the MFA system is over-determined, as it was the case in the presented study, and information about the uncertainties of each measurement data is given. This information was obtained from statistical analysis of measurement values and/or the precision of used measurement devices.

3. RESULTS

In following section, selected results of the analyses are presented. Exemplary the share on the heavy metal input through waste plastics, the outcomes of the MFA (after data reconciliation) and the transfer coefficients for cadmium for one specific year are highlighted.

3.1 Share of heavy metals inserted by waste plastics

Fig. 2 shows the distribution of cadmium, zinc, lead and mercury of the different input materials. The presented values are average values for a period of four years.

The input of Cd through waste plastics is more than 60 % whereas the input through the iron ores is less than 21 %. The mercury input comes mainly from different oil products (more than 60 %). The share of the mercury input from waste plastics is about 30 %, for zinc and lead it is less than 12 %.

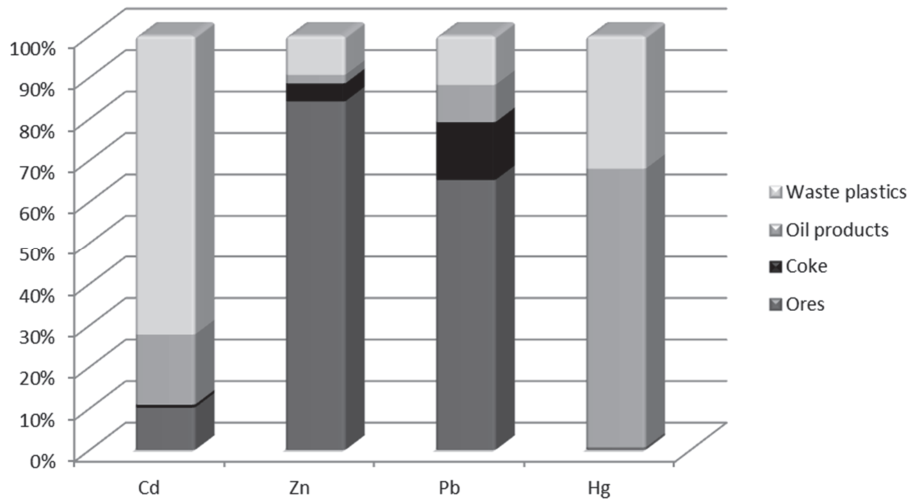

Fig. 2 Share heavy metal (Cd, Zn, Pb, Hg) input by waste plastics

However, it must be noted that the Cd concentrations of the utilized waste plastics are always below the legal limit.

3.2 Material Flow Analysis (after reconciliation)

Fig. 3 shows the results of the MFA for Cadmium. There the cadmium flows through the chosen system including the blast furnace process, the top gas cleaning processes as well as the casthouse dedusting system are represented.

From **Fig. 3** it is obvious, that cadmium is inserted into the blast furnace mainly through the utilization of waste plastics as an alternative reducing agent. The contribution of the waste plastics to the total cadmium input is about 53 %.The iron ores contribute to the cadmium input only to a low proportion. However, it must be noted that especially cadmium concentrations in the different iron ores as well as in other high quantitative flows are very often below the limit of quantification and cannot be evidenced, therefore. Thus, the contribution of the iron ores to the total cadmium input could be slightly higher.

Cadmium is leaving the blast furnace mainly through the top gas. Only a small amount can be detected in the casthouse dust. Within the top gas scrubber Cadmium is split up into the scrubber water and sludge. The distribution between both can vary considerably for the different years under consideration.

