



## **Doctoral Thesis**

Challenges and Potentials for Material Flow Analyses at Plant Level -  
Case Study: Blast Furnace Process

submitted in satisfaction of the requirements for the degree of Doctor of Science of the  
Vienna University of Technology, Faculty of Civil Engineering

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## **Dissertation**

Herausforderungen und Potentiale für Stoffflussanalysen auf  
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## Abstract

Material Flow Analysis (MFA) is a widely used tool for tracing material flows on different scales. On the one hand, there are macro scale level MFA which are utilized to investigate, e.g., the use pattern of materials and the development of the material stocks. On the other hand, MFA at a plant level is applied for optimizing material flows in processes and for tracing environmentally relevant substance flows. The main difference between these two types of applications are the data sources. Macro scale MFA are often based on heterogeneous data sources, such as official statistics, mathematical models, and expert estimations. For MFA on plant level, in contrast, typically extensive measurement data sets are available. Nevertheless, MFA on a plant level faces different challenges in its application.

The aim of this thesis is to investigate different aspects influencing the data quality and thus also the quality of the results of MFA. To do so, MFA is applied to the blast furnace process in order to trace the heavy metals Cd, Cr, Hg, Ni, Pb and Zn, which appear in minor amounts in the inputs and outputs of the furnace. The principal behavior of the respective elements is investigated in an extensive literature study (Paper I). Based on these investigations, the blast furnace sludge is identified as one of the main output flows for Pb and Zn and is investigated in terms of the particle size and metal distribution (Paper II). As the Hot Metal (HM) also constitutes an important output flow, especially for the Pb, it is characterized in detail (Paper III). Observed differences between metal input and output flows resulted in investigations of the blast furnace lining as a potential sink for Pb und Zn (Paper IV). Finally, the applicability of Transfer Coefficients (TCs) for low concentrated output flows is investigated (Paper V).

The results show that the heavy metals investigated behave differently under blast

furnace conditions. Furthermore, differences in balances (total input is unequal to total output) for the heavy metals can be recognized. It can also be seen that the resulting output paths are strongly dependent on their physical and chemical characteristics. Due to the fact that Pb and Zn are the most important elements in terms of process stability, their main output flows (blast furnace sludge and the HM) have been characterized in detail. These investigations show that the blast furnace sludge is extremely heterogeneous. The particle size ranges from less than 20  $\mu\text{m}$  to 250  $\mu\text{m}$  and the particles show different heavy metal concentrations depending on the size (e.g., higher Zn concentrations for smaller particles). Thus, a representative sampling of the sludge is challenging, which has been also confirmed by comparing two different sampling points for the blast furnace sludge. The investigations on the determination of Pb in the HM indicate that the currently applied method needs to be improved (e.g. sample preparation) or replaced by a more suitable analytical method. Furthermore it has been shown that HM samples are heterogeneous regarding their Pb content (Pb is unequally distributed and shows its concentration in the surface layers of the sample). The accumulation of Pb and Zn in the blast furnace process, however, should not affect the balances for these elements. In addition, the applicability of TCs to low concentrated output flows seems to be restricted mainly due to the fact that no linear correlation between the total input and minor output flows could have been identified.

The results obtained allow potentials for improving MFA for the blast furnace process with respect to sampling, analytical efforts as well as the uncertainty of results to be identified. Moreover, further research questions, such as the need for thermodynamic modeling and improved sampling, sample preparation and measurement of HM samples, have been developed.

Besides case study specific recommendations, general aspects for the application of MFA at a plant level are also derived. These include, e.g., the need of closed balances in order to conduct data reconciliation, which is necessary to obtain high quality MFA results. In this context further research questions such as, e.g., the determination of data uncertainty and the application of statistical methods for censored data are also addressed.

## Kurzfassung

Die Methode der Stoffflussanalyse (SFA) ermöglicht die Beschreibung von Güter- und Stoffflüssen auf unterschiedlichen Ebenen: SFA werden einerseits auf einer regionalen, nationalen und globalen Ebene angewendet, um die Nutzung von Ressourcen und damit im Zusammenhang stehenden Änderungen geogener und anthropogener Materiallager zu untersuchen. Andererseits können SFA auch für Industrieprozesse angewendet werden. Dabei steht die Optimierung der Material- und Stoffflüsse innerhalb des Betriebes im Vordergrund, jedoch können auch Emissionspfade untersucht werden. Der größte Unterschied zwischen den beiden Anwendungsgebieten stellen die verfügbaren Datenquellen dar. Während für SFA auf Makroebene zumeist sehr heterogene Datenquellen (offizielle Statistiken, mathematische Modelle, Expertenschätzungen) herangezogen werden, beruhen SFA auf betrieblicher Ebene auf gemessenen Daten. Trotz der meist umfangreichen Messdaten bringt auch die Anwendung der SFA auf betrieblicher Ebene unterschiedliche Herausforderungen mit sich.

Ziel dieser Arbeit ist es, verschiedene Aspekte, die die Qualität von betrieblichen SFA negativ beeinflussen können, aufzuzeigen, zu diskutieren und Lösungsvorschläge abzuleiten. Dafür wird der Hochofenprozess als Fallstudie herangezogen und die Schwermetallflüsse Cd, Cr, Hg, Ni, Pb und Zn werden erforscht. Zu Beginn wird auf Basis einer umfangreichen Literaturstudie das Verhalten dieser Elemente im Hochofen untersucht (Paper I). Basierend auf diesen Untersuchungen wurden der Hochofenschlamm (aus der Abgasreinigung) und das Roheisen als wichtige Outputflüsse für Zn und Pb identifiziert und detaillierter charakterisiert (Paper II bzw. Paper III). Des Weiteren ist auf Grund der Literaturstudie ersichtlich, dass Pb und Zn sich im Hochofen (Ausmauerung) anreichern können. Daher wurde deren Konzentra-

tionen in der Schamotte untersucht (Paper IV) und die im Hochofen verbleibende Menge abgeschätzt. Zusätzlich wurde die Anwendbarkeit von Transferkoeffizienten für niedrig konzentrierte Outputflüsse untersucht (Paper V).

Die Ergebnisse zeigen, dass das Verhalten der untersuchten Schwermetalle sich unterscheidet und häufig Bilanzdifferenzen (Gesamtinput ist ungleich Gesamtoutput) auftreten. Als wichtigste Outputflüsse des Hochofenprozesses für Pb und Zn konnten der Hochofenschlamm und das Roheisen charakterisiert werden. Eine detaillierte Charakterisierung des Hochofenschlammes zeigt, dass es sich dabei um ein sehr heterogenes Material handelt (Partikelgrößenverteilung zwischen 20 und 250  $\mu\text{m}$ ; Pb, Zn Konzentrationen nehmen mit abnehmender Partikelgröße zu), das während der Beprobung bzw. Probenaufbereitung zur Entmischung neigt. Dieser Aspekt konnte auch durch den Vergleich der Ergebnisse von zwei unterschiedlichen Messstellen für den Hochofenschlamm bestätigt werden.

Die Untersuchungen für das Roheisen zeigen, dass Pb in den Proben ungleichmäßig verteilt ist und die aktuell verwendete Messmethode (inkl. Probenaufbereitung) zu einer systematischen Überschätzung des Pb Gehaltes führt. Daher bedarf es einer detaillierten Untersuchung der Pb Verteilung in der Roheisenprobe sowie einer Änderung im Messverfahren.

Die Untersuchungen hinsichtlich des Verbleibs der Elemente Zn und Pb im Hochofen zeigen, dass dieser Effekt sich nicht signifikant auf die Differenz zwischen Gesamtinput und -output auswirkt.

Die durchgeführten Analysen zur Anwendbarkeit von Transferkoeffizienten zeigen, dass zwischen Input- und Outputflüssen, die nur sehr geringe Anteile ( $< 1\%$  zum Gesamtoutput beitragen), kein identifizierbarer Zusammenhang besteht.

Die Ergebnisse der durchgeführten Untersuchungen zeigen Verbesserungspotentiale für SFA für den Hochofenprozess auf (z.B. Verbesserung der Probenahme für den Hochofenschlamm) und sprechen weitere Forschungsfragen, wie z.B. thermodynamische Modellierung, verbesserte Probenahme, Probenvorbereitung und Messmethoden für Roheisenproben an. Des Weiteren können allgemeine Schlüsselaspekte für die SFA auf betrieblicher Ebene abgeleitet werden. Diese umfassen u.a. die Notwendigkeit

von geschlossenen Bilanzen zur Durchführung von Datenausgleichsberechnungen und die Anwendung von statistischen Methoden für Datensätze, die Messwerte unter der Bestimmungsgrenze aufweisen.

## Published articles and author's contribution

- I. V. Trinkel, O. Mallow, C. Thaler, J. Schenk, H. Rechberger and J. Fellner. Behavior of Chromium, Nickel, Lead, Zinc, Cadmium and Mercury in the Blast Furnace - A Critical Review of Literature Data Plant Investigations. *Ind. Eng. Chem. Res.*, 54 (47): 11759-11771, 2015. DOI:10.1021/acs.iecr.5b03442
- II. V. Trinkel, O. Mallow, P. Aschenbrenner, H. Rechberger and J. Fellner. Characterization of blast furnace sludge with respect to heavy metal distribution. *Ind. Eng. Chem. Res.*, accepted 23.4.2016.
- III. V. Trinkel, O. Mallow, N. Kieberger and J. Fellner. Herausforderungen für die Stoffflussanalyse bei Industrieprozessen - Fallstudie: Pb im Hochofenprozess. 6. *Wissenschaftskongress "Abfall- und Ressourcenwirtschaft"*, Berlin; 10.03.2016 - 11.03.2016.
- IV. V. Trinkel, , P. Aschenbrenner, C. Thaler, H. Rechberger, O. Mallow and J. Fellner. Distribution of Zn, Pb, K and Cl in blast furnace lining. *Steel Res. Int.*, 2016. submitted
- V. V. Trinkel, N. Kieberger, T. Bürgler, H. Rechberger and J. Fellner. Influence of waste plastic utilisation in blast furnace on heavy metal emissions. *J. Cleaner Prod.*, 94: 312-320, 2015. DOI: 10.1016/j.jclepro.2015.02.018

- I, V     Responsible for literature research, data evaluation and writing  
III     Responsible for experiment design, data evaluation and writing;  
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## Related publications and conference contributions

- V. Trinkel, C. Thaler, H. Rechberger and J. Fellner. Challenges for the Application of Material Flow Analysis at the Level of Production Processes – Case Study: Blast furnace process. *Materiaux & Techniques*, 104, 2016. DOI: 10.1051/mattech/2016001
- V. Trinkel, O. Cencic, N. Kieberger. Herausforderungen für die Stoffflussanalyse auf betrieblicher Ebene. *Österreichische Wasser- und Abfallwirtschaft*, 67, 43-53, 2015. DOI: 10.1007/s00506-014-0204-9
- V. Trinkel, H. Rechberger, J. Fellner. Comparing the Utilization of Waste Plastics in Hot Metal and Cement Production. In: *Sardinia 2015, 15th International Waste Management and Landfill Symposium*, S. Margherita di Pula, Italy, 2015.
- V. Trinkel, H. Rechberger, J. Fellner, N. Kieberger, T. Bürgler. Heavy Metals Flows Induced by Plastics Utilisation in the Blast Furnace Process. In: *DepoTech 2014 Abfallwirtschaft, Abfallverwertung und Recycling, Deponietechnik und Altlasten*, November 4 - 7, Leoben, Austria: 319-324, 2014.
- V. Trinkel, H. Rechberger and J. Fellner. Distribution of heavy metals in blast furnace in- and outputs with respect to the utilisation of waste plastics. In: *Proceedings of METAL 2014 - 23rd International Conference on Metallurgy and Materials*, Mai 21-23, Brno, Czech Republic: 33-38, 2014.
- V. Trinkel, O. Cencic, H. Rechberger, N. Kieberger, T. Bürgler, J. Fellner. Challenges in material flow accounting - Case study iron production process.

In: 1st ESTAD & 31st JSI, Join New European Steel Industry Conference,  
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## List of Abbreviations

<b>MFA</b>	Material Flow Analysis
<b>TC</b>	Transfer Coefficient
<b>HM</b>	Hot Metal
<b>PCI</b>	Pulverized Coal
<b>RDF</b>	Refuse Derived Fuels
<b>LOD</b>	Limit of Detection
<b>XRF</b>	X-ray fluorescence spectroscopy
<b>ICP-OES</b>	Inductively Coupled Plasma Optical Emission Spectroscopy
<b>OES</b>	Optical Emission Spectroscopy
<b>LA-ICP-MS</b>	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
<b>AAS</b>	Atomic Absorption Spectroscopy



# 1 Introduction

## 1.1 Background

The blast furnace is an important instrument in the crude steel production.<sup>[1,38,50]</sup> In 2015 around 70% of the worldwide crude steel production was produced by means of the blast furnace - basic oxygen furnace route.<sup>[50]</sup> Beside the significant contribution to worldwide CO<sub>2</sub> emissions<sup>1</sup>, this process causes the emission of other environmentally relevant elements, such as heavy metals.<sup>e.g [9,21,30,48,49]</sup> Thus, there is an interest in tracing the heavy metals through the entire process in order to determine their source of origin, their fate and their final destination in the different output flows of the blast furnace process. Material Flow Analysis (MFA) constitutes a suitable method for such investigations.

MFA is a widely used tool for tracking material and substance flows on different scales. In general, a distinction can be made between macro level and plant level MFA.<sup>[4]</sup> MFA at a macro level can be conducted on a regional, national or international scale and addresses different research questions regarding, e.g., the development of the material stock in societies and the use pattern of materials<sup>e.g [7,17,33]</sup>, as well as questions concerning resource management<sup>e.g [19,28,34]</sup> as well as socio-economic issues<sup>e.g [2,4,23]</sup>.

The motivation for conducting MFA at a plant level is mainly to optimize materials flows with respect to resource recovery<sup>e.g [20,35,37]</sup> as well as to trace substances of environmental<sup>e.g [51]</sup> interest.

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<sup>1</sup>Contribution of iron and steel production to total anthropogenic energy and process CO<sub>2</sub> emissions almost reaches 9%<sup>[29]</sup>

Henseler et al.<sup>[20]</sup> applied MFA to a paper production plant. Their main objective was to evaluate whether this method is a suitable tool for material flow accounting at plant level and to verify the economic viability. They focused on the elements C, S, Al, Zn and Fe as these substances are of economic concern for the process considered. The data utilized on their model was, on the one hand, based on relevant documents from accounting. The chemical composition, on the other hand, was determined by their own chemical analyses, product declarations and literature values. They concluded that MFA is a suitable tool for recording distribution patterns of relevant substance flows, for carrying out investigations regarding resource and energy consumption as well as for assessing environmental impacts.

Another example is the application of MFA to municipal solid waste incineration plants.<sup>[32,36]</sup> The goal of these studies was to determine the heterogeneous composition of the waste feed by analyzing the far more homogeneous incineration residues. The mass balance was established by measuring all input and output mass and volume flows. Chemical analysis of the different elements under investigation (e.g. Cd, Pb, Zn) were conducted for the output flows (except for the scrap metal). Morf et al.<sup>[32]</sup> and Schachermayer et al.<sup>[36]</sup> derived Transfer Coefficients (TCs), which enable the composition of the waste to be calculated by utilizing the chemical analysis conducted for the residues at the output.

MFA can also be applied to separation techniques for demolition waste to identify the influence of the sorting method on the quality of the recyclable material.<sup>[37]</sup> To this end the substance flows for different metals (e.g. Fe, Zn and Pb), S, the total inorganic carbon and the total carbon were traced. This investigation was based on data obtained during five measurement campaigns in which the mass flows were obtained over a sampling time of about 2 hours by weighting or measurement, and the chemical composition was determined by different analysis methods (e.g. XRF, AAS).

Another example is the application of MFA to a waste splitting plant producing RDF (Refuse Derived Fuels). Rotter et al.<sup>[35]</sup> carried out a process evaluation based

on MFA which considers the aspect of minimizing hazardous substances in the RDF. Within their work they compared different treatment options with respect to the RDF quality by applying MFA. The data used for MFA is based on four sorting campaigns of household waste. These investigations were carried out during four seasons and at four different locations in Saxony (Germany). For each campaign around 1-2 tons of household waste were sorted into around 50 components, which were analyzed according to their mass and chemical composition.

Velis et al.<sup>[47]</sup> applied MFA on a mechanical-biological treatment plant producing RDF in order to identify the links among material flows, plant configuration and fuel quality. They also determined TCs to model the sorting and upgrading processes of the RDF production plant. The necessary data were obtained by sampling of 16 individual flows. These flows were characterized by manual sorting, chemical and fuel properties characterization. However, they were not able to establish a sound model based on TCs, due to highly uncertain input data, which lead to unrealistic results.

Xu et al.<sup>[51]</sup> utilized MFA to investigate the CO<sub>2</sub> emissions of the blast furnace and basic oxygen furnace steelmaking systems in China.

The feasibility and the quality of MFA results always depend on the availability and the quality of data<sup>[25]</sup>, independently of its field of application. For macro scale MFA, such as international and national material flow balances, the data originate from heterogeneous sources such as official statistics, mathematical models and expert estimations. Typically, these data are isolated values rather than extensive data sets.<sup>[39]</sup> For balancing industrial processes, as mentioned above, most often particular sampling and measurement campaigns are conducted to obtain the necessary data to compare and improve different plant operating options and material flows as well as to determine TCs.

In connection with the quality of the results of MFA, data uncertainties<sup>e.g [25,26]</sup> are a widely discussed topic since they allow data reconciliations to be carried out if an over-determined system and normally distributed data are present. This can be

done by utilizing the data reconciliation algorithm in the software STAN<sup>[22]</sup>, which applies a weighted least-square optimization to the model. This procedure offers not only the possibility to balance the model but also to reduce the uncertainties of the flows.<sup>[6,10]</sup> However, the applicability of data reconciliation is limited. When utilizing highly uncertain input data for the MFA model, the data reconciliation can lead to negative flows, which are physically impossible. In such cases the input data has to be refined accordingly and the congruence of the material flow model has to be checked against the physical material flows.<sup>[24]</sup>

In the case of the blast furnace process, extensive measurement data are available for process control, quality control and environmental protection reasons. These measurement data include volume- and mass-flow measurements as well as concentration measurements for several substances. Although a complete and extensive data set for the blast furnace model's input and output flows is readily available, the application of MFA faces some challenges, which influence the quality of the results. These respective influencing factors for MFA at a plant level have been insufficiently discussed in the literature so far.

## 1.2 Objective

The objective of this thesis is to apply MFA<sup>2</sup> to the blast furnace process in order to trace elements which occur in minor quantities in the system investigated. Thereby the major challenges for the application of MFA at a plant level should become evident.

The blast furnace process serves as a sufficiently complex case study since this process involves a high variety on input and output flows whose composition varies to a great extent. Furthermore, the relationships between input and output flows are only partly known.

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<sup>2</sup>MFA is utilized as an umbrella term including material and substance flow analysis. For the blast furnace process the substances Cd, Cr, Hg, Ni, Pb and Zn have been traced.

MFA is conducted for several heavy metals, including Cd, Cr, Hg, Ni, Pb and Zn. These elements belong to so-called micro elements since their respective concentrations in the different materials is less than 1 wt%.<sup>[12]</sup> The heavy metals considered have the potential to influence the process stability (e.g. Pb, Zn)<sup>e.g[8,52]</sup>, the product quality (e.g. Cr, Ni)<sup>e.g[8]</sup> and/or are of interest for environmental reasons (e.g. Cd<sup>e.g[46]</sup>, Hg<sup>e.g[14]</sup>).

Zn, for example, can lead to an increased wear of the lining material, can reduce the strength of the coke, increases the generation and accumulation of coke fines and can attack the copper blast furnace tuyeres.

Pb is relevant as it may destroy the refractory lining at the hearth and at the bottom of the blast furnace.<sup>[1]</sup>

If Cr enters the blast furnace process as  $\text{Cr}_2\text{O}_3$ , it is reduced by C. This reduction is an endothermic process and requires a lot of energy, which leads to increased coke consumption.<sup>[1,42]</sup> Furthermore, Cr as well as Ni are alloying elements and important for the production of high quality steels.<sup>[38]</sup>

Cd and Hg are relevant for environmental reasons<sup>[42]</sup> since both elements end up to a large extent in the dust produced during the top gas cleaning, which is partly landfilled.<sup>[42]</sup>

In particular, the thesis addresses the following research questions:

- How do the heavy metals Cd, Cr, Hg, Ni, Pb and Zn behave in the blast furnace process?
  - What are the most important input and output flows for these elements?
  - Do the heavy metals in the blast furnace investigated behave similarly to metals in other studies conducted at other blast furnaces?
- How can sampling procedures and/or analytical measurements be improved to enhance the robustness and reliability of MFA results?
  - Which input and output flows are at risk regarding non-representative

sampling?

- How may sampling and applied analytical methods for these flows influence the results of MFA?
- Do processes occurring inside the furnace influence the imbalances and thus the quality of the results of MFA?
- Is it possible to define TCs for the heavy metals investigated for the blast furnace process in order to reduce the measurement effort?

To answer these questions MFA is applied for the heavy metals Cd, Cr, Hg, Ni, Pb and Zn to the blast furnace process using measurement data provided by the plant operator. In order to interpret the results of MFA for the blast furnace correctly, fundamental knowledge of the behavior of the elements under investigation is necessary. Therefore, an extensive literature review (Paper I) is carried out comparing the results of different research studies with our own plant observations. Thereby, balance errors and changes in balances have been identified, which could hardly be explained by the behavior of the elements under investigation.

Based on these findings, MFA for Pb and Zn have been investigated in more detail since these elements are relevant for process stability. As Zn is mainly carried out of the process via the scrubber sludge, this output flow has been identified as critical for the quality of MFA for Zn and is characterized in more detail. In particular, the distribution and content of heavy metals have been analyzed (Paper II). For Pb the Hot Metal (HM) could be identified as a crucial output flow with respect to the result of MFA. Therefore, the content of heavy metals in the HM was investigated in more detail by validating the analytical measurement procedure and investigating the sample homogeneity (Paper III).

Furthermore, some elements tend to remain in the blast furnace, e.g. in the form of accretions and/or by penetrating into the lining material. Consequently, the blast furnace lining is investigated during an overhaul with respect to the concentrations of the respective heavy metals to identify whether the residual amounts in the furnace

might be relevant with respect to the heavy metal imbalances (Paper IV).

Since the determination of reliable transfer coefficients (TC) would mean a significant reduction of measurement effort (reduced costs for sampling and analyses) for industrial processes, the applicability of TCs is assessed for the chosen system and heavy metals investigated (Paper V).

From these investigations conclusions are drawn regarding the challenges and opportunities of applying MFA at a plant level.

## 2 Fundamentals of the blast furnace process

The blast furnace process is a continuously working process, which is based on the counter flow principle. The raw materials, including coke and burden, are charged at the top of the furnace and need 5 to 7 hours to descend within the furnace. The reducing gas, which is generated in front of the tuyeres at the bottom of the furnace, needs around 5 to 10 seconds to ascend to the top. Within the furnace several reactions take place to obtain the Hot Metal (HM).<sup>[1]</sup> The fundamentals, including possible reactions of iron oxides and heavy metals within the blast furnace process, are briefly explained in the following.

### 2.1 Zone model

In an idealized way, the blast furnace can be divided into seven zones in which different chemical reactions take place (see Figure 2.1).

The heating zone shows the lowest temperature. The burden is heated up and dried, chemically bounded water is stripped and the dissociation of  $\text{MgCO}_3$  and  $\text{FeCO}_3$  takes place.<sup>[38]</sup> Furthermore, higher iron oxides such as hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) react (via a direct reduction) with  $\text{CO}$  and  $\text{H}_2$  to wustite ( $\text{FeO}$ ) in the upper part of the furnace (chemical equations given in Figure 2.1).<sup>[27,38]</sup>

In the soaking zone the temperature ranges from between 800 to 1000 °C. This temperature is enough to force the dissociation of  $\text{CaCO}_3$  and the direct reduction of wustite to iron. The composition of the gas phase is influenced from the water-gas-reaction ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ).

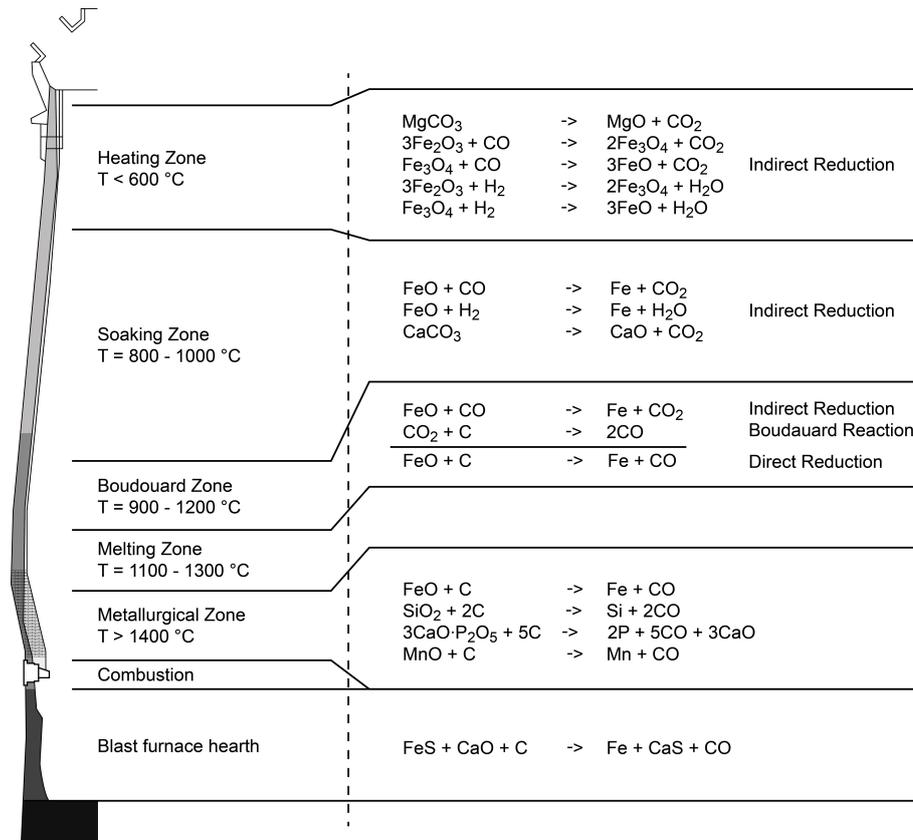


Figure 2.1: Zones model of blast furnace (based on Babich et al.<sup>[1]</sup>, Schenk<sup>[38]</sup>).

At temperatures from between 900 and 1200 °C (Boudouard Zone), the indirect reduction of wustite takes place. The generated CO<sub>2</sub> reacts with C to CO according to the Boudouard equilibrium.

In the melting zone the temperature ranges between 1100 and 1300 °C. In this zone the burden materials soften and begin to melt. Furthermore, first slag phases occur.

At temperatures above 1400 °C, the molten FeO and slag components such as SiO<sub>2</sub>, 3 CaO · P<sub>2</sub>O<sub>5</sub> and MnO are reduced (direct reduction) by the coke. Here a non-reactive zone is formed (dead man), which is no longer involved in any chemical reactions.

The dead man is important for the distribution of the reduction gas within the blast furnace.

In front of the blast furnace tuyeres the race way, which represents a cavity, is built (combustion zone). There coke particles fall into the race way and react with the available O<sub>2</sub> from the hot blast to form the reduction gas.

Below the tuyeres, the carburization and the desulphurization of the HM takes place.<sup>[38]</sup>

## 2.2 Reactions in the blast furnace process

In the following the main reactions of the iron oxides and the heavy metals investigated are briefly specified:

### 2.2.1 Reduction of iron oxides

Iron bearing materials consist of three differing iron oxides: FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> with an O<sub>2</sub> content of 30.06, 27.64 and 22.28 %, respectively. In the blast furnace the reduction of the iron oxides occurs at temperatures above 570 °C from Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> to FeO to Fe.<sup>[1,38]</sup>

The main reactions in the blast furnace process are the direct and the indirect reduction:

- Direct Reduction:

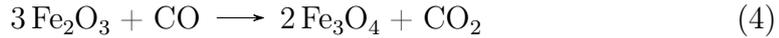
The direct reduction is described by the following endothermic reactions<sup>[1,38,53]</sup>:



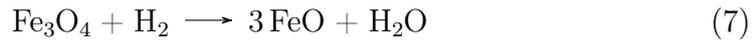


- Indirect Reduction: The indirect reduction of the iron oxides takes place as follows<sup>[1,38,53]</sup>:

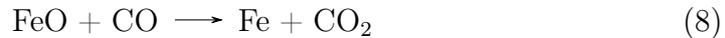
Hematite to magnetite



Magnetite to wustite



Wustite to iron



The reduction of hematite is exothermic and irreversible. The reduction of magnetite and wustite, however, are reversible processes and strongly depend on the temperature and the CO:CO<sub>2</sub>-ratio.

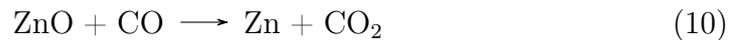
### 2.2.2 Reactions of trace elements

In the following the main reactions of the heavy metals considered in this thesis are summarized (based on Trinkel et al.<sup>[42]</sup>).

- Zinc

Zn belongs to the circulating elements in the blast furnace. In the case that Zn enters the blast furnace with the burden material, it will descend to zones with higher temperatures, where it is reduced. The metallic Zn vaporizes and ascends with the reducing gas. In regions with lower temperatures Zn re-oxidizes and condenses again onto the burden material.

Temperature range 800 - 1000 °C



Temperature range 900 - 1300 °C



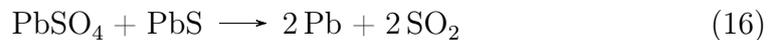
- Lead

Similar to Zn, Pb belongs to the elements which take part in an inner circulation process.

Temperature range 400 - 700 °C



Temperature range 650 - 900 °C



Temperature range 1000 - 1200 °C



- Chromium

$\text{Cr}_2\text{O}_3$  is reduced at temperatures around  $1220\text{ }^\circ\text{C}$ <sup>[16]</sup> according to:



- Nickel

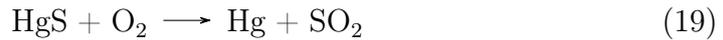
$\text{NiO}$  is slightly easier to reduce than  $\text{FeO}$ . Thus it will be reduced by  $\text{CO}$  at temperatures around  $500\text{ }^\circ\text{C}$ .

- Cadmium

In the case of  $\text{Cd}$  entering the blast furnace in the form of  $\text{CdO}$ , it will easily be reduced by  $\text{CO}$ . Furthermore  $\text{Cd}$  might react with  $\text{Cl}_2$  at temperatures below  $1000\text{ }^\circ\text{C}$  and leave the blast furnace with the top gas as  $\text{CdCl}_2$ .  $\text{Cd}$  can also react with  $\text{S}$  to  $\text{CdS}$ , which is able to rise with the gas stream in the blast furnace. At lower temperature zones at which  $\text{O}_2$  is present, it can be oxidized or solidify and get to zones of higher temperatures. Thus  $\text{Cd}$ , similar to  $\text{Pb}$  and  $\text{Zn}$ , also takes part in an inner circulation processes.

- Mercury

$\text{HgS}$  can be reduced to  $\text{Hg}$  according to:



Furthermore,  $\text{HgS}$  also moves downward to zones with temperatures of more than  $800\text{ }^\circ\text{C}$ . There  $\text{HgS}$  can be transferred into the liquid state and be reduced. The metallic  $\text{Hg}$  formed vaporizes and rises with the reducing gas.

## 3 Materials and Methods

### 3.1 Materials

#### 3.1.1 Investigated blast furnaces

The blast furnace process investigated in Paper I, II, III and V not only includes the blast furnace itself, but also different off-gas cleaning devices. The blast furnace has a hearth diameter of 12 m and a daily production rate of 8500 t HM. This furnace is operated under a counter pressure of approximately 2.5 bar. The top gas is cleaned from coarse particles by a dust bag and further cleaned by a wet scrubber. Furthermore, the cast house dedusting system is considered (see Figure 3.1).

The investigations presented in Paper IV have been carried out at another blast furnace. This furnace has a hearth diameter of 8 m and a daily production rate of 2500 t HM. The pressure at the tuyere level of this furnace is around 1.5 bar. The characterization of the lining material has been carried out at this furnace because it reached the end of the blast furnace campaign after five years of operation.

#### 3.1.2 Paper I

To investigate the behavior of the heavy metals in the blast furnace process, an extensive literature study has been conducted. The findings based on the papers reviewed have been further compared to our own observations. These observations were conducted for the years 2010 to 2012 and are based on measurement data provided by the plant operator (see also Chapter 3.1.6).

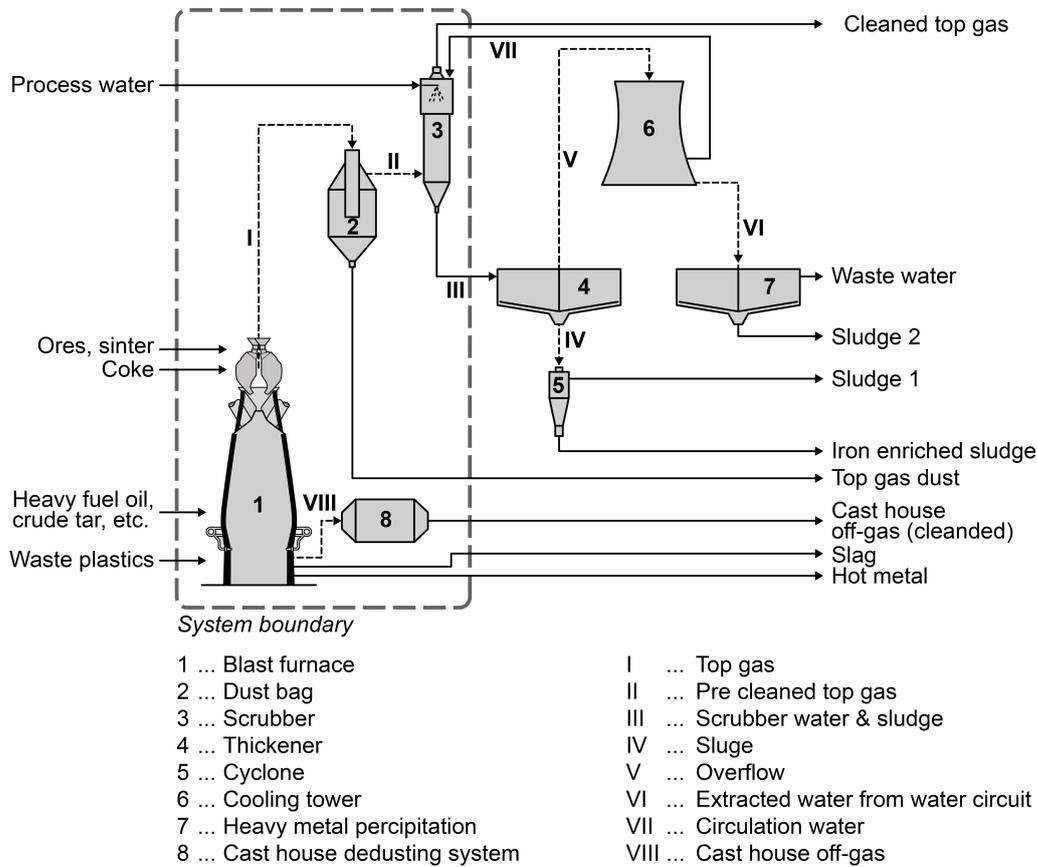


Figure 3.1: Blast furnace model (based on Trinkel et al.<sup>[41]</sup>).

### 3.1.3 Paper II

The characterization of the blast furnace sludge (Paper II) regarding the distribution of the heavy metals Cd, Pb, Zn and the elements C and Fe was carried out for sludge generated at the wet scrubber. The sampling point was chosen directly before a hydro cyclone (indicated with 5 in Figure 3.1). The samples were taken under regular operating conditions at the integrated steel plant on different working days during a time period of 4 weeks. In total 76 samples, each containing around 750 ml of sludge, were taken.

#### **3.1.4 Paper III**

The MFA for Pb has been conducted utilizing annual mean values for a time period of 9 years (2005 - 2013). The annual mean values are based on measurement values provided by the plant operator. Additional HM samples have been taken according to the standard procedure with a lollipop sampler and analyzed regarding the Pb content.

#### **3.1.5 Paper IV**

The blast furnace lining material was characterized regarding its Pb, Zn, Cl and K content. Therefore, 18 samples of the lining material have been taken over the blast furnace height to determine the distribution of these elements. In order to characterize the penetration depth of these elements, all samples were manually split into three subsamples, which were approximately equal in size.

#### **3.1.6 Paper V**

The investigations carried out in Paper V have been based on the measurement data provided by the plant operator. Hence, qualitative (concentration measurements) and quantitative (volume-flow and mass-flow measurements) measurement data from all input and output flows were available due to quality, environmental and/or process control reasons. The measurement frequency of the materials varies and is listed in Trinkel et al.<sup>[41]</sup>. For the analysis the mean values and the uncertainties based on the given measured values were determined and further used for our investigations.

### 3.1.7 Additional samples measured

In order to evaluate the sampling points for the blast furnace sludge after the wet scrubber and directly before the hydro cyclone regarding the representativeness of these sampling points, an additional measurement campaign was carried out. During a total time period of four weeks daily samples were taken at all input and output flows, which are regularly measured by the plant operator. In addition to these flows, the circulation water (indicated with VII in Figure 3.1) and the intake of the hydro cyclone (indicated with IV in Figure 3.1) were sampled and analyzed.

## 3.2 Methods

Table 3.1 gives an overview of the methods applied for certain parts of the work. These methods are subsequently described in detail.

Table 3.1: Applied methods

Method	Paper I	Paper II	Paper III	Paper IV	Paper V	Additional samples
MFA	X		X		X	
Milling				X		
Wet Sieving		X				
ICP-OES		X		X		X
Elemental Analysis		X				
XRF			X	X		
OES			X			
LA-ICP-MS			X			

### 3.2.1 Material Flow Analysis

MFA is a tool to quantify material flows and stocks in arbitrarily complex system defined in space and time and is based on the law of the conservation of mass. To perform MFA, data about the mass flows and the respective concentration of the substances are utilized. With these data MFA allows goods and substances to be traced through an entire system. The method of MFA is applied in Paper I, III and V.

In general, a MFA system can be described by Equation 20:

$$\sum_{K_I} \dot{m}_{Input} = \sum_{K_O} \dot{m}_{Output} + \dot{m}_{Stock} \quad (20)$$

Whereby  $K_I$  is the number of input flows,  $K_O$  the number of output flows,  $\dot{m}_{Input}$  the input mass flow,  $\dot{m}_{Output}$  the output mass flow and  $\dot{m}_{Stock}$  describes the mass flow which enters the stock.<sup>[6]</sup>

Over-determined systems (all input and output flows as well as the stock change is measured) and consideration of data uncertainties allow the application of data reconciliation. The reconciliation algorithm in STAN<sup>[22]</sup> (software which allows data uncertainty in MFA to be considered) applies a weighted least-square optimization to the model. This procedure not only offers the possibility to balance the model but also to reduce the uncertainties of the flows.<sup>[6,10]</sup>

In the case of the blast furnace process, the mass flow which enters the stock is assumed to be zero. This assumption can be made since the time period considered is sufficiently long and thus it can be assumed that although the process conditions may vary, the total amount of substances inserted will be found in the different output flows of the processes. This assumption of a steady-state flow process changes Equation 20 to 21:

$$\sum_{K_I} \dot{m}_{Input} = \sum_{K_O} \dot{m}_{Output} + \Delta B \quad (21)$$

Whereby  $\Delta B$  describes the imbalance between the input and the output of the blast furnace process. The imbalance is of interest since it can be seen as an indicator for the quality of MFA results and thus also for the quality of sampling and analyses of the elements of interest.

Furthermore, MFA allows TCs to be defined. TCs describe the share of the input which is transferred into a specific output of the process (see Equation 22)<sup>[6]</sup>:

$$TC_{k,j} = \frac{m_{Output_j} * c_{k,j}}{\sum_{i=1}^n m_{Input_i} * c_{k,i}} \quad (22)$$

where  $TC_{k,j}$  is the TC for substance k to output flow j,  $c_{k,j}$  the concentration of substance k in output flow j,  $m_{Output_j}$  the mass/volume of output flow j,  $c_{k,i}$  the concentration of substance k in input flow i,  $m_{Input_i}$  the mass/volume of input flow i.

If TCs can be determined and validated for a system, they offer the possibility to reduce the number of measurements at the industrial plant. The reduction of the measurement effort is given by means of reduced workload for chemical analyses and sampling. Thus, the identification of applicable TCs offers the possibility to reduce costs, which is always a key factor for companies regarding their competitiveness.

### 3.2.2 Analytical Methods

For the different samples taken, the following sample preparation processes and chemical analyses have been conducted:

- Sample Preparation

– Milling:

The blast furnace lining samples (Paper IV) were milled to a grain size of 250  $\mu\text{m}$  using a vibratory disc mill (Fritsch Pulverisette 9 with an agate stone inset).

– Wet sieving:

The particle size distribution (Paper II) was obtained by wet sieving. Two sieving towers, consisting of sieves with mesh sizes from 20  $\mu\text{m}$  to 250  $\mu\text{m}$ , were utilized at a vibratory sieve shaker (Fritsch Analysette 3Pro). Ethanol (VWR Chemicals, 96 %vol, c.p.) was used as an auxiliary sieving agent.

• Chemical Analyses

– ICP-OES:

The blast furnace sludge (Paper II) and the blast furnace lining (Paper IV) were analyzed regarding the concentration of the respective elements by means of ICP-OES. Around 71 g of each sample was digested in PTFE vessels (HPR 1000) using 2 ml  $\text{H}_2\text{O}$ , 1 ml  $\text{HNO}_3$ , and 7 ml  $\text{HCl}$  in a microwave oven (Modell: MLS Start 1500). The digestion parameters are given in the Supporting Information of Paper II and IV. The measurements were carried out by using the following wavelength: Cd: 228.802 nm, Cr: 267.716 nm, Fe: 234.349 nm, Ni: 221.647 nm, Pb: 220.353 nm, Zn: 213.856 nm. The results were obtained by applying a max-mode function and by determining the average over a triple determination.

The same procedure was applied for the samples obtained during the additional measurement campaign (see Chapter 3.1.7).

– Elemental analysis:

To obtain the C content of the blast furnace sludge (Paper II), an el-

elementary analyzer (Elementar VARIO Macro analyzer, equipped for CHNS-analyses) was utilized. Around 20 mg of each sample was used for the analyses. The calibration was carried out with 10 mg of sulfanilamide.

– XRF:

K and Cl contents (Paper IV) in the blast furnace lining were determined by means of a mobile XRF handheld device on a portable test stand (Thermo Niton XL3t Air).

The characterization of the HM samples with regard to the Pb content (Paper III) was conducted utilizing an industrial XRF (Thermo Fisher ARL 9800 XP, COMET 3GN).

– OES:

The Pb content of the HM samples (Paper III) have additionally been characterized by an optical emission spectroscope (OBLF QSG750).

– LA-ICP-MS:

The HM samples are further analyzed by means of Laser Ablation-ICP-MS. The elements Cr, Ni, Pb and Zn have been considered. However, the investigations focus on the distribution of Pb in the samples. For these analyses, up to five layers (each around  $3\ \mu\text{m}$  are ablated from the sample surface, starting with a  $1000\ \mu\text{m} \times 1000\ \mu\text{m}$  spot, resulting in a  $600\ \mu\text{m} \times 600\ \mu\text{m}$  spot at the fifth level. The laser parameters are:

- \* 85 % Laser power
- \* 5 Hz Frequency
- \*  $100\ \mu$  Beam diameter
- \*  $10\ \mu/\text{s}$  Scan speed

\* 18 J/cm<sup>2</sup> Energy density

The isotopes measured include <sup>50</sup>Cr, <sup>53</sup>Cr, <sup>60</sup>Ni, <sup>62</sup>Ni, <sup>64</sup>Zn, <sup>66</sup>Zn, <sup>206</sup>Pb, <sup>208</sup>Pb and <sup>57</sup>Fe, whereby the <sup>57</sup>Fe isotope is used for calibration.

Further details on the method applied are given in Bauer and Limbeck<sup>[3]</sup>.

## 4 Results and Discussion

### 4.1 Behavior of heavy metals in the blast furnace process

The heavy metals Cd, Cr, Hg, Ni, Pb and Zn behave differently in the blast furnace process. On the one hand, their respective behavior depends on the location at which they are inserted into the blast furnace (at the top of the furnace or through the blast furnace tuyeres). On the other hand, their behavior is determined by the chemical form introduced. In comparison to the bulk elements (C, Fe), the heavy metals take part in several reactions in the blast furnace, which will most likely not reach the equilibrium state.

The elements Pb and Zn have been chosen since they present the most important ones for process stability. Additionally, the distribution of Cr is discussed since this element behaves in a totally different way compared to the other two. For detailed information on the behavior of all heavy metals under investigation, the reader is referred to Trinkel et al.<sup>[42]</sup>.

The sinter constitutes the main input material for Zn (often far more than 40% of the total input). Within our investigations the sinter contributes between 64 to 72% to the total Zn input. Zn is also inserted via iron bearing materials (up to 40%), coke (less than 4.5%) and alternative reducing agents (up to 13%). The main output for Zn is the HM and the top gas dust (see Figure 4.1)<sup>3</sup>, which is at least partly recycled at the sinter plant.

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<sup>3</sup>In our investigations the top gas dust includes the dry dust from the dust bag, the scrubber sludge and water from the wet scrubber

By comparing the distribution pattern of Zn based on our own investigations with those described in the literature, it turns out that the behavior of Zn can be very different. The amount of Zn which ends up in the HM and in the top gas dust is significantly different for the plants compared. The amount of Zn which is transferred into the HM can range from around 7<sup>[40]</sup> up to 63 %<sup>[31]</sup> of the total amount inserted into the process. For our investigations, the share of the HM in the total Zn output ranges between 28 and 38 %. The share of the total Zn input which is transferred to the top gas dust lies between 3.4<sup>[31]</sup> and 90 %<sup>[40]</sup>; for our investigation the top gas dust holds a share of between 46 to 59 % of the total Zn output. It can be concluded that the distribution of Zn within the process strongly depends on the process conditions<sup>[42]</sup> and it is hardly possible to draw a general conclusion to which extent Zn is transferred into a certain output flow.

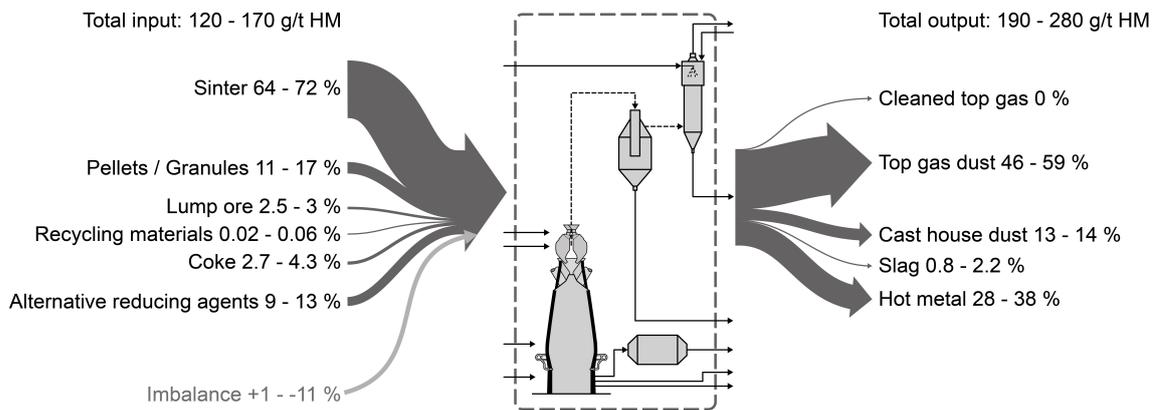


Figure 4.1: Distribution of Zn in blast furnace process (based on data given in Trinkel et al.<sup>[42]</sup> as our own investigations); The percentages given reflect the minimum and the maximum of the respective input and output flow observed for our investigations.