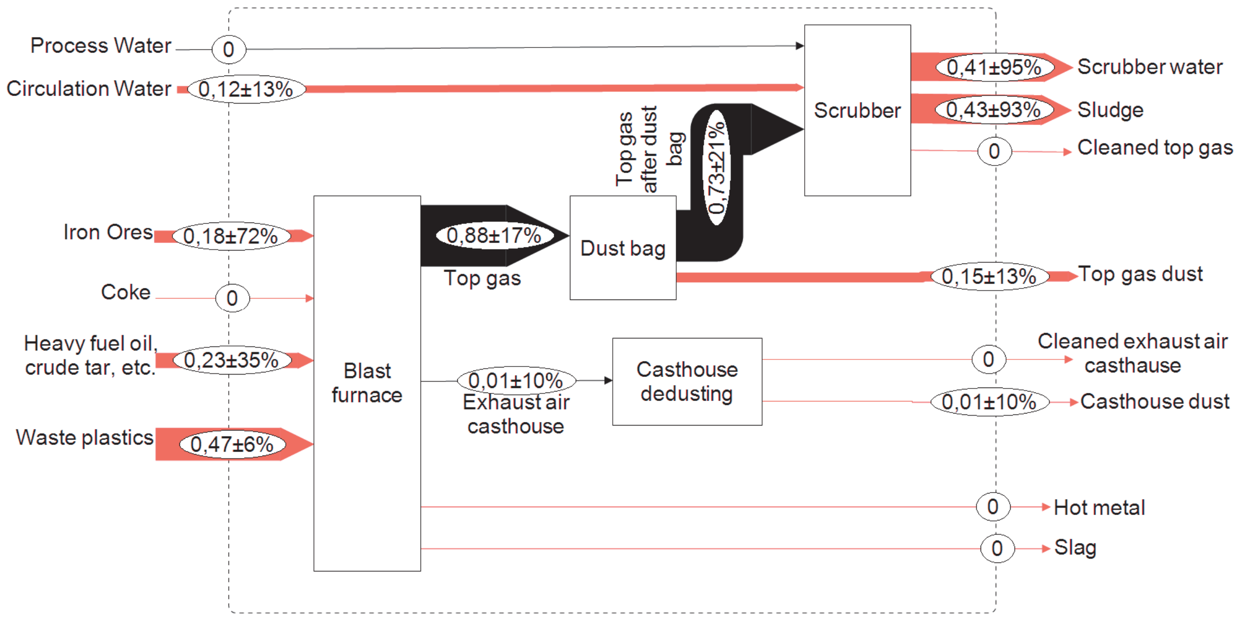

Fig. 3 MFA diagram for Cadmium (demonstrated for 1 kg input of Cadmium)

One major outcome of the MFA application to the blast furnace process was the finding that data reconciliation is largely driven by the quality of the measurement data. For instance, according to the measured/reported data the mass flow of the hot metal was reconciled significantly by more than 12 % (not shown within this manuscript). This result seemed rather unrealistic, considering the fact that hot metal represents the product of economic interest, whose amount will be determined fairly precise.

3.3 Transfer coefficients

In order to reduce the measurement effort, the definition of fixed transfer coefficients describing the portioning of heavy metals to different output flow would be helpful. However, based on the reported data and the MFA system established transfer coefficients for some heavy metals (e.g. Zn and Pb) were varying considerably for the different years investigated.

In contrast for Cadmium fairly constant transfer coefficients could be determined for the different years under consideration. From **Fig. 4** it is obvious that about 82 % of the cadmium input is transferred into the scrubber water and sludge.

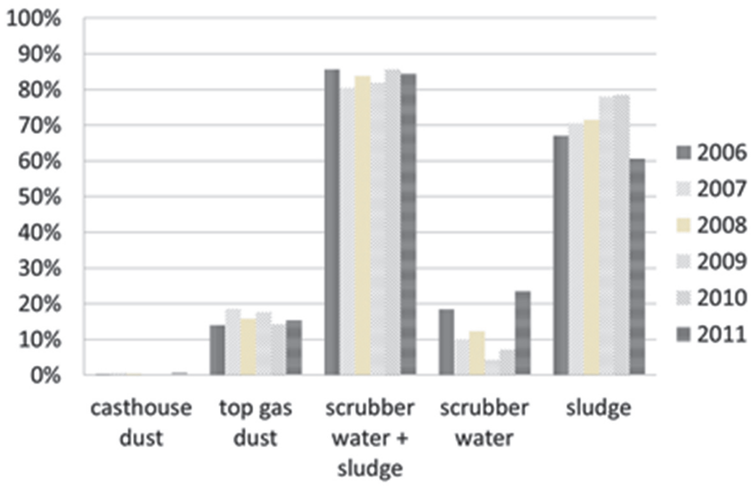

Fig. 4 Transfer coefficients for Cadmium (based on annual averages for the period 2006 until 2011)

CONCLUSION

The results clearly indicate that the contribution of waste plastics to the total input of the considered heavy metals (Cr, Ni, Zn, Pb, Hg, Cd) is for most elements of minor significance. Only for cadmium the share of waste plastics on the total cadmium input is significant with more than 50 %. However, cadmium is leaving the process mainly through the top gas and therefore it is accumulated in the scrubber water and sludge. Due to the chemical properties of cadmium (comparatively low boiling point), the element is not found in the process product. Moreover, it is commonly known that cadmium does not influence the process stability of the blast furnace.

The application of the Material Flow Analysis demonstrates that the outcomes of the mathematically based data reconciliation are largely dependent on the quality of available measurement data. Determination of reliable measurement data for input and output flows of heavy metals from a blast furnace, however, represents a major challenge, mainly due to large quantities of low concentrated input and output flows (e.g. detection limit problem) and high fluctuating output flows (e.g. scrubber water).

Besides that, it must be considered that the share of the investigated heavy metals on the total material flows is less than 0.1 %. Thus, many different chemical reactions which influence the behavior of heavy metals in the blast furnace and its satellite processes can occur. Therefore, from the current knowledge, thermodynamical and chemical knowledge should be combined with the mathematical tool of data reconciliation in order to predict reliable transfer coefficients that could subsquently be used to reduce measurement efforts.

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