The imbalance (shown in Figure 4.1) is defined as:  $(\text{total input} - \text{total output}) / (\text{total output})$ . A positive value describes the fact that the total amount inserted in the blast furnace is larger than the total output. For Zn the observed imbalance is either positive or negative (see Figure 4.1).

The different input materials (utilized during the time period of our own investigations) contribute a similar amount (around 10 to 30 %) to the total Pb input, which allows no identification of a main input material. However, in other studies reviewed the contributions of the sinter material to the overall Pb input might be twice as high (up to 60 %).<sup>[11]</sup> Similarly to Zn, the main output flows are the HM and the top gas dust. In our own investigations up to 75 % of the Pb inserted end up in the top gas dust and up to 37 % are transferred to the HM. Literature results concerning the distribution of Pb show different behavior patterns. Morf<sup>[31]</sup> demonstrated, for example, that around 10 % are transferred into the HM and around 84 % can be found in the top gas dust. Taking these results into account, it is not possible to draw a general conclusion for the behavior of Pb in the blast furnace process.

The Pb balances show relatively high differences between the total input and output, which ranges from between 31 to 39 %<sup>4</sup>. These imbalances indicate errors either for sampling and/or analytical measurements.

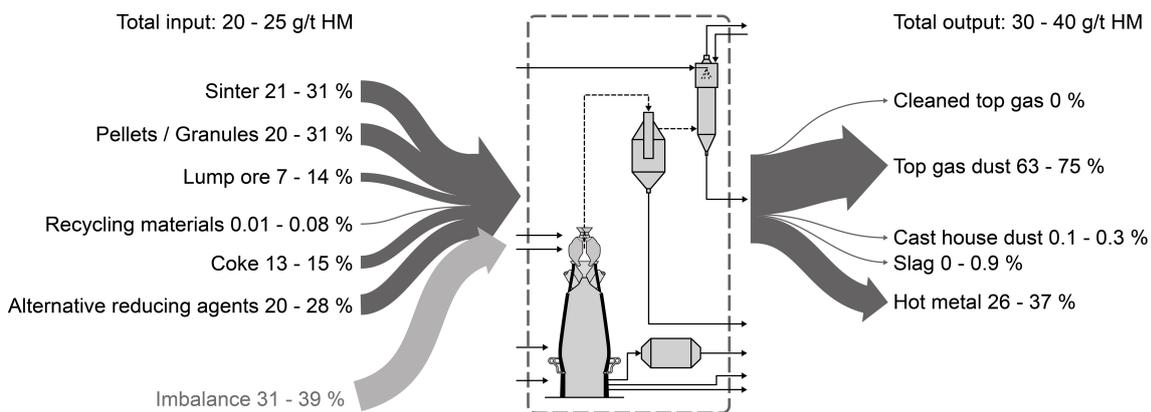


Figure 4.2: Distribution of Pb in blast furnace process (based on data given in Trinkel et al.<sup>[42]</sup> as our own investigations); The percentages given reflect the minimum and the maximum of the respective input and output flow observed for our investigations.

The distribution pattern of Cr is different compared to those of Pb and Zn. The

<sup>4</sup>imbalance = (total input - total output)/(total output)

most important Cr input flows are the iron bearing materials (including sinter, pellets/granules, and lump ores), which have a share of more than 90 % of the total input. In the output, Cr is mainly found in the HM. Our investigations indicate that more than 90 % of the total Cr input is transferred into the HM (see Figure 4.3). Its behavior pattern observed in our own investigations is very similar to the results reported in the other studies, which indicates that the behavior of Cr is most likely independent of process conditions.

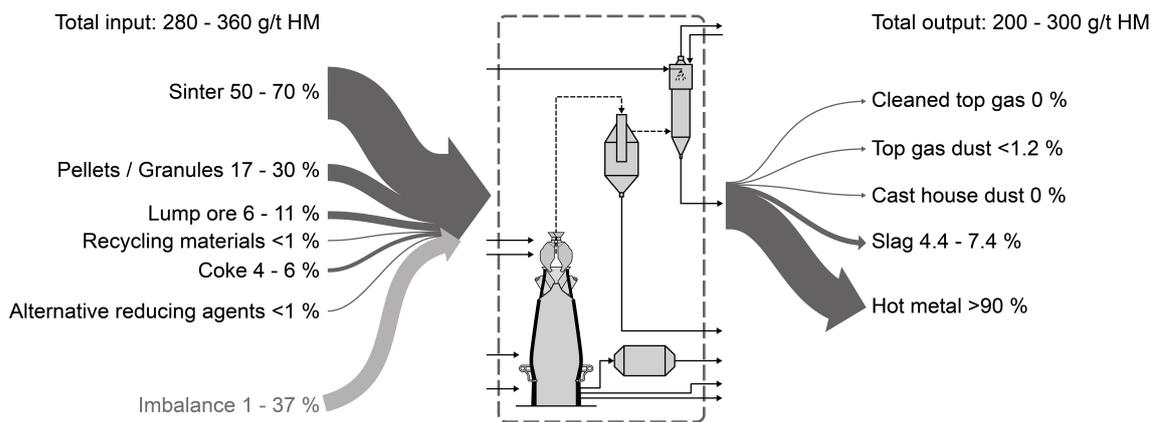


Figure 4.3: Distribution of Cr in blast furnace process (based on data given in Trinkel et al.<sup>[42]</sup> as our own investigations); The percentages given reflect the minimum and the maximum of the respective input and output flow observed for our investigations.

Another aspect, hardly discussed in the literature reviewed, is the differences in total inputs and outputs for the heavy metals investigated. Nevertheless, these differences are important for MFA with regard to the quality of the results since the imbalance indicates whether sampling, sample preparation and/or analytical measurements are carried out accurately. These imbalances have only been mentioned in a few cases in the literature considered and were explained either by the analytical challenges due to the low concentrations of the respective elements (e.g. Cd, Hg, Pb) or due to the characteristics of some elements (e.g. Pb and Zn) remaining within the blast furnace (e.g. in the lining material or in accretions). The aspects of sampling and sample preparation influencing the results, however, have not been mentioned.

To improve the MFA results for the blast furnace process (minimization of differences in balances), the behavior of the heavy metals Pb and Zn is investigated in more detail. Since the top gas dust and the HM are important output flows for Zn and/or Pb, these materials are characterized (Paper II, Paper III) in terms of the content and distribution of heavy metals. Moreover, the blast furnace lining is analyzed regarding the contents of Zn and Pb (Paper IV) to investigate whether the amounts accumulating in the furnace will affect the results of the MFA.

## 4.2 Characterization of blast furnace sludge with respect to heavy metal distribution

The blast furnace sludge accrues at the second stage of the top gas cleaning system (wet scrubber) and is, as already indicated in Chapter 4.1, an important output flow for the heavy metals Cd, Hg, Pb and Zn. On this account, the blast furnace sludge is characterized in detail in terms of the particle sizes and the distribution of the heavy metals as well as the main components Fe and C.

The results of the sieving analyses show, that more than 60 % of the particles are smaller than 40  $\mu\text{m}$ . Furthermore, the concentrations of the different elements under investigations depend on the particle size. Cr and Ni, for example, are equally distributed over the different particle fractions, whereas the Cd, Fe, Pb and Zn concentrations significantly decrease with increasing particle size. The C distribution shows an opposite concentration trend compared to the aforementioned elements<sup>[43]</sup>. The results of the particle size distribution and the concentration patterns for Zn and Cr are shown for one sample in Figure 4.4.

The results of the investigations demonstrate that the blast furnace sludge is an extremely heterogeneous material. Thus, representative sampling is important in order to achieve significant results which can be utilized to conduct MFA.

For the evaluation of the regular sampling point, located directly after the wet

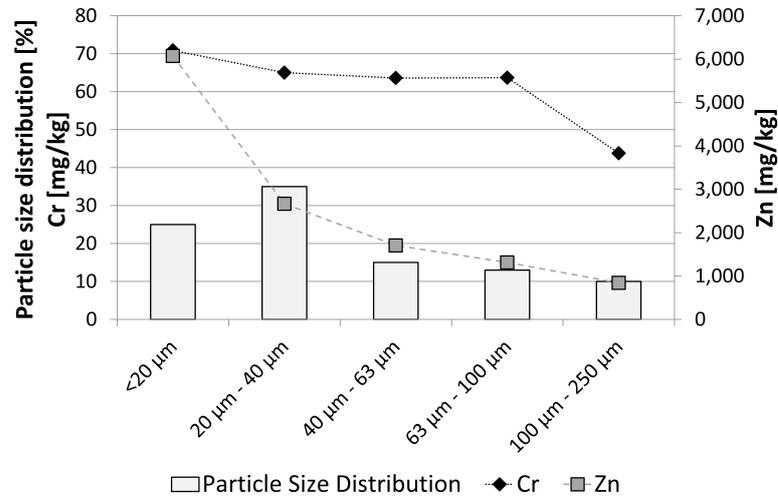


Figure 4.4: Particle size distribution of one blast furnace sludge sample investigated in [%] and its Cr and Zn content given in [mg/kg] (based on Trinkel et al.<sup>[43]</sup>)

scrubber, the results obtained from the sludge characterization (sampling point located directly before the hydro cyclone, see Chapter 3.1.3) are compared with compositioned data determined for the regular sampling point. At both sampling points different results for the mass flows and for the concentration measurements are obtained. The mean flows of solids at the sampling point directly after the wet scrubber is around 2.5 times higher than at the sampling point before the hydro cyclone<sup>5</sup> (see Figure 4.5). Furthermore, the calculated standard deviation for the measurement data at the sampling point located after the wet scrubber is much higher (indicated with gray areas in Figure 4.5).<sup>6</sup>

Comparing the mass flows of solids determined at the two different sampling points,

<sup>5</sup>During the measurement campaign.

<sup>6</sup>It must be noted that the amount of dust particles carried out of the blast furnace and the corresponding concentration of elements under investigation depends on the operating conditions and on the input materials utilized. If these two factors vary, the amount as well as the composition of flue dust will also change. Thus, the mean value and the standard deviation not only include the fluctuation due to sampling errors, but also fluctuations due to changes in the process itself.

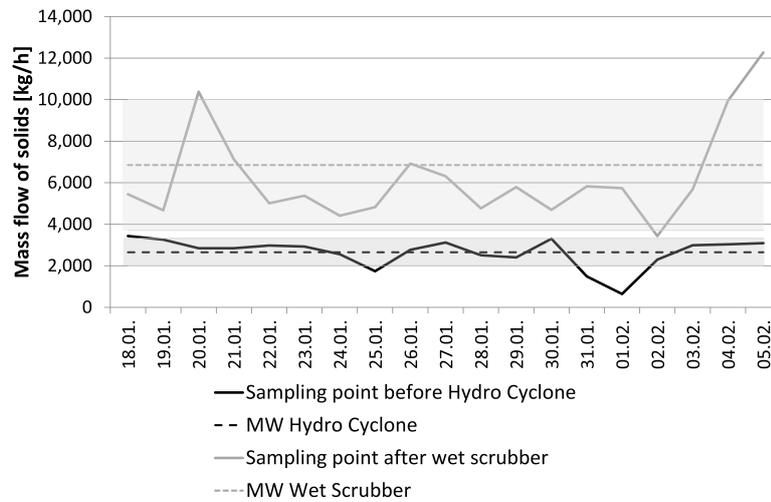


Figure 4.5: Mass flows of solids at the sampling point after the wet scrubber and before the hydro cyclone given in  $[kg/h]$ , measured during a 4 week measurement campaign; Gray areas represent the standard deviation

it is demonstrated that the mass flow determined directly after the wet scrubber shows significant differences within the time period considered. The results also indicate that the mass flows of solids are most likely overestimated at the sampling point after the wet scrubber.

The measured Zn concentrations are also different for the samples taken at these two sampling points (see Figure 4.6). The concentration measured for the samples taken directly after the wet scrubber is significantly smaller than the Zn concentration obtained for the samples taken before the hydro cyclone. The mean concentration of the samples taken directly before the hydro cyclone is more than 1.5 times higher than the mean concentration based on the measurements performed after the wet scrubber. Similar results have been obtained for the elements Pb and Cd.

If one considers the distribution pattern within the blast furnace sludge presented by Trinkel et al.<sup>[43]</sup>, it is most likely that sampling directly after the wet scrubber is selective in terms of particle size. The samples obtained most likely contain more

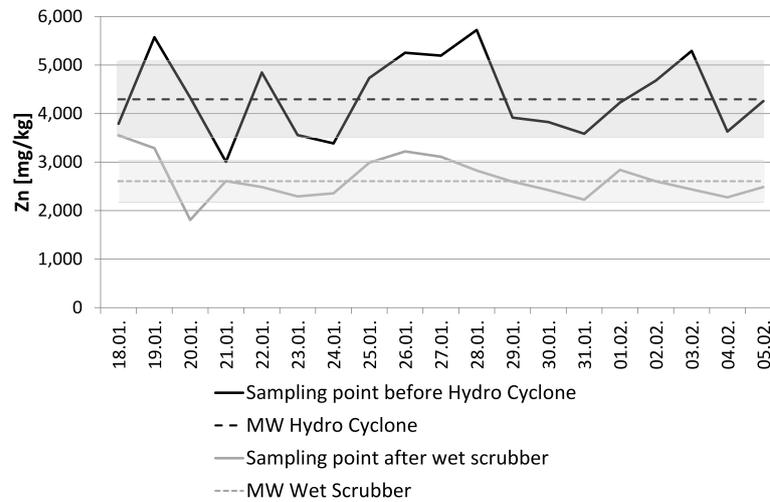


Figure 4.6: Zn concentration at the sampling point after the wet scrubber and before the hydro cyclone given in  $[mg/kg]$  measured during a 4 week measurement campaign; Gray areas represent the standard deviation

coarse particles than fine ones. As the latter show higher, e.g., Zn concentrations, the Zn content measured for these samples is most likely underestimated.

In contrast to Zn, the results for the chemical analyses of Cr (see Figure 4.7) and also for Ni are quite similar for the samples obtained at both points. These results can be explained by the equal distribution of these two elements in the blast furnace sludge.<sup>[43]</sup>

Generally, it can be noted that more highly concentrated flows (in terms of the solid content as well as the concentration of the respective element) are better suited to obtain representative samples (the probability of sampling only a certain type of particle is lower).

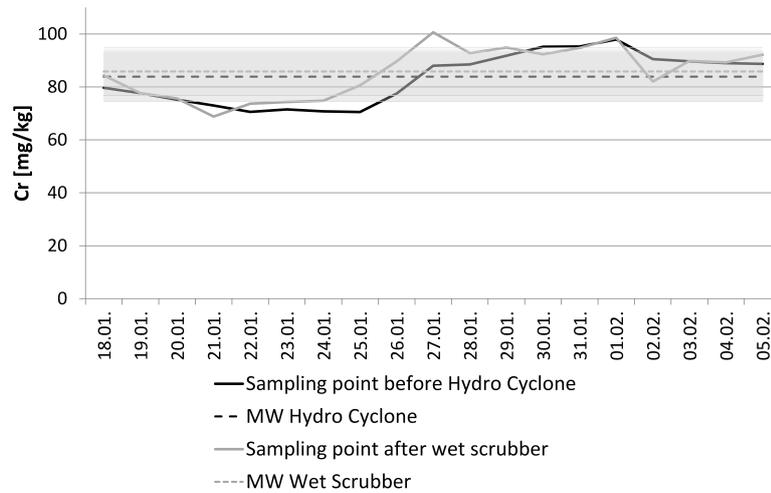


Figure 4.7: Cr concentration at the sampling point after the wet scrubber and before the hydro cyclone given in  $[mg/kg]$  measured during a 4 week measurement campaign; Gray areas represent the standard deviation

### 4.3 Characterization of Pb in Hot Metal samples

MFA has been conducted for Pb for a time period of 6 years. In this time period the differences in balances for Pb have significantly increased year by year. In the beginning of the investigation, the difference in balance amounted to around 15 % in 2009 and increased to more than 45 % in 2012 (see Figure 4.8).

During the same time interval it has been noticed that the Pb concentration in the HM increased from around 2 mg/kg to more than 12 mg/kg.<sup>[44]</sup> Such an increase can neither be explained by the chemical and thermodynamic behavior of Pb in the blast furnace process nor by changing compositions of the burden materials (see also Trinkel et al.<sup>[42]</sup>). In order to check the accuracy of the measurement methods routinely utilized, HM samples are analyzed with two different measurement methods (namely XRF, which represents the routine measurement method, and OES). The measurement results obtained by OES are significantly lower than the Pb concentration measured by means of XRF. In this context it has to be noted,

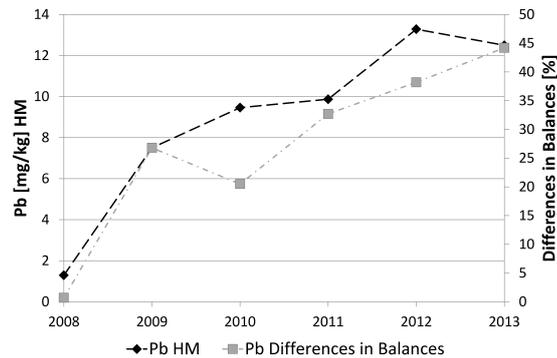


Figure 4.8: Pb concentration in HM given in  $[mg/kg]$ ; Differences in Balances 2008 - 2013 (based on<sup>[44]</sup>)

that the Pb concentrations in the HM samples are very low and close to the LOD of the XRF (LOD XRF = 20 mg/kg). Measurement values close to the LOD show high errors (uncertainties) compared to the measurement (even if small in absolute terms), which will have a disproportionately large influence on the value.<sup>[5]</sup> Thus, these values are not very strong from a statistical point of view.

The homogeneity of the HM concerning the distribution of Pb is investigated by XRF measurements. The samples are measured from both sample sides. The Pb concentrations obtained are, however, different for both sample sides. In a next step HM samples are analyzed by means of LA-ICP-MS in order to prove the presumption that Pb is unequally distributed in the sample. Five layers (one layer is equal to a depth of around  $2\ \mu\text{m}$ ) from the surface of a HM sample are vaporized by laser and analyzed via ICP-MS. The results indicate Pb only in the first layer, meaning all lower layers hardly contain any Pb (see Figure 4.9<sup>7</sup>).

Based on the investigations it can be stated that different results for the Pb concentrations are obtained by different measurement methods (XRF and OES) and it has to be proven which method (either one of the two used or a different one) provides more reliable results. Furthermore, it can be concluded that Pb is not

<sup>7</sup>It has to be noted that in Figure 4.9 Pb is not presented as a concentration in  $[mg/kg]$ , but as a signal intensity normalized to  $^{57}\text{Fe}$

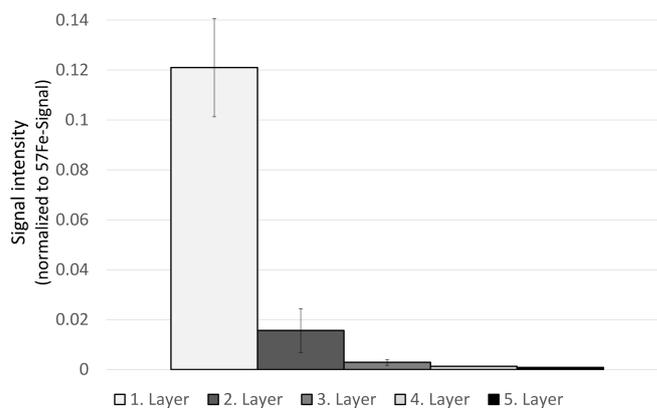


Figure 4.9: Signal intensities for Pb for the different layers investigated of one HM sample obtained by LA-ICP-MS

equally distributed in the HM samples.

To clarify whether sampling, sample preparation and/or the measurement method applied can be optimized and improved, further research is needed. The investigations should focus on the optimization of the sampling procedure to obtain more homogeneous samples (with respect to Pb). The research work should also consider the influence of the sample preparation procedure on the Pb measurements. Additionally, it has to be investigated whether the XRF measurement method can be optimized to measure the low Pb concentration present in the samples or if another routinely used method would provide more reliable results.

The following conclusions can be drawn for MFA at a plant level: The accuracy of measured values should always be questioned, especially if measurement values are utilized which are obtained by routine measurements conducted for reasons of quality assurance. For these kinds of measurements, the bulk elements are often of interest. Thus, the analytical method utilized might not be applicable for minor content elements since their concentrations might be close or even below the LOD and/or the bulk elements might influence the measurement (depending on the analytical method chosen). Furthermore, sampling (representative and homogeneous sample) and

sample preparation (falsification of measurement results due to sample preparation) should be considered.

#### 4.4 Distribution of Zn and Pb in blast furnace lining

Pb and Zn are able to shorten the blast furnace campaign due to various damage mechanisms (e.g. destruction of lining material, increased wear)<sup>[45]</sup> and are able to accumulate in the blast furnace lining as well as in scaffolds.<sup>[13,15]</sup>

In order to investigate the distribution of these heavy metals in the lining material and to be able to estimate the amount of Pb and Zn which remain in the furnace, a measurement campaign was carried out during an overhaul of a blast furnace. During this measurement campaign samples were taken from 18 sampling positions distributed over the height of the blast furnace. These samples are split into three equally sized subsamples in order to determine the penetration depth of the respective elements.

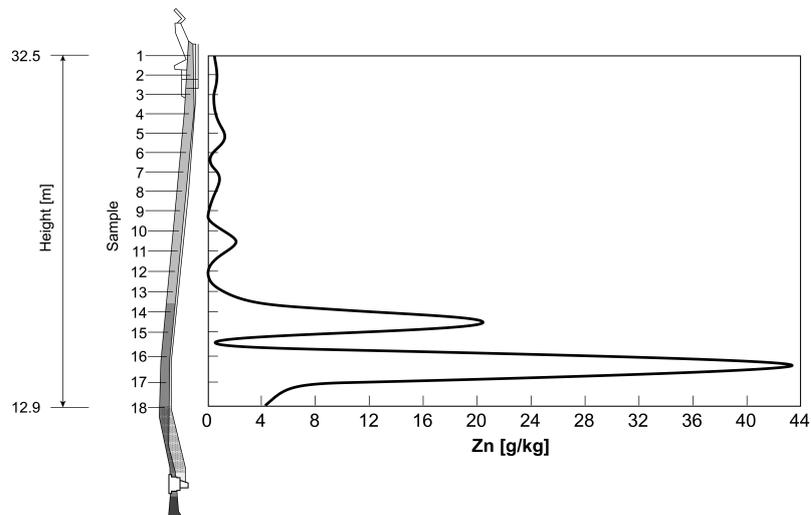


Figure 4.10: Zn content [g/kg] in blast furnace lining of subsample 1 (based on Trinkel et al.<sup>[45]</sup>)

The chemical analyses show that both elements can be mainly detected at the inner (hot) part of the lining brick (subsample 1).

For Zn the highest concentrations have been measured between the samples 13 to 16<sup>8</sup> located approximately 10 to 5 m above the tuyeres (see Figure 4.10).<sup>[45]</sup>

The distribution pattern of Pb over the blast furnace height is similar to that of Zn. The highest Pb concentrations have been detected for sample 3 (around 21 m above the tuyeres) and between the samples 14 to 16 (around 7 to 10 m above the tuyeres) (see Figure 4.11). The concentration detected for Pb is an order of one magnitude smaller than for Zn. This might be explained by the physico-chemical behavior of this element. Pb will more likely accumulate in the refractories located below the tuyeres.<sup>[45]</sup>

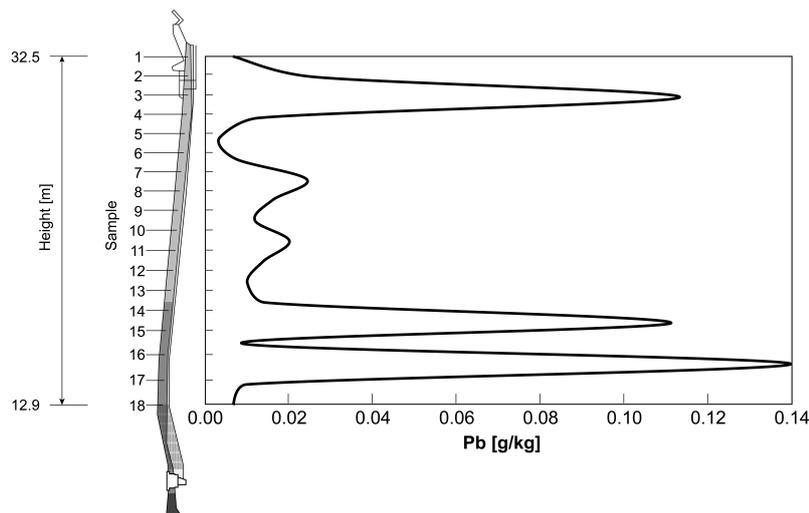


Figure 4.11: Pb content [ $g/kg$ ] in blast furnace lining of subsample 1 (based on Trinkel et al.<sup>[45]</sup>)

Based on these investigations and an estimation of the lining material remaining at the end of the blast furnace campaign, it is possible to assess the amount of Zn and

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<sup>8</sup> Sample 1 is taken at the top of the blast furnace at a height of 32.5 m, and sample 18 at 12.9 m, which is around 2 m above the blast furnace tuyeres

Pb accumulating in the blast furnace. The amount of the lining material is roughly estimated to be around 820 t<sup>9</sup>. The heavy metal concentrations utilized are mean values (Zn = 1.6 g/kg, Pb = 0.01 g/kg) based on all measurements performed (all three subsamples are included). Multiplying these contents by the mass of the lining material, 1350 kg Zn and 8.9 kg Pb remains in the furnace after 5 years of operation. These amounts are negligible and do not explain the imbalances observed.

For Zn, however, accretions within in the blast furnace are often discussed in the literature<sup>[1,15]</sup> and might be of importance for the imbalance. Since the measurement campaign was conducted during the ongoing maintenance work, representative sampling of the accretions was impossible. The randomly taken samples show Zn concentrations of between 0.05 g/kg and 11 g/kg, and Pb concentrations of between 0.006 g/kg and 0.4 g/kg.

For the accumulation of Pb, the amount which remains in the carbon refractories (below the blast furnace tuyeres) is of importance. For the randomly picked samples, Pb concentrations of between 0.005 g/kg and 0.14 g/kg have been determined. Additionally, thin Zn layers have been found during maintenance work, consisting of more than 99 % Zn. The plant operator estimated the amount to be less than 15 kg and stated that determining the origin of these Zn layers was impossible. The reason for this might be found in the fact that these Zn layers are formed behind the lining material, near the cooling plates.

Based on all these results, it may be concluded that the accumulation of the heavy metals considered within the furnace does not effect the quality of the MFA in terms of closing the balance for Zn and Pb.

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<sup>9</sup> Estimated amount is based on the volume of the lining material which has been removed during the overhaul (given by the plant operator) and an average density (based on data sheets provided by the plant operator) for a typical lining material of 1700 kg/m<sup>3</sup>.

## 4.5 Applicability of transfer coefficients to the blast furnace process

When applying MFA at plant level, the determination and utilization of TCs is often of interest since TCs may allow measurement efforts to be reduced, as described in Chapter 3.2.1. The applicability of TCs to the blast furnace process is discussed in the paper "Influence of waste plastic utilization in blast furnace on heavy metal emissions", in which the gaseous and liquid emissions of Cd, Hg, Pb and Zn are directly related to the specific inputs of the heavy metals.<sup>[41]</sup> If TCs are valid for the system investigated, a significant relationship between the emission levels of the heavy metals and their respective inputs is expected. The investigations conducted indicate no correlation between the emissions of the respective heavy metals and their input amounts. As an example of these results, the Zn and Pb emissions to the atmosphere (emissions via the cleaned top gas), depending on the input of the respective heavy metal, are shown in Figure 4.12. These results show that an increased input does not lead to higher emissions of the respective element. The results even indicate an independence of the emissions from the amount of heavy metals inserted into the blast furnace process. Thus, the top-gas cleaning device utilized shows an increasing cleaning efficiency for the concentration range considered.

Low heavy metal concentrations challenge the applied analytical method (e.g., for ICP-MS, ICP-OES due to matrix effects) and the concentration, are often below the LOD<sup>10</sup>. This does not significantly influence the imbalance for the respective element, but affects the determination of the TC for the respective output.

For MFA at plant level, the application of TCs for substances which occur in very low concentrations is most likely inappropriate for the following reasons:

- An increased input amount does not necessarily result in an increased output and no correlation might be determined.

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<sup>10</sup>This has become obvious for the investigations of the specific emission for Cd to the cleaned top gas and for the specific Hg emissions to the waste water.<sup>[41]</sup>

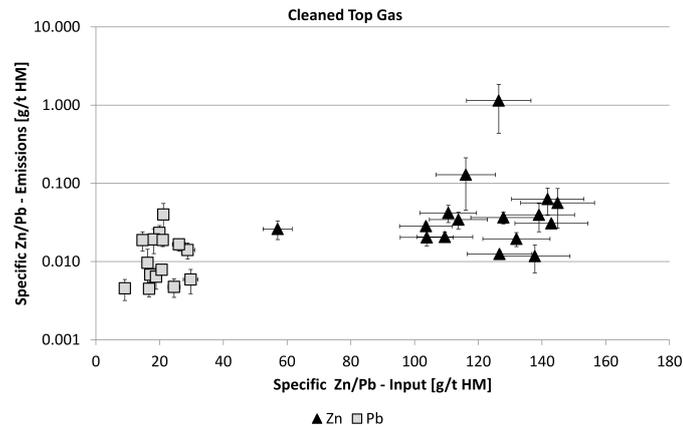


Figure 4.12: Specific Zn/Pb emissions versus specific Zn/Pb input (based on Trinkel et al.<sup>[41]</sup>)

- Very low concentrations are difficult to measure and are often below the LOD. Thus, the exact amount of a substance transferred to a certain output flow might not be determined accurately.

## 5 Conclusions

MFA has been applied to a blast furnace to trace the heavy metals Cd, Cr, Hg, Ni, Pb and Zn through the process. Based on the research work conducted, the following conclusion can be drawn regarding the application of the MFA to the blast furnace process in particular and to a plant level in general:

The literature study (Paper I) revealed the different behavior of heavy metals in the blast furnace process depending on their physico-chemical properties. The results reported in the literature and those based on our own investigations differ significantly, especially for the elements Pb and Zn.

Beside the different behavior of the heavy metals, differences in the overall inputs and outputs (imbalances) have been noted. The reasons for these imbalances have hardly been discussed in the literature so far. Nevertheless, these differences relate to the quality of the data determined. Minor differences in balances indicate that the determination of the necessary data (including mass, volume and concentration measurements) has been carried out accurately, whereby the determination of the data includes the sampling, sample preparation, concentration and volume/mass flow measurements. Thus small imbalances of MFA indicate good data quality, which also affects the overall robustness of results.

Further research into the behavior of different heavy metals in blast furnace processes is of interest as fundamental knowledge of their reactions is required in order to predict the affects of changing amounts of heavy metals entering the furnace. A higher input of heavy metals can be caused, for instance, by an increased utilization of alternative reducing agents (e.g. waste plastics) or alternative input materials (e.g. different slags from iron and steel production).

Such an in-depth understanding of the behavior of heavy metals in the process may be generated by thermochemical modeling. As these models also allow sensitivity analyses, the influence of an increasing input of heavy metal on the amount transferred into the different outputs of the process can be simulated. Furthermore, inner circulation processes (as they occur for Pb and Zn) can be investigated in more detail. Thereby the influence of an increased input of the heavy metals on the amount taking part in the inner circulation processes could also be assessed.

However, the development of a blast furnace model for thermochemical modeling is challenging, on the one hand, because of the multitude of reactions and, on the other, due to limited information available about the conditions prevailing in different zones of the furnace. Especially for heavy metals, which belong to the micro elements ( $< 1\% \text{wt}^{[12]}$  in the particular input materials), many different reactions occur and their reaction processes strongly depend on the conditions prevailing (e.g. different behavior if the heavy metals are inserted on the top of the furnace or through the blast furnace tuyeres). The different reaction zones and the circulation process strongly influence the set up of the model. It must be noted that a overly detailed model challenges the computing performance and also the input data required. Other limiting factors are the limited availability of a substance data basis for the different heavy metals and the need for reliable measurement data for model validation.

The emphasis of detailed investigations conducted has been given to the elements Pb and Zn due to the fact that these elements are the most important ones for the process stability. Based on data provided by the literature study, the outputs "blast furnace sludge" and "HM" have been identified as the main outputs for Pb and/or Zn and investigated in more detail.

The blast furnace sludge has been characterized in terms of the particle size and the distribution of the heavy metals (Paper II). The results show that this material is highly heterogeneous. The heavy metal concentrations depend on the particle size, which ranges from  $250\ \mu\text{m}$  to less than  $20\ \mu\text{m}$ , whereby the smaller particles show higher Pb and Zn concentrations. Based on these results it can be concluded that

the sampling of this material must take into account that the different particle size may lead to a demixing of sludge. Coarse particles tend to accumulate at the bottom of the sampling devices.

Due to the fact that the Pb and Zn balances show differences in balances, two different sampling points (one close to the wet scrubber; the other one directly before the hydro cyclone) have been chosen and the results obtained have been compared. At the sampling point located at the hydro cyclone, far more concentrated (in terms of solid particles) samples are obtained. Moreover, the Pb and Zn concentrations measured for these samples are significantly higher than those obtained at the sampling point directly after the wet scrubber.

In order to check which sampling point after the wet scrubber is more suitable, the concentrations of the different elements as well as the mass flow should be determined at both sampling points (sampling point directly after wet scrubber and before hydro cyclone) over a sufficient time period. It is recommended that during this time period at least 10 samples are taken at both sampling points to be able to conduct statistical analyses. Utilizing these data, MFA has to be conducted for both systems. By comparing the results it should become obvious that by utilizing the sampling point located before the hydro cyclone, the difference between the total input and output of the Zn balance can be decreased.

Another important factor influencing MFA for Pb is the HM. This has become obvious by comparing the results of annually conducted MFA (from 2008 to 2013). Within this period the difference in balances has increased by the same extent as the Pb output via the HM. Such an increase is most unlikely due to the behavior of Pb in the blast furnace. Therefore the measurement method for determining the Pb content as well as the homogeneity of the HM samples were investigated in detail. These investigations show that the currently applied XRF is most likely not suitable to detect minor contents of Pb in the HM. The results also show the unequal distribution of Pb in the samples.

As a consequence of this observation, it is recommended investigating whether a more suitable method could be applied for routine measurements. Additionally, an

evaluation of the influence of the sample preparation methods (e.g. milling of sample surface, coolant agent) on the analyses results should be conducted. In order to obtain a more homogeneous sample, influencing factors concerning the sampling (e.g. influence of sample cooling rate, immersion depth of lollipop sampler) should be investigated. From a scientific point of view it is of interest to create Pb maps of HM samples which display the Pb distribution. Such maps could allow cross sections of the sample representative of the overall Pb content to be determined. It is also of interest to investigate chemical form and the location (e.g. between the metal lattice) at which Pb is present in the samples.

Pb and Zn tend to accumulate in the blast furnace. Based on our own investigations on the blast furnace lining (Paper IV), it can be concluded that accumulations of Zn and Pb are almost negligible (e.g. amount of Zn remaining in the furnace has been estimated to be less than 1.5 t during a blast furnace campaign of 5 years) and do not explain the imbalance (difference between input and output) of the MFA.

Further research on the amount of the accretions and their link to process parameters (e.g. temperature distribution in blast furnace) would be of interest. A detailed study on the influencing factors of the C based refractories could provide information whether Pb effects the duration of the blast furnace campaign.

The last aspect investigated is the applicability of TCs (Paper V) on the blast furnace process. The investigations show that there is no correlation between low concentrated output flows (emission) and the inserted amount of a respective heavy metal (for the considered concentration range). Thus, TCs are not applicable for the prediction of low concentrated flows<sup>11</sup>.

Based on the aforementioned results, sampling (points and procedure) and analytical methods should be improved. To assess these improvements, it is recommended that the measurement data be recorded during a time interval of around a year and that MFA be conducted based on such data. A better data quality should result in reduced imbalances.

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<sup>11</sup>In terms of elemental concentrations and the solid share (for suspensions)

It has to be noted that if the analytical methods cannot be improved so as to determine very low heavy metal concentrations, statistical methods for censored data<sup>[18]</sup> which allow measurement values below the LOD to be considered (of the applied measurement method), should be applied.

Generally, the following aspects can be derived from the work concerning MFA at plant level:

- The behavior of the element in the process should always be considered when conducting a MFA. This knowledge can be utilized to assess the reliability of the data available.
- Closed balances can be seen as a quality measure for the data utilized in MFA. The data quality is important to be able to apply data reconciliation, which influences the quality of the results obtained by MFA.
- Differences in balances often indicate that sampling and analytical measurements are not conducted with significant accuracy. Thus, sampling points should be questioned regarding their limitations for representative sampling (e.g. a representative sample is more easily obtained for higher concentrated suspensions (in terms of the solid content) than for low concentrated ones).
- The applicability of measurement methods utilized for elements under investigation has to be proven. This is especially important if the respective elements occur in a very low amount in the respective flow. Thereby the LOD of the respective analytical method as well as influencing factors such as matrix effects have to be considered.
- Low concentrated flows often result in measurement values which are below the LOD. This problem should be tackled by applying statistical methods for censored data if the measurement method cannot be improved.
- The application of data reconciliation is desirable in order to obtain significant

results from MFA. The calculation is only possible if data uncertainties are given and can be assigned on the basis of meaningful measurement data. However, the uncertainties calculated always include natural scattering (e.g. due to changes in the concentration in the inputs based on geological circumstances because of variation of the output concentration due to changes in the process conditions)

- It should be investigated whether inner accumulation processes for an element of interest may occur and if these processes affect the extent of the imbalances.
- In order to determine TCs, the relationship between the input and output has to be verified.

In general, MFA is a powerful tool to trace elements which belong to the main substances in an industrial system. The method can be used to point out challenges regarding sampling and the analytical methods applied to certain elements. It allows environmental, process and quality relevant elements to be traced throughout the entire process. The behavior of bulk elements may be described by TCs, which can help to reduce the measurement effort required in terms of chemicals, equipment and manpower utilized.

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## Appendix

# Behavior of Chromium, Nickel, Lead, Zinc, Cadmium, and Mercury in the Blast Furnace—A Critical Review of Literature Data and Plant Investigations

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## Supporting Information

**ABSTRACT:** Blast furnaces have a huge turnover of materials. Besides the transformation of the main elements iron and carbon, a large variety of other elements (present at low concentrations in different input materials) are undesirably inserted into blast furnaces. Heavy metals, such as chromium, nickel, lead, zinc, cadmium, and mercury, belong to these unwanted elements that are inserted. In the present paper, the behavior of these heavy metals in the blast furnace process has been investigated in detail, since they may influence the quality of the product, the byproduct, the process stability, and the environmental impact of hot metal production (e.g., emissions of heavy metals). Thereto, a detailed literature review has been carried out and its results have been subsequently compared with long-term investigations (over 3 years) conducted at an Austrian blast furnace. The results of the study indicate that nickel and chromium are very affine to the hot metal and thus to a large extent (>84%) transferred into it. Contrary to this, mercury and cadmium are mainly discharged via the top gas dust (>87%) and thus accumulate in the residues of the top gas cleaning system. For zinc and lead, no main discharge route could be detected. The results for lead and zinc varied considerably, which indicates the dependency of their transformation on the process conditions.

## 1. INTRODUCTION

The blast furnace is still at the center of the hot metal (HM) production process. In 2013, an amount of 1168 million tons of HM (or almost 94% of total HM production) was produced by means of blast furnaces worldwide.<sup>1</sup> Because of its overall importance, numerous research studies aiming at a better understanding and optimization of its processes have been carried out. The latest investigations addressing the blast furnace process have focused on the simulation of the process. Thus, different models describing the flows of the different phases occurring in the blast furnace (see, for example, refs 2 and 3), investigating the chemical and physical phenomena in the raceway (see, for example, refs 4 and 5), or focusing on process control based on neural networks (see, for example, refs 6 and 7) have been developed and applied. Other recent studies have investigated the injection of different alternative reducing agents, thereby aiming at a reduction of greenhouse gas emissions or raw material costs through the utilization of biomass (see, for example, refs 8–10) or waste materials, such as waste plastics (see, for example, refs 11–13). However, only a few recently conducted studies involve the behavior of heavy metals in the blast furnace process. Because of the very low amounts present, heavy metals, according to Chernousov et al.,<sup>14</sup> belong to the so-called “microelements”. Microelements in an industrial process are characterized by concentrations of <0.1 wt %.<sup>14,15</sup> Although the amounts of heavy metals inserted

unintentionally (as they are present at low contents in different input materials) are very small, compared to the major elements iron and carbon, their impacts are complex. On the one hand, they may influence process stability (e.g., zinc, lead) and product and byproduct quality (e.g., chromium, nickel).<sup>16</sup> On the other hand, they are also important from an environmental perspective (e.g., gaseous emissions of mercury<sup>17</sup> or cadmium<sup>18</sup>).

Research studies investigating the behavior of heavy metals in the blast furnace have aimed to evaluate the pathways as well as the sinks of the heavy metals inserted. Although a significant number of surveys on heavy metals during HM production have been carried out so far, a comprehensive analysis and discussion of the different results, also with respect to the transferability of the observations made to other blast furnaces, is lacking.

Hence, the major objective of this paper is to critically review existing studies investigating the behavior of the heavy metals zinc, lead, chromium, nickel, cadmium, and mercury in the blast furnace and their transfer into the different outputs. Besides the review, results from own investigations (over a period of 3

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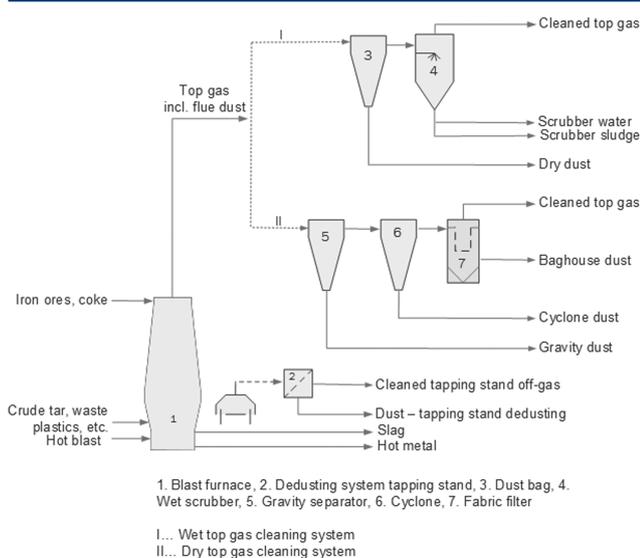
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years) conducted at an Austrian blast furnace are presented and compared to the literature data.

The present study should allow common patterns for the behavior and transformation of the selected heavy metals in the blast furnace process to be identified.

## 2. SYSTEM DESCRIPTION

The papers reviewed investigated blast furnace processes equipped with different top gas cleaning systems. The top gas dust is removed using either a wet or dry top gas cleaning system. In Figure 1, both types of top gas cleaning are



**Figure 1.** System description of the blast furnace process and its top gas cleaning devices.

illustrated. The path indicated with “I” shows the wet cleaning devices; the other path, indicated with “II”, refers to the dry top gas cleaning system.

The blast furnace process investigated by the authors and indicated in the following as “own investigations” is characterized by a daily production rate of ~8500 Mg of HM and a hearth diameter of 12 m. It uses a counter pressure at the throat of ~2.5 bar. The top gas of the furnace is cleaned by a wet system. The scrubber water generated thereby is treated (not shown in Figure 1) and, to a large extent, recirculated.

## 3. BEHAVIOR OF HEAVY METALS IN THE BLAST FURNACE

The literature review and our own plant investigations focus on the following heavy metals: chromium, nickel, zinc, lead, cadmium, and mercury, as they are either relevant for the environment, process stability, or product and byproduct quality. In the following, their input sources, their mode of occurrence, their behavior in the blast furnace, and their distribution in the blast furnace output flows are discussed.

**3.1. Zinc.** **3.1.1. Zinc in the Input of the Blast Furnace.** The amount of zinc inserted into different blast furnaces can range from 120 g/Mg HM to 650 g/Mg HM (see the Supporting Information (Table S1)). The sinter represents the main source for the zinc input (in most cases, more than two-thirds of the inserted zinc can be attributed to the sinter material), followed by the other iron-bearing materials (pellets/granules and lump ores), which contribute between 1% and

40% to the overall zinc input. In the case that alternative reducing agents (including, e.g., crude tar and waste plastics) are utilized, they contribute ~10% to the overall zinc input.

In iron ores, zinc is mainly found as ferrites (such as  $(\text{Zn},\text{Fe})\text{O}\cdot\text{Fe}_2\text{O}_3$  or  $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ ), silicates (e.g.,  $2\text{ZnO}\cdot\text{SiO}_2$ ), and sulfides (e.g.,  $(\text{Zn},\text{Fe})\text{S}$  or  $\text{ZnS}$ ). The ferrites are more easily reduced than the silicates.<sup>19</sup>

At the sinter plant, iron ore fines, coke, limestone, and dolomite (as a source for  $\text{MgCO}_3$  and  $\text{CaCO}_3$ ) are utilized, as well as internally recycled sludge and dusts.<sup>20</sup> In iron ore fines, zinc occurs in the same modes as in the iron ores. Because of the process conditions at the sinter plant, the oxidation of  $\text{ZnS}$  can occur at temperatures between 500 °C and 870 °C.<sup>21</sup> Thus, in the sinter, zinc most likely will be present as  $\text{ZnO}$ . Moreover, the presence of zinc as zinc ferrites is possible.

Within the internally recycled sludge and dusts, zinc occurs as  $\text{ZnO}$ . CO can be used to reduce  $\text{ZnO}$  to zinc. The metallic zinc can evaporate under the given temperature conditions. Thus, some of the zinc may be found in the off-gas of the sinter plant. The metallic zinc, however, may also be reoxidized and remain as  $\text{ZnO}$  in the sinter. However, note that the zinc content in the sinter is mainly dependent on the share of dust and sludge recycled at the sinter plant. These materials might show zinc concentrations between 0.03 wt % and 20 wt %.<sup>22</sup>

In limestone, zinc may be present as  $\text{ZnS}$  and  $\text{ZnCO}_3$ .<sup>23,24</sup>

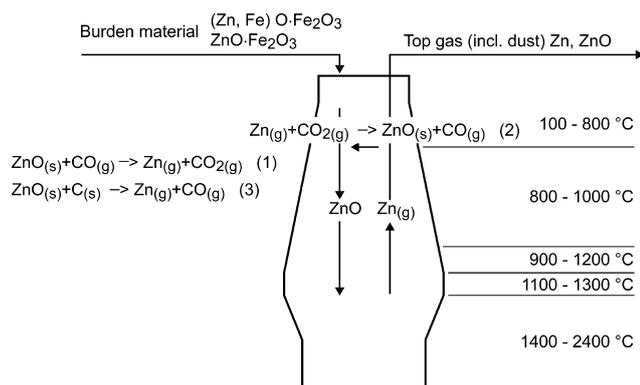
In coal, zinc shows an inorganic affinity, which means it is present together with iron sulfides.<sup>25</sup> Thus, it can be assumed that, in coal, zinc occurs as  $\text{ZnS}$ , since the coking process takes place in an oxygen-free atmosphere.

Zinc can also be found in the alternative reducing agents. In crude tar, for example, zinc will be most likely present as  $\text{ZnS}$ , since the crude tar is a byproduct from the coking process. If waste plastics are utilized, they include, e.g., polypropylene (PP) (stemming from, e.g., automotive parts, yoghurt pots), polyethylene (PE) (including low-density polyethylene (LDPE) and high-density polyethylene (HDPE), which are used, e.g., for pipes and toys), and polyvinyl chloride (PVC) (from, e.g., window frames, automotive parts, and medical products).<sup>26</sup> Thus, zinc can occur in many different forms. In PVC, for example, zinc is used as a stabilizer such as a Ca–Zn compound.<sup>27</sup> In PP, zinc may be used, e.g., as a fire retardant additive in the form of zinc borates (e.g.,  $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ ),<sup>28</sup> and, in PVC, zinc might also be used as a fire retardant additive in such forms as  $\text{ZnS}$ ,  $\text{ZnCl}_2$ , and  $\text{Zn}(\text{BO}_2)_2\cdot\text{H}_2\text{O}$ .<sup>29</sup>  $\text{ZnO}$  is also used in PP, HDPE, and PVC as a stabilizer.<sup>30</sup> Furthermore, zinc might be utilized as a pigment in plastics (for instance, in the form of  $\text{ZnO}$ ,  $\text{ZnS}\cdot\text{BaSO}_4$ , or  $\text{ZnFe}_2\text{O}_4$ ).<sup>29</sup>

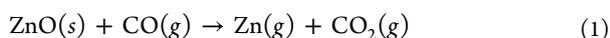
**3.1.2. Behavior of Zinc in the Blast Furnace.** Zinc is able to circulate within the blast furnace (see Figure 2). For this reason, several studies have been carried out to investigate its behavior in more detail (see, for example, refs 19 and 31–33).

The melting temperature of metallic zinc is ~420 °C; the boiling point is ~910 °C.<sup>34</sup> Therefore, it is easily vaporized at the temperatures present in the blast furnace. However, if metallic zinc reaches colder temperature zones again, it condenses, e.g., at the surface of the burden material, or it is oxidized.

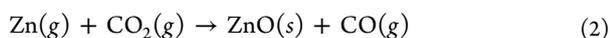
If zinc enters the blast furnace in the form of  $\text{ZnO}$ , it will move downward with the burden until it enters zones with higher temperatures. Between 800 °C and 1000 °C,  $\text{ZnO}$  can be reduced by CO, according to the following chemical reaction:



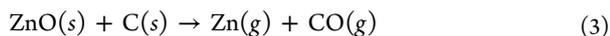
**Figure 2.** Behavior of zinc in a blast furnace (on the basis of Deike et al.<sup>58</sup>); the given temperature refers to the gas temperature.



However, within this temperature range (800–1000 °C), metallic zinc vapor may reduce  $\text{CO}_2$  and thereby oxidize again to  $\text{ZnO}$ :

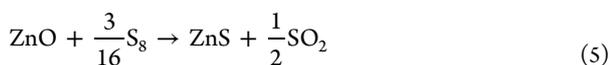


At temperatures between 900 and 1300 °C,  $\text{ZnO}$  can easily be reduced by carbon to metallic zinc, which evaporates:



Moreover, small amounts of  $\text{ZnCl}_2$  may be formed if chlorine is present under oxidizing conditions at temperatures between 700 °C and 1200 °C.<sup>35</sup>

In addition, zinc and  $\text{ZnO}$  may react with sulfur to form  $\text{ZnS}$ , according to the following reactions:<sup>36</sup>



$\text{ZnS}$  has a sublimation point of 1180 °C.<sup>24</sup> Thus,  $\text{ZnS}$  will rise up with the gas stream to zones of lower temperatures and solidify there again.

The possible reactions of zinc in the blast furnace have also been investigated by Zhang et al.<sup>37</sup> In their work, they studied the thermodynamic properties of zinc by means of the FactSage thermodynamic database.

Investigation of the zinc content in the lining material of the blast furnace started in the 1950s.<sup>32</sup> However, recent studies have also addressed this issue. Besta et al.,<sup>39,40</sup> for instance, measured the zinc content throughout the height of the blast furnace during an overhaul. They discovered that the zinc content of the lining was highest in the upper parts of the furnace (7–10 m from the top of the furnace), followed by the bottom of the furnace (19–22 m from the top of the furnace). This observation has been confirmed by Dai et al.,<sup>41</sup> who investigated the zinc distribution in a blast furnace during an overhaul. They also reported that the zinc content is quite high in the slag that solidified in the inner surface of carbon bricks at the tuyere's height and in the upper furnace zone and riser pipes. Moreover, they also observed  $\text{ZnO}$  in the bottom carbon brick gap sediment, with a content of ~8.4 wt %.

The amount of zinc accumulating in the lining is dependent on several factors, e.g., top gas temperature, moisture content of the top gas, and the charging mechanism.<sup>42</sup> Zinc might also accumulate in the tuyere coke, since zinc vapor penetrates into the coke pores. This penetration reduces the strength of the coke and increases the generation and accumulation of coke fine.<sup>43</sup> Several studies have also investigated the lining surface.<sup>39,40,44</sup> Thereby, they identified cracks that might be a consequence of the volume increase of zinc when condensing in the pores of the furnace lining. This mechanism also takes place in the carbon bricks at the furnace bottom. Zinc intruding into the refractory linings may cause internal stress, volume expansion, and material damage.<sup>41</sup>

Moreover, zinc as well as  $\text{ZnO}$  condenses on the surface of the iron-bearing materials and coke. The pores are thereby

**Table 1.** Distribution of Zinc to the Different Outputs of the Blast Furnace

distribution of zinc [%]	Zhang et al. <sup>47</sup>	Stepin et al. <sup>45 a</sup>			Besta et al. <sup>40</sup>	Mertins <sup>31</sup>	Besta et al. <sup>39</sup>	Morf <sup>46</sup>	Own Investigations		
		I	II	III					2010	2011	2012
hot metal	9.4	6.9	9.3	11.1	22.1	28	63	32	28	38	
slag	3.3	3.8	7.3	7.3	8.1	24	6.8	6.5	1.0	0.8	2.2
top gas dust	83	89.3	83.6	81.7	69.8	76	65.8	3.4	56	59	46
gravity dust	19										
cyclone dust	22										
baghouse dust	42										
dry dust		6.0	10.5	0.8	8.4	13	6.8	1.6	8.7	6.5	4.8
scrubber sludge		83.3	73.1	80.9	61.4	63	59	1.6	47	37	17
scrubber water								0.2	0	15	24
cleaned top gas	4.3	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0.2	0	0	0
dust tapping stand dedusting	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	23.8	13	13	14
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	531	289	215	181	<i>c</i>	<i>c</i>	111	<i>c</i>	284	195	189
remains in furnace and imbalance [%] <sup>d</sup>	+22	+44	+58	+65			+13		+1.0	+2.1	-11

<sup>a</sup>I, balance for blast furnace No. 1 from Severstal; II, balance for blast furnace No. 4 from Severstal immediately before the blast furnace was shut down for an overhaul; and III, balance for blast furnace No. 4 from Severstal after the overhaul. <sup>b</sup>Not detected. <sup>c</sup>Not specified. <sup>d</sup>Remains in furnace and imbalance are defined as follows: (total input – total output)/(total output). A positive value means that the total input is larger than the output.

blocked and the gas permeability decreases, which may result in increased coke consumption and decreased productivity.<sup>20</sup>

All these facts (increased stress for linings, reduction of the mechanical strength of coke as well as reduction of gas permeability) denote the significance of zinc for the blast furnace process, although its input is <1%, in comparison to iron.

**3.1.3. Zinc in the Outputs of the Blast Furnace.** The distribution of zinc to the different blast furnace output flows has been investigated in several studies (see Table 1). Mertins<sup>31</sup> reported, in conjunction with investigations into the processing and recycling of dust and sludge from top gas cleaning, an approximate distribution of zinc to the different output flows. According to his results, most of the zinc (63%) finally ends up in the sludge generated by wet top gas cleaning. The remaining part is transferred into the dry dust (13%), as well as into the HM and slag (24%).

Deike and Hillmann<sup>38</sup> studied the behavior of zinc during the recycling of dust and sludge from the iron production process. Their investigations showed that ~5 kg Zn/Mg HM is transferred into the top gas dust and ~20 kg Zn/Mg HM accumulates in the sludge generated by the wet scrubber. These output amounts seem rather high, compared to the other studies investigated (see Table 1). However, the input amount of zinc was ~30 kg Zn/Mg HM, which also is much higher. The amount of zinc transferred into slag and HM was rather low. Less than 1 kg Zn/Mg HM was found in the slag. The amount transferred into the HM was even below 0.1 kg Zn/Mg HM.<sup>38</sup>

Stepin et al.<sup>45</sup> determined zinc balances for blast furnace No. 1 at Severstal (Russia) and for blast furnace No. 4 at Severstal (Russia) immediately before and after an overhaul. For their investigations, they determined the zinc content of the different input materials and output flows. Because of this setup (measurement of all input and output flows), they were able to report an imbalance of ~30%. They also stated that this imbalance may partly be attributed to the amount of zinc that remains within the furnace (see Table 1). However, measurement errors (mainly due to nonrepresentative sampling of inputs and outputs) have been considered to be the main reason for the imbalances observed.<sup>45</sup>

Morf<sup>46</sup> carried out extensive measurements of input and output flows over a time period of more than 100 days to investigate balances for different elements for a blast furnace process. According to his results, more than 60% of the total zinc output accumulates in the HM, which is quite high, compared to other studies (see Table 1). The second-largest output flow, according to Morf,<sup>46</sup> represents the dust from the dust cleaning device at the tapping stand, with a total zinc output of ~24%.

Zhang et al.<sup>47</sup> also published a zinc balance for a blast furnace. However, the top gas at this plant was cleaned by a dry cleaning system, whereas the other plants investigated were equipped with a wet dedusting system. Nevertheless, the zinc distribution is similar to other studies. Only the total inserted amount of zinc, with more than 500 g Zn/Mg HM, is almost twice as high, compared to other studies.

Besta et al.<sup>39,40</sup> investigated the effect of harmful elements and thereby the cycle and effect of zinc on the blast furnace process. They found that the most important output flow for zinc is the blast furnace scrubber sludge (59%–61%), followed by the HM (22%–28%). The remaining part of the zinc is transferred into the slag and the dry dust. The total output of

zinc at the plant investigated by Besta et al.<sup>39</sup> was only 111 g Zn/Mg HM and, thus, resides at the lower end of the scale, in comparison to the other blast furnaces.

Our own investigations (conducted over a period of 3 years) indicate that the most important output for zinc is the top gas dust. However, in contrast to the other studies, our investigations show that the zinc output via the scrubber water is not negligible. The results demonstrate that outputs obtained via scrubber water are larger than those obtained via scrubber sludge. The content of dissolved zinc, which remains in the scrubber water, reached up to 32 mg/L (or ~73 g Zn/Mg HM). The HM constitutes the second-largest output for zinc (32%–38% of the total output). Our investigations show an increase of the zinc output in the HM for the different years investigated. The zinc content in the HM increased from 41 g Zn/Mg HM in 2010 to 70.9 g Zn/Mg HM in 2012. The amount of zinc transferred into the scrubber sludge decreased during the same time. The output via the dust from the tapping stand remained fairly constant (at ~13%) over several years.

From Table 1, it is evident that most of the studies considered reported the occurrence of an imbalance. These imbalances can be as high as +65%.

**3.2. Lead.** **3.2.1. Lead in the Input of the Blast Furnace.** The main input of lead originates from the iron-bearing materials such as sinter, pellets/granules, and lump ore (~50%–100% of the overall lead input; see Table S2 in the Supporting Information). Alternative reducing agents (such as, e.g., crude tar, heavy fuel oil, and waste plastics) represent an additional source for lead. Results from our investigations denote that alternative reducing agents might contribute up to 28% to the total lead input. However, it must be noted that, although alternative reducing agents cause an additional input of lead, the overall amount of lead inserted into this furnace was low (~20 g Pb/Mg HM), in comparison to other plants. For instance, Zhang et al.<sup>47</sup> reported a total lead input of 370 g Pb/Mg HM.

Lead enters the blast furnace mainly in the form of the following compounds: PbO, PbS, and PbSO<sub>4</sub>,<sup>20,48,49</sup> whereby PbS and PbSO<sub>4</sub> predominate in the iron-bearing material. PbO in the input originates mainly from the dust of the top gas or sludge (in the case of a wet cleaning system) utilized in the sinter plant.<sup>20,25,50</sup>

In coal, lead, similar to zinc, shows an inorganic affinity and is present as a trace metal in clay minerals, feldspars, and sulfides.<sup>25</sup> Because of the conditions prevailing in the coking process and the affinity of lead to sulfur, lead is most likely to be present as PbS in coke.

The use of waste plastics as alternative reducing agents includes several types of plastics, as already described in the case of zinc. In PVC, lead stabilizers such as, e.g., PbO, 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> and 3PbO·PbSO<sub>4</sub>·H<sub>2</sub>O, have been used.<sup>51</sup> Different lead compounds are also used as pigments in plastics.<sup>52</sup> Because of the conditions at the blast furnace tuyeres (high O<sub>2</sub> content of the hot blast), lead most likely enters the blast furnace mainly in an oxide form.

However, it must be noted that lead stabilizers in PVC have been increasingly replaced with calcium-based stabilizers. A complete replacement of lead stabilizers in PVC will be realized by the end of 2015.<sup>53</sup>

**3.2.2. Behavior of Lead in the Blast Furnace.** Similar to zinc, lead also circulates within the blast furnace. At high temperatures, it is reduced to metallic lead, which evaporates and ascends to lower temperature zones (see Figure 3), where

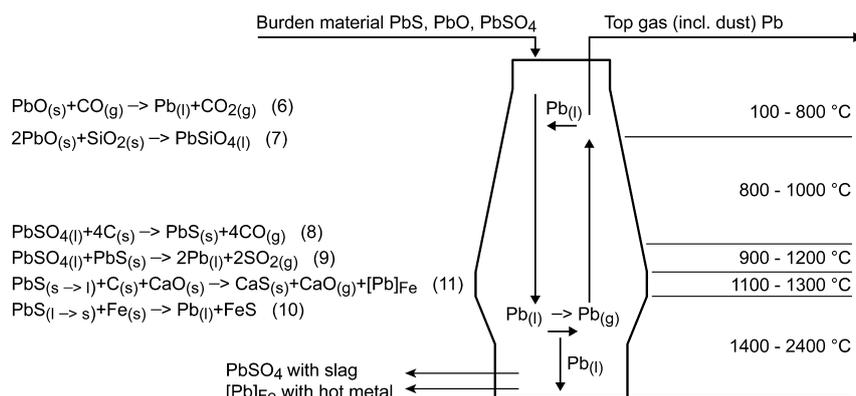


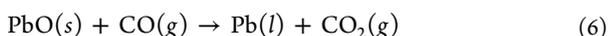
Figure 3. Behavior of lead in the blast furnace (based on the work of Chernousov et al.<sup>48</sup>); the given temperature refers to the gas temperature.

Table 2. Distribution of Lead to Different Outputs of the Blast Furnace Process

distribution of lead [%]	Zhang et al. <sup>47</sup>	Chernousov et al. <sup>48 a</sup>				Own Investigations		
		I	II	III	Morf <sup>46</sup>	2010	2011	2012
hot metal	38	38	75	67	10	32	26	37
slag	51	13	8.3	nd <sup>b</sup>	3.1	0	0	0.9
top gas dust	11	50	17	33	84	67	75	63
gravity dust	2.2							
cyclone dust	3.1							
baghouse dust	5.2							
dry dust					7.9	9.5	5.3	5.2
scrubber sludge		50	17	33	75	57	66	58
scrubber water					1.5	0	2.2	0.5
cleaned top gas	0.74	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	1.8	0	0.1	0.1
dust tapping stand dedusting	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0.8	0.3	0.1	0.3
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	130	8	60	15	<i>d</i>	30	38	36
remains in furnace and imbalance [%] <sup>c</sup>	+183	+20	+25	+40	<i>d</i>	-31	-34	-39

<sup>a</sup>Investigations for different integrated steel plants: I, Severstal (Russia); II, Tulachermert (Russia); and III, EKO-Stahl (Germany). <sup>b</sup>Not detected. <sup>c</sup>Remains in furnace and imbalance are defined as follows: (total input – total output)/(total output). A positive value means that the input is larger than the output. <sup>d</sup>Not specified.

it condenses on the surface of burden material and coke. According to the Ellingham diagram, PbO is less stable than FeO and therefore is easily reduced by CO and H<sub>2</sub> gas in the upper part of the blast furnace.<sup>54</sup> The reduction of PbO with CO to metallic lead may already occur at temperatures of ~400 °C.<sup>54,55</sup> According to Chernousov et al.,<sup>48</sup> the following chemical reaction takes place within a temperature range of 400–700 °C:

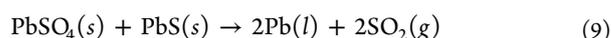
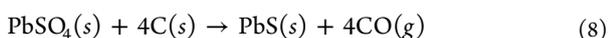


Lead, as a product of this reaction, is present as a liquid, because of its relatively low melting point (only 330 °C).<sup>34</sup>

Beside the reduction of PbO, the oxide can also react with SiO<sub>2</sub> at temperatures of 400–700 °C, which is illustrated in Figure 3:

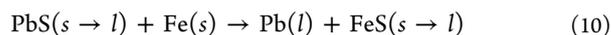


PbSiO<sub>4</sub> may partially pass directly into the slag (the melting point of PbSiO<sub>4</sub> is ~743 °C<sup>34</sup>), but it might also be reduced to PbS and lead at higher temperatures (650–900 °C):



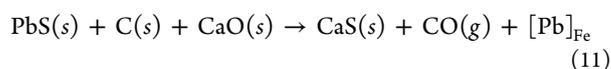
The molten metallic lead passes into higher temperature zones, where it is vaporized (the boiling point of lead is ~1749 °C<sup>34</sup>) and subsequently rises up into zones of lower temperatures, where it condenses again. This results in an inner circulation of lead.<sup>48</sup>

Besides the reduction of lead glance PbS (melting point of 1113 °C<sup>34</sup>) by PbSO<sub>4</sub>, it is also reduced by metallic iron at 1000–1200 °C, according to<sup>20</sup>



However, Chernousov et al.<sup>48</sup> reported that this reaction may already occur at temperatures of 400–700 °C.

In addition, PbS is reduced by carbon in the presence of CaO (decomposition temperature of >2000 °C<sup>34</sup>) at temperatures from 1000 °C to 1200 °C:

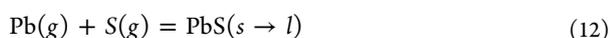


It is also possible that the gaseous lead will react with gaseous sulfur to form PbS again:

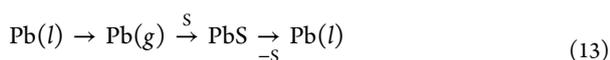
Table 3. Distribution of Chromium to the Different Outputs of the Blast Furnace Process

distribution of chromium [%]	Chernousov and Golubev <sup>15 a</sup>					Own Investigations		
	I	II	III	IV	Morf <sup>46</sup>	2010	2011	2012
hot metal	89	91	85	84	97	92	95	94
slag	8.7	6.4	12.1	15.1	2.6	7.4	4.3	4.4
top gas dust	2.6	2.7	3.0	1.2	0.9	0.9	0.8	1.2
dry dust	1.5	1.8	1.8	0.7	0.4	0.5	0.5	0.9
scrubber sludge	1.1	0.9	1.2	0.5	0.5	0.4	0.3	0.3
scrubber water	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0	0	0	0
cleaned top gas	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0	0	0	0
dust tapping stand dedusting	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0	0	0	0
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	265	110	165	430	<i>d</i>	205	206	304
imbalance [%] <sup>c</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	<i>d</i>	+40	+42	+18

<sup>a</sup>Investigations for different integrated steel plants: I, Severstal (Russia); II, NLMK (Russia); III, Tulachermet (Russia); and IV, EKO-Stahl (Germany). <sup>b</sup>Not detected. <sup>c</sup>Remains in furnace and imbalance are defined as follows: (total input – total output)/(total output). A positive value means that the input is larger than the output. <sup>d</sup>Not specified.



Thus, PbS can take part in an inner circulation loop, according to<sup>48</sup>



Lead is insoluble in cold iron and, because of its considerably higher density (11.3 g/cm<sup>3</sup>), compared to iron, it will accumulate in the hearth bottom, where it might seep into the refractory lining and thereby destroy it.<sup>20</sup> According to the literature, however, some of the lead is carried out by the top gas.<sup>e.g.31,47,48,56,57</sup>

**3.2.3. Lead in the Outputs of the Blast Furnace.** The distribution of lead to the different blast furnace outputs, according to the studies of Zhang et al.,<sup>47</sup> Chernousov et al.,<sup>48</sup> Morf,<sup>46</sup> and our own investigations is summarized in Table 2. The results of Chernousov et al.<sup>48</sup> for plant II and plant III indicate that the largest portion of lead leaves the furnace via the HM (>66%). For plant I, the output of lead via the HM is similar to the result reported by Zhang et al.,<sup>47</sup> as well as in the same range as our plant observations. A significantly lower output of lead via the HM (only 10% of the total lead output occurs via the HM) was reported by Morf.<sup>46</sup> Thus, the range of lead transferred into the HM shows a large range, from 10% up to 75%, in reference to the studies considered. The discharge of lead via the slag and via the top gas dust also exhibits a wide range of variation (lead transfer into the slag = 0%–51%; transfer into the top gas dust = 10%–84%). The highest transfer of lead into the slag was observed by Zhang et al.<sup>47</sup> at a plant that showed, by far, the highest throughput of lead. All other studies cited report a transfer coefficient for lead into slag of <13% and, for the top gas, a transfer of at least one-third of the total output. From Table 2, it is evident that the imbalance is quite different among the studies considered. Zhang et al.<sup>47</sup> and Chernousov et al.<sup>48</sup> determined positive imbalances. This means that the total input of lead observed is larger than the total output. The lead imbalance reported by Zhang et al.<sup>47</sup> exceeds +180%. In comparison, our own investigations denote a negative imbalance, meaning that more lead is detected in the output flows of the process than in the input materials. Possible causes for these imbalances include, for example, difficulties in

sampling, because of heterogeneous input materials, or concentrations below the limit of detection (LOD).

**3.3. Chromium.** **3.3.1. Chromium in the Input of the Blast Furnace.** Iron-bearing materials (sinter, pellets, granules, and lump ores) represent the main source for chromium (input share of more than 90%) in the input materials. The second-largest source is coke, which contributes between 2% and 10% to the overall chromium input. The analyzed data show a total input of chromium into the blast furnaces in the range of 110–430 g/Mg HM (see Table S3 in the Supporting Information).

In iron ores (the dominant source for chromium), chromium might be present as chromite (FeO·Cr<sub>2</sub>O<sub>3</sub>),<sup>20,23</sup> PbCrO<sub>4</sub>, and Cr<sub>2</sub>O<sub>3</sub>.<sup>24</sup>

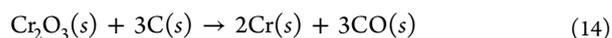
In the sinter, it is most likely that chromium is also present in the same modes as in the iron ores, because of the fine ores utilized. Moreover, the sludge and dusts recycled at the sinter plant hardly contain any chromium.

In the coal used for the coking process, chromium is largely bound in the inorganic portion. Thereby, chromium appears mainly in clay minerals (e.g., chrome spinel ((Mg,Fe)-(Cr,Al,Fe)<sub>2</sub>O<sub>4</sub>), kemmerite ((Mg,Fe)<sub>5</sub>(Al,Cr)[AlSi<sub>3</sub>O<sub>10</sub>]-[OH]<sub>8</sub>)<sup>58</sup>) and feldspars.<sup>25</sup>

In waste plastics, chromium is used as a pigment in its oxidized form (e.g., Cr<sub>2</sub>O<sub>3</sub>, Cu(Cr,Fe)<sub>2</sub>O<sub>4</sub>, (Ti,Sb,Cr)O<sub>2</sub>).<sup>29</sup>

**3.3.2. Behavior of Chromium in the Blast Furnace.** Metallic chromium is characterized by a melting point of 1907 °C and a boiling point of 2671 °C.<sup>34</sup>

The reduction of Cr<sub>2</sub>O<sub>3</sub> occurs in the blast furnace hearth at temperatures of ~1700 °C.



This reaction is highly endothermic; therefore, a lot of energy is required, which increases coke consumption.<sup>20,54</sup>

**3.3.3. Chromium in the Outputs of the Blast Furnace.** The investigations of Chernousov and Golubev<sup>15</sup> into the distribution of chromium to the different outputs of the blast furnace (see Table 3) demonstrate that more than 84% of the chromium accumulates in the HM. The second-largest output represents the slag, covering 6%–15% of the total chromium output. Minor amounts of chromium have also been detected in the dry dust of the dust bag and in the sludge of the wet cleaning system. Our own investigations indicate that more

Table 4. Distribution of Nickel to the Different Outputs of the Blast Furnace process

distribution of nickel [%]	Chernousov et al. <sup>14a</sup>					Own Investigations		
	I	II	III	IV	Morf <sup>46</sup>	2010	2011	2012
hot metal	92	94	92	97	93	98	98	96
slag	0	0	0	0	3.3	0.5	0.3	2.9
top gas dust	8	6	8	3	3.2	1.5	1.1	2
dry dust	2	1	2	1	0.6	0.5	0.4	1.3
scrubber sludge	6	5	6	2	2.5	0.7	0.6	0.6
scrubber water	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0.1	0.3	0.3	0.1
cleaned top gas	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0.2	0	0	0
dust tapping stand dedusting	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	0.1	0.2	0.1	0.1
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	65	80	65	170	<i>d</i>	41	47	58
imbalance [%] <sup>c</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	<i>d</i>	+37	+1.0	+10

<sup>a</sup>Investigations for different integrated steel plants: I, Severstal (Russia); II, NLMK (Russia); III, Tulachermet (Russia); and IV, EKO-Stahl (Germany). <sup>b</sup>Not detected. <sup>c</sup>Remains in furnace and imbalance are defined as follows: (total input – total output)/(total output). A positive value means that the input is larger than the output. <sup>d</sup>Not specified.

than 90% of the chromium entering the blast furnace ends up in the HM. A very small amount of chromium exits the blast furnace via the top gas dust (<1.2%). These results are also consistent with the data presented by Morf.<sup>46</sup>

The imbalance observed in our investigations amounted to ~40% for 2010 and 2011 and decreased to 18% for the year 2012. For the other studies, no chromium balance (input versus output) has been established.

**3.4. Nickel.** **3.4.1. Nickel in the Input of the Blast Furnace.** Nickel is mainly inserted into the process by the sinter (>50%). The pellets/granules and the lump ore contribute, ~10% each, to the total nickel input. The coke amounts to 12%–23% of the total nickel input; a higher contribution of the coke (31% of the total nickel input) has been observed only for one plant (see Table S4 in the Supporting Information).

The specific input rate of nickel ranged from 47 g Ni/Mg HM to 170 g Ni/Mg HM, whereby, at most plants, input rates have not exceeded 80 g/Mg HM.

Nickel can occur in nature in a massive form, e.g., in the Earth's core. However, in the lithosphere, it is mostly present in nickel–iron ores or nickel-bearing iron ores.<sup>24</sup>

In coals, nickel is likely to occur in sulfide minerals and is related to carbonate minerals.<sup>50</sup> Thus, it is most likely that nickel occurs in the same species in the coke.

Since iron ore fines and coke are used at the sinter plant, it is most likely that the sinter contains nickel in the same species, since it is present in these input materials of the sinter plant.

In waste plastics, nickel may be used as a pigment (e.g., (Ti,Sb,Ni)O<sub>2</sub>, (Co,Ni,Zn)<sub>2</sub>(Ti,Al)O<sub>4</sub>).<sup>29</sup> Organic nickel complexes are used in plastics as light stabilizers. Nickel-coated chopped carbon or glass fibers are used as a conductivity additive.<sup>52</sup>

**3.4.2. Behavior of Nickel in the Blast Furnace.** The melting point of metallic nickel is 1455 °C, and the boiling point is 2913 °C,<sup>34</sup> whereby the latter is not reached in the blast furnace. Thus, nickel leaving the blast furnace through the top gas is most likely associated with the discharge of fine particles resulting from abrasion of the charging materials.

If nickel enters the blast furnace process, it is reduced by CO already at temperatures of ~500 °C (according to the Ellingham diagram given in Froberg,<sup>55</sup> which is valid for a CO:CO<sub>2</sub> ratio of 50:50. However, the reaction can already

occur at lower temperatures if the CO content is higher). This means that NiO is slightly easier to reduce than FeO, which starts to be reduced by CO at temperatures above 600 °C.<sup>55</sup>

**3.4.3. Nickel in the Outputs of the Blast Furnace.** Chernousov et al.<sup>14</sup> investigated the behavior of nickel in different integrated steel plants (see Table 4). They noted that nickel is easily reduced under blast furnace conditions and almost entirely dissolves in iron. Thus, nickel is almost exclusively transferred into the HM. They also reported that the transfer of nickel into a gaseous form is only possible if nickel is bound to the organic part of the coke. Moreover, this is only possible at temperatures of 1300–1600 °C, at which gaseous nickel hydride may develop and Ni atoms from the coke are gasified.<sup>14</sup>

Morf<sup>46</sup> also reported that nickel will mostly accumulate in the HM (93%). Just 3.3% of the total nickel output has been detected in the slag. The sludge generated in the wet scrubber process contains ~2.5% of the total nickel discharged. The contribution of the other output flows investigated was <1% of the total nickel output (see Table 4)

Our own observations also demonstrate that the main amount (>95%) of nickel is transferred into the HM and just a small portion leaves the process via the slag (<3%). However, the plant data for the year 2010 indicate an imbalance of ~37% between the total input and output flows.

**3.5. Cadmium.** **3.5.1. Cadmium in the Input of the Blast Furnace.** Our own investigations denote that cadmium enters the blast furnace process mainly due to the utilization of alternative reducing agents (see Table S5 in the Supporting Information). In addition, iron-bearing materials also contribute, to some extent, to the overall input of cadmium (up to 21% of the overall cadmium input). Thereby, it must be noted that their contribution might be higher, because of the fact that, for many samples of iron-bearing material, cadmium concentrations were below the LOD. For simplicity reasons, the cadmium content of these samples has been assumed to be zero, which definitely results in an underestimation of the annual mean cadmium content of iron-bearing materials.

The chemical behavior of cadmium is similar to that of zinc. Both elements do not occur in nature in metallic form, but mainly in chemical compounds such as sulfides and carbonates. CdS or CdCO<sub>3</sub> mainly accompany ZnS and ZnCO<sub>3</sub>.<sup>24</sup>

In coal, cadmium occurs mainly as a solid solution in sphalerite and pyrite. It might also occur in association with clays, carbonates, and together with organic matter.<sup>59</sup> However, because of the coking process, it is most likely that cadmium will be removed (because of the high volatility of cadmium at higher temperatures) and thus not be present anymore in the coke.

In plastics, cadmium has been used in mixed-metal stabilizers. These stabilizers are used as heat stabilizers in PVC in which they are present as CdCl<sub>2</sub>. Cadmium has also been utilized as a pigment in plastics. However, because of stringent regulations and greater environmental concern, pigments based on cadmium have been phased out.<sup>52</sup>

**3.5.2. Behavior of Cadmium in the Blast Furnace.** Cadmium is characterized by a melting point of 320 °C and a boiling point of ~770 °C.<sup>34</sup> If cadmium enters the blast furnace as CdO, it is reduced by CO at a temperature of ~800 °C. Because of the relatively low boiling point of cadmium, it is most likely that it will exit the plant via the top gas.

To the knowledge of the authors, the overall behavior of cadmium (potential chemical reaction) in the blast furnace has not been investigated so far. Until now, several studies have only reported the cadmium content in different output flows of the blast furnace process (as described in section 3.5.3).

Based on investigations on the behavior of cadmium in waste incineration plants by Zhang et al.,<sup>60</sup> one can draw the following conclusions for the blast furnace process:

- Above 950 °C, cadmium is predominate and coexists with small fractions of CdO. CdO is the only species present below 800 °C in oxidizing condition predominating in waste incineration plants. Since, in the blast furnace, reducing conditions are present, CdO will most likely be reduced to cadmium by CO.

- If Cl is present, CdCl<sub>2</sub> is formed and exists at temperatures below 1000 °C. Thus, cadmium might leave the blast furnace with the top gas as CdCl<sub>2</sub>.

- Together with sulfur, cadmium can react to CdS. The sublimation point of CdS is 1000 °C.<sup>24</sup> Thus, CdS is able to rise up with the gas stream in the blast furnace process. If O<sub>2</sub> is present in lower temperature zones, CdS may oxidize to CdO or solidify again and get to zones of higher temperatures. Following these reactions, cadmium could also form an inner circulation process, similar to zinc and lead.

**3.5.3. Cadmium in the Outputs of the Blast Furnace.** Prater<sup>61</sup> carried out cadmium measurements in the output flows of HM, slag, sludge, and scrubber water from top gas cleaning. The cadmium content of the HM and the slag were below the analytical detection limit. For the effluent of the top gas washing process (scrubber water), no measurement value has been reported. Hence, only for the solids derived from top gas cleaning have cadmium contents been determined. The reported mean value amounts to 51 mg cadmium/kg of dry matter of scrubber sludge.<sup>61</sup>

By comparison, the cadmium content of the blast furnace dust investigated by Asadi Zeydabadi et al.<sup>62</sup> was much lower (5.6 mg/kg). However, they analyzed only one sample from a steel-producing company.

Proctor et al.<sup>63</sup> investigated the physical and chemical characteristics of different slags in the steel industry. Within their study they also analyzed the blast furnace slag, with respect to its cadmium content. Similar to the studies of Prater,<sup>61</sup> they were not able to detect cadmium in the slag, because of its low concentration.

Mansfeldt and Dohrmann<sup>56</sup> characterized 32 samples of blast furnace sludge from an abandoned landfill. Their results indicate cadmium contents ranging from 31 mg/kg up to 227 mg/kg, with a mean value of 81 mg/kg.

Chernousov and Golubev<sup>15</sup> investigated the cadmium content in the blast furnace sludge for different metallurgical combines from Russia. They reported cadmium concentrations of the blast furnace sludge in the range of 1–5 mg/kg.

Kretschmar et al.<sup>64</sup> analyzed the blast furnace sludge from former sedimentation ponds that were operated between 1930 and 1982. The selected samples (a total of 36 samples) showed cadmium concentrations from below the detection limit up to 95 mg/kg (32 samples showed cadmium contents between 5.6 and 95 mg/kg).

All these studies did not report the specific amounts of sludge or dust generated. Thus, the cadmium contents observed cannot be translated into specific cadmium flows that might be comparable to our own observations.

The investigations of Morf<sup>46</sup> during an intensive measurement campaign over 118 days demonstrated that cadmium leaves the blast furnace mainly via the top gas. According to his results, cadmium accumulates in the sludge from the wet top gas scrubber (75% of the total cadmium output ends up there). In addition, the scrubber water contains ~13% of the total cadmium output. Only a minor portion (~11% of the total output) is transferred into the coarser dust from the dust bag and just 1% remains in the cleaned top gas and is emitted (see Table 5).

**Table 5. Distribution of Cadmium to the Different Outputs of the Blast Furnace Process**

distribution of cadmium [%]	Morf <sup>46</sup>	Own Investigations		
		2010	2011	2012
hot metal	0	0	0	0
slag	0	0	0	0
top gas dust	99.0	99.8	99.6	99.6
dry dust	11	17	12	14
scrubber sludge	75	78	54	84
scrubber water	13	5.0	34	0.7
cleaned top gas	1	0	0	0.2
dust tapping stand dedusting	0	0.2	0.4	0.2
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	<i>b</i>	0.30	0.42	0.31
imbalance [%] <sup>a</sup>	<i>b</i>	-48	-31	-60

<sup>a</sup>Remains in furnace and imbalance are defined as follows: (total input – total output)/(total output). A positive value means that the input is larger than the output. <sup>b</sup>Not specified.

Our own investigations indicate a similar partitioning of cadmium to the different output flows of the blast furnace process (see Table 5). Only for one year (2011) did the distribution of cadmium between the scrubber sludge and the scrubber water differ significantly from the other investigations. In that year, a higher amount of cadmium was transferred into the scrubber water (34%, instead of 0.7%–13%) and a lower amount into the scrubber sludge (54% instead of 75%–84%).

When comparing the total input and output of cadmium, significant imbalances have been observed, ranging from –31% to –60%. These consistently negative imbalances indicate that the cadmium content in the input materials is most likely

underestimated. Reasons for this might be the fact that, for many iron ore or coke samples analyzed, a cadmium concentration of zero had to be assumed because concentrations were below the limit of quantification.<sup>65</sup>

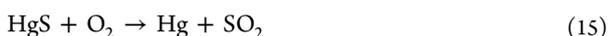
**3.6. Mercury.** **3.6.1. Mercury in the Input of the Blast Furnace.** Similar to cadmium, mercury is mainly introduced into the process by alternative reducing agents utilized (the contribution to the overall mercury input is >97%; see Table S6 in the Supporting Information). The iron-bearing materials hardly contribute to the overall input (up to 3% of the total mercury input).

Mercury occurs in nature mainly bound in sulfides (HgS, Hg[Sb<sub>2</sub>S<sub>7</sub>]) and can rarely be found in an unbound or metallic form.<sup>24</sup>

In coal, mercury might be present as HgS, metallic mercury, and organometallic compounds.<sup>59</sup> After the coking process, mercury will be mainly present in the crude tar. The crude is tar is a byproduct of this process and may be used as an alternative reducing agent.

**3.6.2. Behavior of Mercury in the Blast Furnace.** At room temperature, metallic mercury is liquid and has a boiling temperature of 357 °C.<sup>24</sup>

HgS can easily be reduced by O<sub>2</sub>, according to the following reaction:<sup>24</sup>

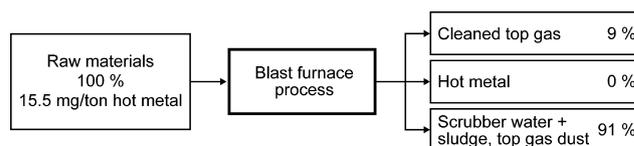


However, because of the reducing conditions present in the blast furnace, it is likely that HgS also moves downward with the burden to temperatures of more than 800 °C. At that point, it might be transformed into a liquid state (melting point of HgS = 850 °C<sup>34</sup>). It is possible that the liquid HgS is reduced and the metallic mercury thereby generated is vaporized, or that the liquid HgS descends to zones with higher temperatures. In the case that mercury enters the blast furnace as an oxide (HgO), it decomposes to mercury and O<sub>2</sub> at temperatures above 400 °C.<sup>24</sup>

**3.6.3. Mercury in the Outputs of the Blast Furnace.** To the knowledge of the authors, Proctor et al.<sup>63</sup> were the first to try to analyze the mercury content in blast furnace slag. They determined the content of different elements in a total of 11 samples taken from different blast furnaces. However, the mercury content in all slag samples was below the LOD.

Fukuda et al.<sup>65</sup> carried out a survey on mercury emissions and its behavior in primary ferrous metal production. They determined the mercury content in different input materials and in the outputs of the blast furnace. Altogether, 32 samples from one blast furnace were taken and analyzed. In particular, the following materials have been analyzed: sinter, coke, iron ore, limestone, powdered coal, pellets, HM, slag, dry dust, scrubber water, scrubber sludge, and cleaned top gas. The mercury concentrations measured in the input materials were in the range of 17–53 µg/kg for iron ore (three samples), 0.10–11 µg/kg for coke (five samples), 0.0–21 µg/kg for sinter (nine samples), 8.9–31 µg/kg for limestone (two samples), 11.0–84 µg/kg for powdered coal (three samples), 0.3–0.4 µg/kg for pellets (two samples) and 0.0–0.6 µg/kg for slag (three samples). Mercury was not detectable in the HM. According to these mercury contents and the respective mass flows of the different outputs, Fukuda et al.<sup>65</sup> derived the mercury mass balance depicted in Figure 4 for the blast furnace process.

The average mercury contents in the blast furnace output flows investigated by Fukuda et al.<sup>65</sup> are presented in the Supporting Information (Table S7).



**Figure 4.** Mercury mass balance for the blast furnace process (based on the work of Fukuda et al.<sup>65</sup>).

Recently, Földi et al.<sup>66</sup> published their investigations on mercury in dumped blast furnace sludge. They determined the total mercury content in blast furnace sludge from different “landfills” in Europe. A total of 65 samples were taken from former blast furnace sludge sedimentation ponds. Furthermore, the mercury content of some charge materials was investigated. The total mercury content of the blast furnace sludge for all 65 samples varied between 0.006 mg/kg and 20.8 mg/kg, with a mean value of 3 mg/kg, which is five times greater than the concentration observed by Fukuda et al.<sup>65</sup> (0.655 mg/kg). However, it must be noted that the mercury contents of the sludge samples analyzed showed a large variability. The mercury concentrations of the coke analyzed (three samples) varied between 0.015 mg/kg and 0.093 mg/kg, with a mean value of 0.06 mg/kg. For iron ores (two samples), the concentrations ranged between 0.019 mg/kg and 0.048 mg/kg, with a mean value of 0.044 mg/kg. For the sinter material (one sample), they reported a mean mercury content of 0.019 mg/kg.<sup>66</sup> The analysis results for the different input materials are almost identical to those presented by Fukuda et al.<sup>65</sup>

Földi et al.<sup>66</sup> also reported that, according to the literature, mercury preferentially resides with organic matter in soil and sediments. Moreover, carbon-based sorbents are found to be most effective for mercury removal from the flue gas.<sup>66</sup> Thus, it might be reasonable to assume that the carbon in the blast furnace process constitutes a sorbent for the metallic mercury vapor.

Morf<sup>46</sup> also investigated the behavior of mercury in a blast furnace. The results of his survey and our own observations are summarized in Table 6.

**Table 6.** Distribution of Mercury to the Different Outputs of the Blast Furnace Process

distribution of mercury [%]	Fukuda et al. <sup>65</sup>	Morf <sup>46</sup>	Own Investigations		
			2010	2011	2012
hot metal	0	0	0	0	0
slag	0	0	0	0	0
top gas dust	91	95	92	91	87
dry dust		5.5	7.0	5.8	13.8
scrubber sludge	91	89	85	85	73
scrubber water		0	0	0	0
cleaned top gas	9	5.6	8.4	9.7	13.3
<b>sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
total output [g/Mg HM]	<i>b</i>	<i>b</i>	0.034	0.16	0.032
imbalance [%] <sup>a</sup>			−36	−44	−24

<sup>a</sup>Remains in furnace and imbalance are defined as (total input – total output)/(total output). A positive value means that the input is larger than the output. <sup>b</sup>Not specified.

The outcomes clearly indicate that mercury leaves the process preferentially via the top gas dust. The main amount of mercury accumulates in the scrubber sludge (up to 89%). Some of the mercury may leave the process via the cleaned top gas (5%–14%).

For our own investigations, the imbalances are quite high, ranging from –24% up to –44%. Thus, a similar picture as that observed for cadmium can be observed (see Table 5): the input of mercury is systematically underestimated. The reasons for this underestimation might be the same as those for cadmium (e.g., concentrations below the LOD in different input materials).

#### 4. DISCUSSION AND CONCLUSIONS

Although the heavy metals zinc, lead, chromium, nickel, mercury, and cadmium occur in very low concentrations in the different input materials of the blast furnace process, compared to the main elements, such as iron or carbon, they may significantly impact the overall process. Several studies have proven the negative effect of, e.g., zinc and lead on the blast furnace operation, with respect to process stability, the service life of the lining and the coke consumption. In addition, all the heavy metals considered are of environmental concern.

Among the heavy metals reviewed, zinc probably represents the best investigated microelement in the blast furnace process. The analysis of the input materials (see Table S1 in the Supporting Information) showed that the main input source represents the sinter. This can be mainly traced back to the utilization of internally recycled dust and sludge from off-gas cleaning devices, which are known as sinks for zinc.

Besides the external recirculation of zinc (due to material recycling via the sinter), the formation of an internal cycle of zinc within the blast furnace has also been observed and described in numerous studies. Since the chemical reactions driving this internal zinc cycle are sensitive to the operating conditions (e.g., top gas temperature, pressure at the throat), the distribution of zinc to the outputs of the blast furnaces was quite diverse for the different studies analyzed (as shown in Table 1). Thus, it can be concluded that the behavior of zinc is strongly dependent on the process conditions and no general conclusion can be drawn regarding to what extent zinc is transferred to the different outputs. Thus, further investigations concerning the impact of process conditions on the behavior and discharge routes of zinc are needed.

Moreover, significant balance errors (input  $\neq$  output) for zinc have been reported, which range from –11% (output > input) to +65% (output < input). They are most likely a consequence of nonrepresentative sampling and improper analysis methods. With respect to the latter, often methods for routine monitoring (e.g., X-ray fluorescence spectroscopy for product quality measurements) have been applied, which are of limited reliability for the determination of specific microelements. Moreover, these elements might also be unequally distributed in the samples taken. Hence, in order to obtain a more reliable picture about the behavior of zinc, sampling and measurement methods must be improved.

Besides sampling and measurement errors (difficult sampling of heterogeneous input and output flows), the observed imbalance may, to a minor extent, also be attributed to a potential accumulation of zinc in the blast furnace lining or due to scaffold formation. However, reliable information about the quantity of zinc remaining in the furnace requires chemical analysis of the lining after a blast furnace shutdown, which has

rarely been conducted so far (see, e.g., Besta et al.<sup>39,40</sup>). Thus, quantitative investigations about the penetration of zinc into the lining material would be required in order to assess its potential impact on the overall zinc balance.

The behavior of lead within the blast furnace is comparable to that of zinc. Lead may also circulate within the blast furnace and destroy the lining as it penetrates into the refractory linings.<sup>20</sup> Hence, it negatively influences the process.

Similar to zinc, the behavior of lead also seems to be highly dependent on the process conditions as the output flows reported in the studies reviewed (see Table 2) are quite different. The output via the flue dust, e.g., may vary from 10%<sup>47</sup> to more than 80%.<sup>46</sup> Moreover, the overall transfer of lead into the HM varied significantly. Chernousov et al.<sup>48</sup> reported that, up to 75% (plant II) of the total lead output accumulate in the HM, whereas other studies as well as our plant investigations came up with significantly lower fractions (in the range of 35%).

Moreover, the reported imbalances for lead are also quite diverse in the studies analyzed. All literature data reviewed indicate a positive error (total lead output is smaller than the total input), whereas our own investigations are characterized by negative balance errors, meaning that the total lead output determined is larger than the total input of lead into the blast furnace. Such negative imbalances (over a longer time period) are physically impossible. They may only be attributed to measurement or sampling errors. However, minor positive balance errors might be explained by the accumulation of lead in the linings of the furnace described in the literature. Nevertheless, the imbalances observed for lead, similar to zinc, are significant and quite diverse. Thus, it can also be concluded for lead that the sampling and the measurement methods used in the studies must be improved to obtain a more reliable picture about the behavior of lead.

Nickel and chromium exhibit a similar behavior in the blast furnace process and are almost exclusively transferred to the HM. All studies reviewed, as well as our own investigations, demonstrate that usually more than 90% of both elements can be found in the HM. This can be explained by the fact that both elements are also alloying elements in steel production. Nickel and chromium are hardly discharged via the reducing gas. Thus, the contents in the flue dust reach only 3% for chromium and 8% for nickel. These minor quantities of nickel and chromium transferred into the top gas dust originate from the abrasion of the burden material, since their boiling temperature is far above the highest temperature observable in the blast furnace process.

For the metals cadmium and mercury, only a few studies have been conducted so far. The results, including our own observations, demonstrate that both metals are inserted only to a minor extent via iron-bearing materials (up to 15% of the total cadmium input, up to 3% of the total mercury input). The alternative reducing agents represent the most important source for both metals (waste plastics in the case of cadmium and crude tar in the case of mercury). However, the share of the iron-bearing materials and coke to the total input of both heavy metals could have been significantly underestimated, because of the fact that their mercury and cadmium contents had often been assumed to be zero, especially since concentrations are frequently below the limit of detection (LOD). Cadmium and mercury are highly volatile metals and, hence, are mostly transferred into the top gas. After the top gas cleaning (dedusting and wet scrubber), both metals accumulate in the sludge generated by the wet scrubber. For cadmium, the

observations indicate that all of the inserted cadmium will exit the blast furnace with the top gas. However, to the knowledge of the authors, no investigations have been carried out yet to determine the cadmium content in HM, which is obviously very low but might still be above zero.

Mercury behaves similar to cadmium; it is mainly discharged via the top gas and accumulates to a large extent in the blast furnace sludge in the case where a wet gas cleaning system is in place. However, minor amounts of mercury might remain in the cleaned top gas. Hence, an increased utilization of alternative reducing agents (e.g., waste plastics, crude tar or heavy fuel oil) containing higher contents of mercury will result in an increased amount of mercury in the blast furnace sludge, which is currently landfilled. To a minor extent, higher inputs of mercury or cadmium may also increase gaseous emissions of both elements. However, this correlation between input and emissions of mercury and cadmium could not be confirmed during detailed investigations conducted by Trinkel et al.<sup>67</sup>

Because of the fact that the heavy metals are inserted at very low concentrations, there might be numerous reactions occurring under the different local conditions present in the furnace. Thus, the reactions of the heavy metals in the blast furnace are not dependent only on the metal compounds inserted but also on whether they are inserted with the burden from the top of the furnace or are injected through the tuyeres.

For a better understanding of the behavior of the heavy metals discussed, in particular for those undergoing various chemical transformations such as zinc and lead, thermodynamical calculations could be beneficial. To some extent such calculations have already been carried out by, e.g., Chernousov and Golubev<sup>15</sup> and Zhang et al.<sup>37,49</sup> However, these calculations also face severe challenges as most input data necessary for thermochemical modeling are not available (e.g., lack thermodynamic data). Moreover, existing models trying to simulate the behavior of trace metals in the blast furnace (see, for example, ref 68) are based on strong simplifications (e.g., flat assertions that no particles are carried out with the top gas), thereby disregarding major processes for the discharge of at least some heavy metals.

Therefore, it is recommended that, in a first step, the concentration measurements in the different input and output flows of the blast furnace should be improved, thereby accounting for the heterogeneous character of the different material flows and the difficulties with regard to the analysis of very low metal contents. Such optimized sampling and analysis of input and outputs will significantly reduce the differences between total metal inputs and outputs. In a second step, existing thermodynamical model approaches should be applied to such an improved dataset of input and output flows.

Both improved plant observations and thermodynamical modeling can be regarded as crucial in order to enhance knowledge of the behavior of heavy metals in the blast furnace process which, in the end, should enable an even more resource efficient production of HM.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b03442.

Input distribution of heavy metals (zinc, lead, chromium, nickel, cadmium, and mercury); mean mercury concentration of the different blast furnace outputs (PDF)

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### Notes

The authors declare no competing financial interest.

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# Supporting Information

## Behavior of Cr, Ni, Pb, Zn, Cd and Hg in the blast furnace – A critical review of literature data and plant investigations

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**Table S 1: Contribution of different input materials to the total Zn input into blast furnaces**

Zn	Zhang et. al. <sup>47</sup>	Stepin et. al. <sup>45 a</sup>			Besta et. al. <sup>40</sup>	Mertins <sup>31</sup>	Besta et. al. <sup>39</sup>	Morf <sup>46</sup>	Own investigations		
	[%]	I [%]	II [%]	III [%]	[%]	[%]	[%]	[%]	2010 [%]	2011 [%]	2012 [%]
Sinter	64	97	98	92	71	40	77	72	70	64	72
Pellets/ Granules	33	0.96	0.09	3.4	7.9	42	6.4	6	11	17	14
Lump ore	1.1	0	0	0	3.6	-	2.7	4	2.8	2.5	2.6
Slag (recycling material)	-	-	-	-	6.5	18	4.7	-	0.02	0.03	0.06
Limestone	-	-	-	-	1.1	-	0.91	-	-	-	-
Coke	1.1	2.3	2.1	4.7	8.9	-	4.4	4	4.3	3.5	2.7
Coal/ Coal Powder	1.1	-	-	-	-	-	-	-	-	-	-
Alternative reducing agents	-	-	-	-	-	-	-	13	12	13	9.1
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	645	416	340	279	116	- <sup>b</sup>	126	- <sup>b</sup>	127	143	168

<sup>a</sup> I: Balance for blast furnace No. 1 from Severstal, II: Balance for blast furnace No.4 from Severstal immediately before the blast furnace was shut down for an overhaul, III: Balance for blast furnace No.4 from Severstal after the overhaul

<sup>b</sup> not specified

**Table S 2: Contribution of different input materials to the total Pb input into blast furnaces**

Pb	Zhang et al. <sup>47</sup>	Chermousov et al. <sup>48 c</sup>			Morf <sup>46</sup>	Own investigations		
	[%]	I [%]	II [%]	III [%]	[%]	2010 [%]	2011 [%]	2012 [%]
Sinter	60				26	32	21	31
Pellets/ Granules	24	100	60	95	10	22	31	20
Lump ore	11				16	8.1	6.8	14
Slag (recycling material)	-	-	-	-	-	0.01	0.02	0.08
Limestone	-	-	-	-	-	-	-	-
Coke	4.6		40	5	20	15	13	15
Coal/ Coal Powder	1.8	-	-	-	-	-	-	-
Alternative reducing agents	-	-	-	-	28	23	28	20
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	370	10	75	21	- <sup>d</sup>	21	25	22

<sup>c</sup> Investigations for different integrated steel plants: I: Severstal (Russia), II: Tulachemet (Russia), III: EKO-Stahl (Germany)

<sup>d</sup> Not specified

**Table S 3: Contribution of different input materials to the total Cr input into blast furnaces**

Cr	Chermousov and Golubev <sup>15 e</sup>				Morf <sup>46</sup>	Own investigations		
	I [%]	II [%]	III [%]	IV [%]	[%]	2010 [%]	2011 [%]	2012 [%]
Sinter					43	52	59	71
Pellets/ Granules	94	95	90	98	25	30	28	17
Lump ore					21	11	6.8	6.6
Slag (recycling material)	-	-	-	-	-	0.6	0.45	0.76
Limestone	-	-	-	-	-	-	-	-
Coke	6	5	10	2	8	6.2	5.2	4.0
Coal/ Coal Powder	-	-	-	-	-	-	-	-
Alternative reducing agents	-	-	-	-	4	0.5	0.87	0.34
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	265	110	165	430	- <sup>f</sup>	287	293	360

<sup>e</sup> Investigations for different integrated steel plants: I: Severstal (Russia), II: NLMK (Russia), III: Tulachemet (Russia), IV: EKO-Stahl (Germany)

<sup>f</sup> not specified

**Table S 4: Contribution of different input materials to the total Ni input into blast furnaces**

Ni	Chernousov et. al. <sup>14 g</sup>				Morf <sup>46</sup>	Own investigations		
	I	II	III	IV		2010	2011	2012
	[%]							
Sinter					54	50	61	65
Pellets/ Granules	69	81	77	88	10	16	10	14
Lump ore					14	14	8.7	6.8
Slag (recycling material)	-	-	-	-	-	-	-	-
Limestone	-	-	-	-	-	-	-	-
Coke	31	19	23	12	16	16	16	13
Coal/ Coal Powder	-	-	-	-	-	-	-	-
Alternative reducing agents	-	-	-	-	6.5	3.8	3.6	1.7
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	65	80	65	170	- <sup>h</sup>	55	47	64

<sup>g</sup> Investigations for different integrated steel plants: I: Severstal (Russia), II: NLMK (Russia), III: Tulachermet (Russia), IV: EKO-Stahl (Germany)

<sup>h</sup> Not specified

**Table S 5: Contribution of different input materials to the total Cd input into blast furnaces**

Cd	Morf <sup>46</sup>	Own investigations		
		2010	2011	2012
	[%]	[%]	[%]	[%]
Sinter		4	15	4
Pellets/ Granules		0	5.6	0
Lump ore		1	0	0
Slag (recycling material)	100 <sup>i</sup>	0	0	0
Limestone		-	-	-
Coke		0	0	0
Coal/ Coal Powder		-	-	-
Alternative reducing agents		95	79	96
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	- <sup>j</sup>	0.16	0.29	0.12

<sup>i</sup> No allocation to the different input materials was provided since the input of Cd into the blast furnace was derived from output measurements (see **Error! Reference source not found.**)

<sup>j</sup> Not specified

**Table S 6: Contribution of different input materials to the total Hg input into blast furnaces**

Hg	Fukuda et. al. <sup>65</sup>	Morf <sup>46</sup>	Own investigations		
			2010	2011	2012
	[%]	[%]	[%]	[%]	[%]
Sinter			0	0	2.8
Pellets/ Granules			0	0	0
Lump ore			0.6	1.8	0
Slag (recycling material)	100 <sup>k</sup>	100 <sup>k</sup>	0	0	0
Limestone			-	-	-
Coke			0	0	0
Coal/ Coal Powder			-	-	-
Alternative reducing agents	-	-	99	98	97
<b>Sum</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
Total Input [g/Mg HM]	- <sup>l</sup>	- <sup>l</sup>	0.018	0.033	0.023

<sup>k</sup> No allocation to the different input materials was performed since total input of Hg was derived from output measurements (see **Error! Reference source not found.**)

<sup>l</sup> Not specified

**Table S 7: Mean Hg concentration of the different blast furnace outputs (on the basis of Fukuda et. al.<sup>65</sup>)**

Hg	Fukuda et. al. <sup>65</sup>			
	Number of samples	[mg/kg]	[µg/l]	[µg/Nm <sup>3</sup> ]
Hot metal	2	0		
Slag	3	0.0002		
Top gas dust	3	0.267		
Scrubber sludge	3	0.655		
Scrubber water	3		n.d.	
Blast furnace gas	3			3.34



# Characterization of Blast Furnace Sludge with Respect to Heavy Metal Distribution

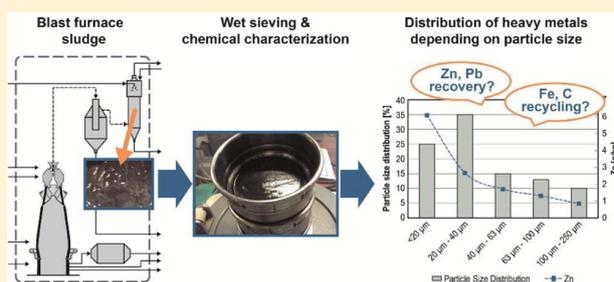
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## Supporting Information

**ABSTRACT:** Blast furnace sludge is a heterogeneous material generated by the wet top gas cleaning process. It consists mainly of Fe, O, and C and contains major amounts of Si, Al, and Mg. Besides these elements, the sludge also contains trace metals such as Cd, Zn, and Pb. Reliable information about the total contents and distribution of the elements present in blast furnace sludge is of importance for hot metal production as some of them should preferably be recycled (Fe, C) and others (Cd, Zn, or Pb) are of environmental concern. Hence, the aim of the present study was to investigate the composition of blast furnace sludge with respect to the separation of desirable from undesirable elements. For this purpose, blast furnace sludge samples have been taken and analyzed with regard to particle size distribution (using wet sieving) and their respective contents of Fe, Zn, Pb, Cr, Ni, Cd, and C. The results of the analyses demonstrate that the concentration of the elements investigated significantly depends on the particle size. Coarser particles (>100  $\mu\text{m}$ ) are characterized by higher contents of C, whereas fine grained particles (<20  $\mu\text{m}$ ) show an enrichment of Fe and a significant accumulation of the heavy metals Zn, Pb, and Cd, which is attributed to their condensation on the particles' surfaces. The content of Cr and Ni in blast furnace sludge is largely independent of the particle size.



## 1. INTRODUCTION

Blast furnace sludge is generated during hot metal (HM) production. It represents an industrial waste derived from wet top gas cleaning of the blast furnace. The blast furnace sludge contains high contents of Fe, C, and O<sup>1-4</sup> and major amounts of Si, Al, Ca, Mg, and K.<sup>3-6</sup> Besides these elements, the sludge is characterized by the contents of various trace metals of environmental concern, including Zn, Pb, Cd,<sup>1-3,5</sup> and Hg.<sup>7</sup> Furthermore, Zn and Pb are also relevant for the blast furnace process itself because these elements may damage the lining<sup>8,9</sup> or the tuyere refractory<sup>8,10</sup> or weaken the strength of tuyere coke (in the case of Zn).<sup>11</sup>

In general, blast furnace sludge contains undesired as well as valuable elements. This distinction, however, depends on the utilization path of the sludge. Blast furnace sludge can either be internally recycled at the sinter plant in order to subsequently utilize Fe and C in the blast furnace, when the Zn and P contents are low enough for the sinter plant, or the sludge can present a potential source for the recovery of Zn or Pb. Hence, several studies addressing the removal of Zn and Pb from blast furnace sludge have been conducted. All of them followed one of the subsequently described approaches. In one group of studies, hydrometallurgical methods (leaching) have been applied to separate Zn and Pb from the sludge. The focus of these studies was either on the recovery of these two elements<sup>4,12-15</sup> or the removal of Zn and Pb from the sludge in order to generate a material that can be internally recycled in

the sinter plant.<sup>5</sup> In another group of studies, the separation of both elements by mechanical methods, e.g., hydrocyclones,<sup>16-18</sup> has been investigated. The aim of these studies was to obtain a sludge fraction with low contents of heavy metals allowing the utilization in the sinter plant.

Not only the heavy metal contents but also the origin of the dust particles is of particular interest for their separation. The sludge can consist of either mechanically or chemically formed particles.<sup>6</sup> The heavy metals themselves may either condense on existing fly ash particles or condense and coalesce as submicron aerosols if local supersaturation conditions exist. Furthermore, they can chemically or physically adsorb to particles. Species with higher vapor pressure may remain in the vapor phase unless they reach condensation temperatures.<sup>19</sup> This might be the case not only within the blast furnace process but also outside the furnace (either in the dust bag or in the wet scrubber).

To the knowledge of the authors, investigations regarding the distribution of heavy metals (e.g., Cd, Ni, Cr, and Pb) in terms of the particle size of the blast furnace sludge are limited. Most studies were carried out in the 1980s e.g. refs 20 and 21. However, since that time not only have process conditions and

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input materials (e.g., utilization of alternative reducing agents that might increase the overall input of heavy metals) changed significantly, but there is evidently an increasing awareness about “harmful” substances utilized in the process.<sup>22–25</sup> Thus, the phasing out of undesirable heavy metals is still of major importance with respect to the management of blast furnace sludge. Furthermore, recycling of the sludge as an instrument to reduce overall resource consumption for HM production has become increasingly important in the last few decades since the iron and steel industry is under pressure to increase its resource efficiency e.g. refs 26–28.

In the present work sludge derived from the wet off-gas cleaning of a blast furnace with a daily production rate of 8,500 t of HM and operated under a counter-pressure at the blast furnace throat was sampled and analyzed. The particle size distribution of the material was obtained by wet sieving. The sieve fractions were characterized with respect to their trace metal contents of Cr, Ni, Pb, Zn, and Cd as well as their major components, Fe and C. Furthermore, the reason for the accumulation of Zn, Pb, and Cd at smaller particles was discussed. Special emphasis was given to the mass distribution of the elements with regards to the separation potential of desirable from undesirable elements present in the sludge.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The material used in this study was blast furnace sludge from a wet off-gas cleaning system installed at an integrated steel plant. The samples were taken from a pipe which is placed directly behind a mixing tank for the scrubber sludge. Each sample contained approximately 750 mL of sludge. The samples were taken under regular operating conditions but on different days so as to reflect different input materials and process conditions. In total, 76 samples were taken during a period of 4 weeks. Since the total content of the elements under investigation did not change significantly, three samples were randomly chosen for the detailed investigations described in this paper.

During the sludge sampling period, the iron bearing materials (including sinter, lump iron ore, pellets and alternative input materials) showed a Fe content of at least 470 g/kg. The Cr and Ni content of the different input materials ranged from 3–560 mg Cr/kg and 7 to 140 mg Ni/kg. For Cd, the chemical analysis of the burden material revealed contents below the limit of quantification (LOQ = 0.5 mg/kg). This, however, does not imply a complete absence of Cd in the burden material. For the alternative reducing agents (e.g., waste plastics, crude tare, and heavy fuel oil), Cd contents between 3 and 12 mg/kg were analyzed.

For the Zn and Pb concentrations in the burden material (including iron ores, iron ore pellets, sinter, etc.), values in the range of 1 to 177 mg Zn/kg and 1 to 8 mg Pb/kg were determined during the period of sampling. In comparison, the alternative reducing agents, which are injected via the tuyeres, reached Zn concentrations of up to 1,000 mg/kg and Pb concentrations of up to 250 mg/kg. Detailed information about the contents of the different elements in the input material utilized is provided in Table S1 of the [Supporting Information](#).

**2.2. Analyses.** The particle size distribution of the blast furnace sludge was determined by wet sieving. The resulting sieve fractions were subsequently analyzed for their concentrations of Fe, Zn, Pb, Cr, Ni, and Cd by means of ICP-OES and the content of C by means of elemental analysis.

The samples were processed and analyzed according to the following procedures:

- **Particle size distribution**

Two sieving towers were used for the wet sieving. The first one consisted of sieves with a mesh size of 63, 100, and 250  $\mu\text{m}$  and a sieve diameter of 150 mm. The second sieving tower included sieves with a mesh size of 40 and 20  $\mu\text{m}$  and a sieve diameter of 80 mm. The sieving amplitude applied was 3 mm for the sieves with the larger mesh size and 8 mm for the smaller ones (utilizing a Fritsch Analysette 3Pro Vibratory Sieve Shaker). Ethanol (VWR Chemicals, 96% vol, c.p.) was used as a sieving auxiliary agent due to the high surface tension of the samples.

The wet sieving was carried out for each sample as follows:

The total sample was homogenized by manually shaking the sampling bottle for 3 min. Approximately half of the sludge sample was placed in the first sieving tower. The suspensions, including undersized particles passing the 63  $\mu\text{m}$  sieve, were collected. This suspension was further sieved by the second sieving tower. The particles smaller than 20  $\mu\text{m}$  (of the second tower) were collected as well.

The total sieving time (for both towers) amounted to approximately 2.5 h. Depending on the behavior of each sample during the sieving procedure, the sieving time had to be slightly adjusted in order to ensure that the liquid phase passed each sieve of the sieving tower. In total, 50 mL of the sieving auxiliary agent was used per sample.

Each of the 6 sieve fractions (<20  $\mu\text{m}$ , 20–40  $\mu\text{m}$ , 40–63  $\mu\text{m}$ , 63–100  $\mu\text{m}$ , 100–250  $\mu\text{m}$ , > 250  $\mu\text{m}$ ) was filtered with a filter paper (Macherey-Nagel, Reference-Number 203012) and subsequently dried at 105 °C until their weight remained constant in order to determine their dry weight.

- **Determination of elemental composition**

The dried fractions were analyzed for their elemental composition. In particular, the contents of Fe, C, Cr, Ni, Zn, and Pb have been determined. Thereto the following procedure has been applied:

- **ICP-OES:**

The dried sludge fractions were homogenized, and a subsample with a mass of 1 g was taken with a spatula from each particle size fraction. The subsamples obtained were used for the closed microwave digestion. The samples were digested in Teflon vessels (HPR 1000) using 2 mL of H<sub>2</sub>O, 1 mL of HNO<sub>3</sub>, and 7 mL of HCl in the microwave oven (Model: MLS Start 1500). The digestion parameters are given in the [Supporting Information](#) Table S3.

The determination of Cr, Ni, Pb, Zn, Cd, and Fe concentrations of the sieve fractions was done using an inductively coupled plasma optical emission spectrometer Horiba Jobin Yvon ULTIMA 2. A customized multielement standard was used for the calibration. This standard was prepared by utilizing single element standards from Merck and Roth for all elements investigated. Furthermore, the calibration standard was doped with 4 g Fe/L by utilizing FeCl<sub>3</sub> for matrix compensation.

For the measurement the following wavelengths were used: Cd: 228.802 nm, Cr: 267.716 nm, Fe: 234.349 nm, Ni: 221.647 nm, Pb: 220.353 nm, Zn: 213.856 nm.

The results were determined using a max-mode function and were averaged over a triple determination.

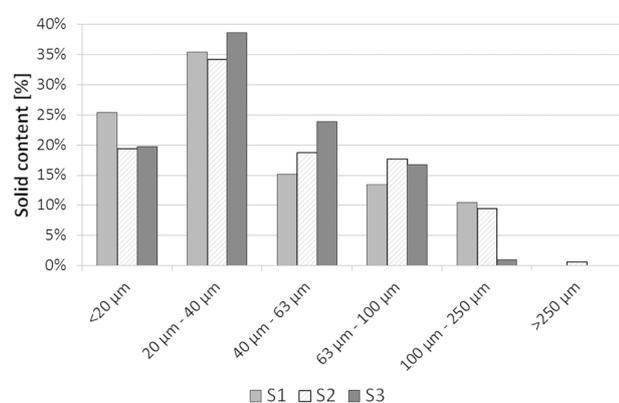
- Elemental analysis:

The C content was determined using an elemental analyzer (Elementar VARIO Macro EA-CHNS analyzer). Thereto 20 mg of the different sludge fractions was utilized. For calibrating the analyzer, around 10 mg of sulfanilamide was utilized.

The utilized chemicals for the analyses include deionized H<sub>2</sub>O (Millipore Direct-Q, 0.05  $\mu$ S/cm at 25 °C), HCl (Merck Suprapure, 30%), HNO<sub>3</sub> (Merck Emsure, 65% for analyses), and FeCl<sub>3</sub> (Fe(III)Cl<sub>3</sub>·H<sub>2</sub>O p.a., Roth).

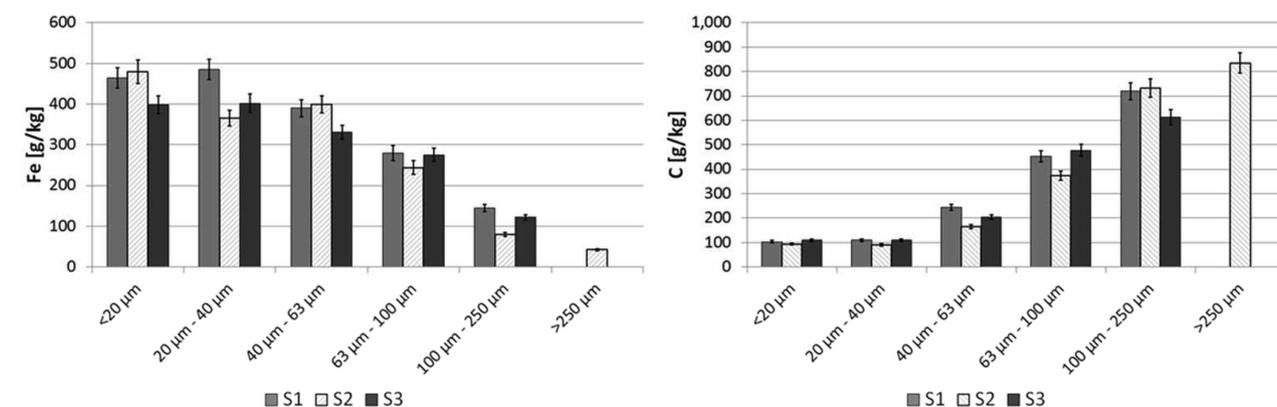
### 3. RESULTS AND DISCUSSION

**3.1. Particle Size Distribution.** Altogether 6 classes of particle sizes are distinguished. The results of these analyses are summarized in Figure 1. Although slight differences in the



**Figure 1.** Particle size distribution for three blast furnace sludge samples.

particle size distribution of the samples analyzed (S1, S2, and S3) are observable, it becomes obvious that the grain size between 20 and 40  $\mu$ m represents the dominant fraction. More than one-third of the solid particles' mass can be attributed to this particular fraction. In total, more than 70% of the sample mass are characterized by a grain size smaller than 63  $\mu$ m. Particles larger than 250  $\mu$ m were only observed for one sample (S2). In contrast, for sample S3 almost all particles were smaller than 100  $\mu$ m.



**Figure 2.** Fe and C content (given in g/kg) in different sieve fractions of three sludge samples.

In general, the particle size distribution (considering all sieve fractions) is rather similar for the three samples, although the process conditions might have been different since the samples were taken on consecutive working days.

**3.2. Elemental Composition of the Sieve Fractions.** Subsequent to the determination of the particle size distribution, the concentrations of Fe, C, Cr, Ni, Cd, and Zn of the different sieve fractions were analyzed.

Our investigations regarding the two major constituents (Fe and C) show opposing trends with respect to the correlation of the concentration and the particle size (see Figure 2). The results clearly indicate that Fe contents are highest in the small grained particles (up to 500 g/kg for <20  $\mu$ m) and decrease with increasing grain size (<150 g/kg for 100–250  $\mu$ m). In contrast, the concentration of C increases from 100 g/kg (<40  $\mu$ m) to more than 600 g/kg (100–250  $\mu$ m) with increasing particle size.

Ni and Cr concentrations observed are nearly equal for all sieve fractions (from <20 to 100  $\mu$ m–250  $\mu$ m), except for sample S3, which shows a 50% higher Ni content in the fraction <20  $\mu$ m.

In general, it can be noticed that the overall Ni and Cr concentrations are slightly different for the different sludge samples S1, S2, and S3 taken (see Figure 3), indicating that the composition of the sludge may have varied over time. This variation can be traced back to the fact that the sludge composition strongly depends on the composition of the different input materials utilized in the blast furnace process.

We also determined the Zn and Pb distribution in the different sieve fraction since these elements are harmful for the blast furnace process and are hence to be phased out. In addition, they also influence the recyclability of the sludge e.g. refs 10, 11, and 29. Zn and Pb contents of the different sieve fractions show a similar behavior as observed for Fe: concentrations decrease with increasing particle sizes. This trend is apparent for all three samples analyzed (see Figure 4).

In comparison to Fe the contents of Pb and Zn significantly increase in the smallest grain fractions. Whereas for Fe only a minor accumulation (<15%) was observed for the sieve fraction <20  $\mu$ m in comparison to the fraction 40–63  $\mu$ m, for Pb and Zn an increase of factor 3 to 6 was detected when comparing the concentration of these two particle sizes.

For almost all sieve fractions analyzed, it turned out that those of sample S3 showed the highest concentrations of Pb and Zn, which might either be attributed to higher Pb and Zn

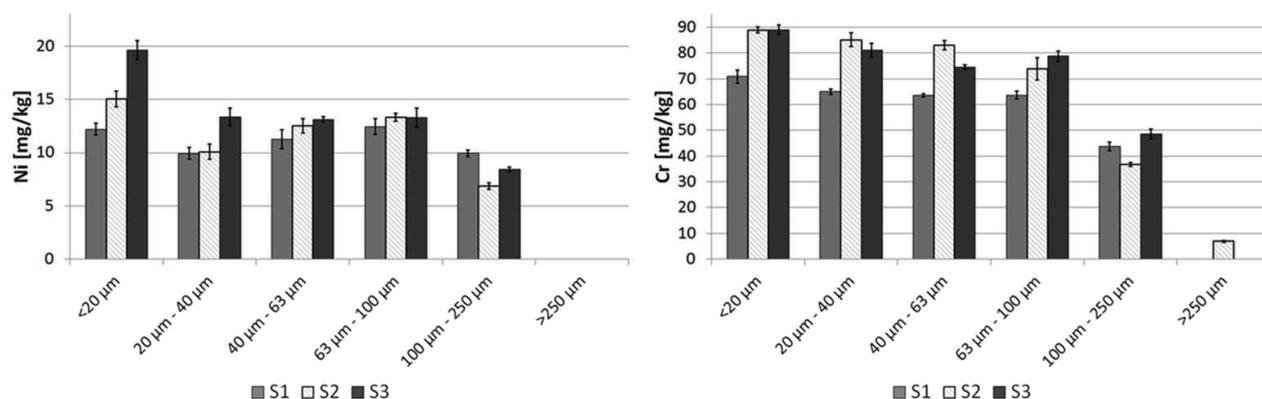


Figure 3. Cr and Ni content (given in mg/kg) in different sieve fractions of three sludge samples.

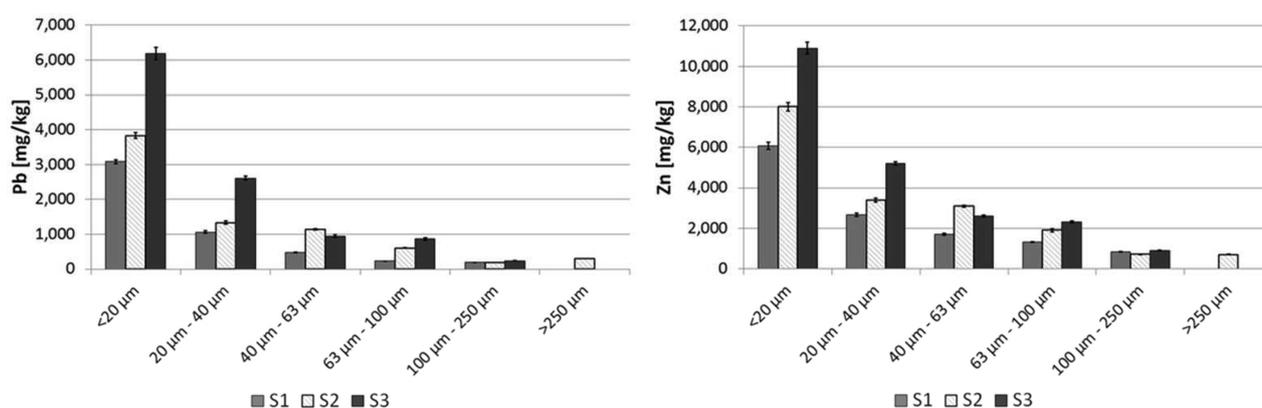


Figure 4. Pb and Zn content (given in mg/kg) in different sieve fractions of three sludge samples.

of the charging materials or (more likely due to the behavior of these elements in the blast furnace) to (slightly) different process conditions, which might have enhanced the discharge of Zn and Pb via the top gas.

The results obtained for Pb and Zn are also in line with observations presented by, e.g., Toda, Furutaku, Takahashi, Futamura, and Kitazawa<sup>20</sup> and Heijwegen and Ijmuiden.<sup>21</sup> They noticed a significant increase in Zn and Pb contents with decreasing particle size. The maximum concentrations determined by Heijwegen and Ijmuiden<sup>21</sup> (Zn  $\sim$  35,000 mg/kg, Pb  $\sim$  10,000 mg/kg for particle size fraction  $<5\ \mu\text{m}$ ), however, were considerably higher than our observations although the specific amounts of Zn inserted into the blast furnace were almost identical (120 to 130 g Zn/t HM reported by Heijwegen and Ijmuiden;<sup>21</sup> our study 131 g Zn/t HM, see Supporting Information Table S2). One explanation for the higher contents of Zn and Pb observed by Heijwegen et al. might be the smaller particle size of the sludge fraction analyzed.

Furthermore, we investigated the distribution of Cd in the blast furnace sludge since this element is of major environmental concern.<sup>30,31</sup> The pattern of the Cd concentration in different sieve fractions is comparable to those observed for Pb and Zn. The content of Cd significantly increases with decreasing particle size (see Figure 5).

Thus, analogous to Zn and Pb, an enrichment of Cd at fine flue dust particles might take place due to inner circulation processes (evaporation and condensation processes).<sup>32</sup> These

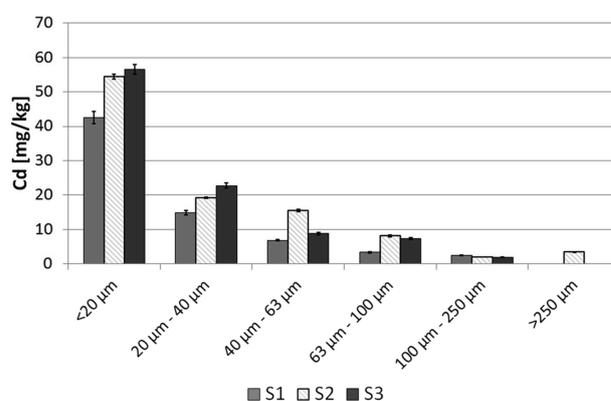


Figure 5. Cd content (given in mg/kg) in different sieve fractions of three sludge samples.

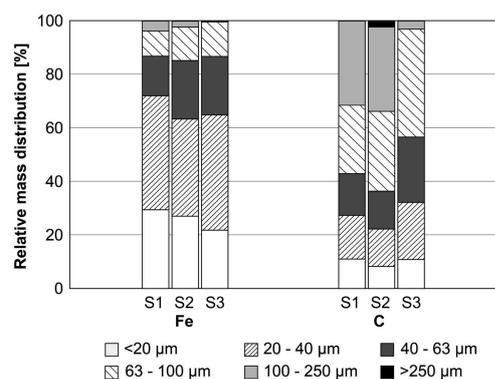
processes and their impacts on the sludge composition are further addressed in section 3.4.

**3.3. Mass Distributions.** In terms of recyclability of the blast furnace sludge, the mass distributions of the elements investigated are of major interest. To obtain the mass distributions, the mean concentration of each sieve fraction of the respective element was multiplied with the mean mass of the respective sieve fraction (see results of Figure 1).

With respect to the sludge recycling at the sinter plant, not only is the mass distribution of the valuable substances (Fe, C) of interest but also those of the problematic elements such as

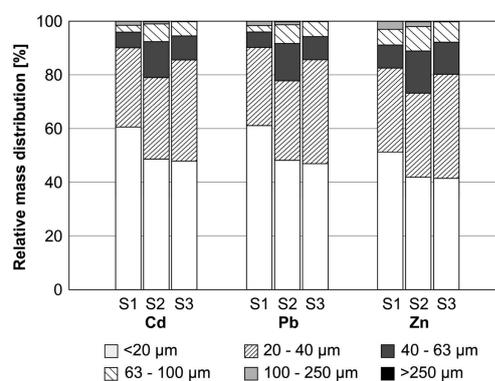
Zn and Pb. Both may negatively influence process stability when recycled since they are able to damage the blast furnace lining as well as the tuyere refractory and weaken the strength of the blast furnace tuyere coke e.g. refs 8–11.

The distribution of the elements that should preferably be recycled (Fe and C) is quite diverse. Whereas for C the major part (more than 45% of total C) is present in particles larger than 63  $\mu\text{m}$ , the biggest share of Fe (about two-thirds of total Fe) is present in the particles <40  $\mu\text{m}$  (see Figure 6).



**Figure 6.** Relative mass distribution of Fe and C in the different particle size fractions of the sludge samples (S1, S2, and S3).

The elements Cd, Pb, and Zn are all characterized by a quite similar mass distribution (see Figure 7). The most important

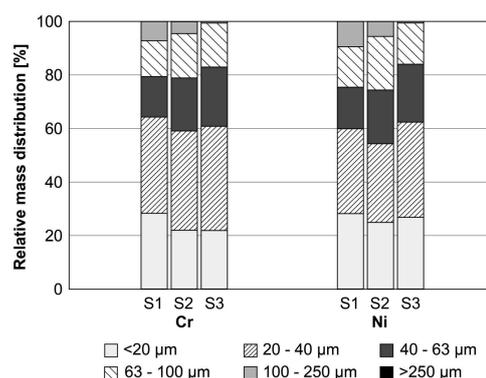


**Figure 7.** Relative mass distribution of Cd, Pb, and Zn in the different particle size fractions of the sludge samples (S1, S2, and S3).

particles in terms of mass fraction for these three metals represent the sieve fraction “<20  $\mu\text{m}$ ”. These fractions contain more than 40% of the total mass of these metals present in the sludge. Another 35% of the total mass of Cd, Pb, and Zn is contained in the second smallest particle fraction, “20–40  $\mu\text{m}$ ”. This means that in order to phase out more than 70% of Cd, Pb, and Zn, particles smaller than 40  $\mu\text{m}$  would have to be separated for disposal, which also implies that more than 40% by mass of Fe present in the sludge would need to be landfilled in the case that a mechanical separation is chosen.

For Cr and Ni the contribution of the different sieve fractions to the total mass is almost identical to the contribution of Fe. Around 60% of total Cr and Ni are present in particles smaller than 40  $\mu\text{m}$  (see Figure 8).

**3.4. Origin of Sludge Particles.** The solid particles of the blast furnace sludge may originate from either the upper part of



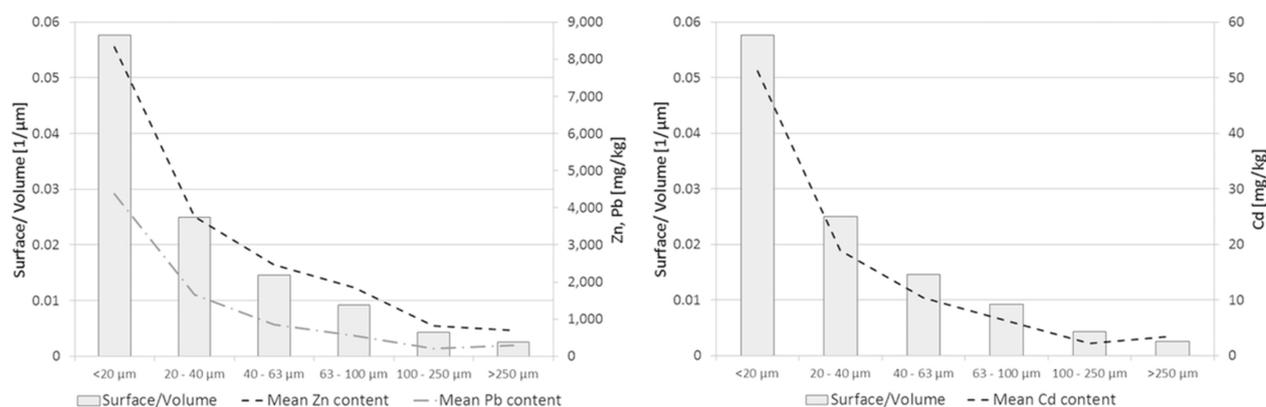
**Figure 8.** Relative mass distribution of Cr and Ni in the different particle size fractions of the sludge samples (S1, S2, and S3).

the blast furnace shaft (due to abrasion during charging) and/or from the lower part of the furnace. In the case that the particles stem from higher temperatures zones (lower part) of the furnace, they might result from abrasion of the charging materials during their downward movement, from fine particles of injected materials or from condensation processes. The condensation may lead to the formation of new solid particles or may alter the composition of existing particles (due to condensation on the particle surface).

The distribution of the elements Ni and Cr in the sludge, however, is only affected by the abrasion of the charging materials. Evaporation and condensation of these two elements can hardly be observed, simply due to their relatively high melting temperature (Cr: 1907  $^{\circ}\text{C}$ , Ni: 1455  $^{\circ}\text{C}$ )<sup>33</sup> and boiling points (Cr: 2671  $^{\circ}\text{C}$ ; Ni: 2913  $^{\circ}\text{C}$ ).<sup>33</sup> The latter are definitely above the temperatures prevailing in the blast furnace. There the highest temperature of about 2400  $^{\circ}\text{C}$  is observed in the front of the blast furnace tuyeres, making it most unlikely that Cr and Ni are transferred via evaporation and condensation to other particles. This hypothesis is supported by the fact that the Ni and Cr concentrations of the different sieving fractions are in the same magnitude as the ones detected in the input materials (the mean concentration of Cr and Ni in the burden materials amounts to 99 mg/kg and 14 mg/kg, respectively).

In contrast, the chemical analyses of the different sieving fractions suggest a different origin of the elements Zn, Pb, and Cd. It is shown that the Zn and Pb contents of the coarse particle fractions (>100  $\mu\text{m}$ ) were the lowest (<1,000 mg Zn/kg and <250 mg Pb/kg). Nevertheless, even these concentrations are higher than the Pb and Zn content of the main burden and alternative reducing materials utilized (see Supporting Information Table S1). This significant increase in Pb and Zn contents in the blast furnace sludge indicates a considerable accumulation of Zn and Pb on the solid particles that are carried out of the furnace and finally end up in the sludge of the wet top gas cleaning.

This accumulation arises from the characteristic behavior of Zn and Pb in the blast furnace process. Both elements are known to take part in an inner circulation process in the blast furnace based on evaporation and condensation processes e.g. refs 34 and 35. Hence, a significant amount of Zn and Pb condenses on the surface of finer particles which subsequently leave the furnace via the top gas and finally end up in the blast furnace sludge. For Cd, such a circulation process might also take place.<sup>32</sup> However, to the knowledge of the authors, in-depth investigations in this context are lacking.



**Figure 9.** Ratio between surface and volume of the particles present in the blast furnace sludge; mean Zn, Pb, and Cd contents for different sieve fractions.

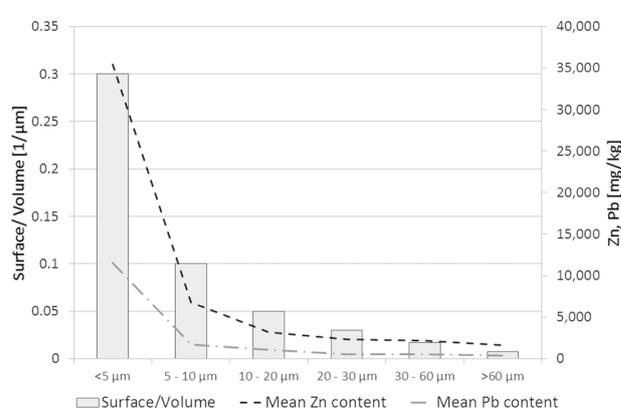
The hypothesis that most of the Pb and Zn as well as Cd present in the sludge results from condensation processes on the particles surface is supported by an almost identical trend of Zn, Pb, and Cd contents and the ratio between surface and volume (mass) of the particles present in the different sieve fraction (see Figure 9). This means that the Zn, Pb, and Cd contents observed are a result of metal condensation: The smaller the sludge particles, the higher the ratio between surface and mass of the particles becomes, which inevitably leads to higher contents of metals that condensate at the particle surface (e.g., Zn, Pb, Cd). Thereby, we did not distinguish between C and Fe based particles. This assumption can be justified by ongoing research work regarding the characterization of the particles by means of LA-ICP-MS (preliminary results are given in Achleitner<sup>36</sup>). These results indicate that heavy metals can be found at the surface of both types of particles. Thus, the more complex structure of the C based particles seems not to enhance the condensation of the heavy metals on these particles.

In Figure 9 the contents of Zn and Pb are compared to the ratios between the surface and volume of the particles present in the different sieve fractions. For this theoretical ratio between the surface and volume of the particles representative for the different sieve fractions, a mean particle size of the respective sieve fraction and an ideal spherical shape of these mean particles were assumed. The values calculated for the surface/volume ratio are given in Table S4 of the Supporting Information.

The correspondence between heavy metal contents (Zn, Pb, and Cd) and the surface/volume ratio of the particles can also be noticed for the investigations conducted by Heijwegen and Ijmuiden.<sup>21</sup> They described the Zn and Pb content of the blast furnace sludge in a particle size range of <5 μm to >60 μm. By calculating the surface to volume ratio and comparing it to the Zn and Pb concentration (using their data reported), a trend similar to our investigations is observable (see Figure 10; Supporting Information Table S5).

#### 4. CONCLUSION

Blast furnace sludge samples were taken under real process conditions on consecutive working days and characterized according to their particle size distribution and chemical constitution (Fe, C, Ni, Cr, Zn, Pb, and Cd). Special emphasis was given to the characterization of the mass distribution of the



**Figure 10.** Ratio between surface and volume of the particles present in the blast furnace sludge; mean Zn and Pb contents for different sieve fractions based on data from Heijwegen and Ijmuiden.<sup>21</sup>

elements investigated since these findings provide valuable information regarding the recyclability of this material.

The particle size distribution obtained shows that a major part of the sludge (70%) is characterized by particles smaller than <40 μm. This result is also in accordance with former studies conducted by, e.g., Ma.<sup>17</sup>

The chemical analysis demonstrated that the concentration of the elements considered strongly depends on the particle size. Thereby, the main elements (Fe and C) exhibited contrary behavior. Fe concentration increases with decreasing particle sizes, while the C concentration decreases with decreasing particle size. The contents of Zn, Pb, and Cd showed a similar trend to that of Fe. Nevertheless, their dependence on the particle size is much more pronounced, which might be attributed to the condensation of these metals on the particle surface (see below). Ni and Cr concentrations observed were nearly equal for all particle size fractions.

Furthermore, comparing Zn, Pb, and Cd contents of the sludge with their concentration in the different input materials utilized indicates a significant enrichment of these metals in the blast furnace sludge. This observation is traced back to the specific behavior of Zn, Pb and Cd, which circulate within the blast furnace by evaporating at higher temperatures and condensing at lower temperatures. The condensation of the metals most likely occurs at the surface of particles, which (depending on their size) may move downward with the

burden material or end up in the scrubber sludge. The hypothesis that contents of Zn, Pb, and Cd observed in the sludge largely result from metal condensation on the particle surface is supported by the fact that differences in metal contents observed between different sieve fractions correspond well to the changes in the ratio of surface to volume of the respective particles. Furthermore, first research results describing the structure of the sludge particles confirmed that the heavy metals are found on the surface of the particles, which might allow leaching the metals from surface using acidic agents. Nevertheless, further research is needed to map the distribution of the different heavy metals on the sludge particles in more detail. These findings would provide a better understanding concerning the dust formation mechanisms in the blast furnace process and also to decide upon the appropriate strategy for metal recovery/separation.

Information about the distribution of the elements in the different particle size fractions of the sludge is crucial for its treatment (separation) and subsequent recycling. The outcomes of the present study demonstrate that by separating the particles " $<40\ \mu\text{m}$ " a reduction in the overall Zn, Pb, and Cd load in the sludge of about 80% would be possible. Although such a separation would be desired for sludge recycling at the sinter plant in order to decrease the contents of undesirable metals (Pb, Zn), in return the separation of particles  $<40\ \mu\text{m}$  would lead to the loss of almost 40% of the Fe present in the sludge. Nevertheless, this share of the sludge (fraction  $<40\ \mu\text{m}$ ) could be interesting for the recovery of Zn and Pb. Several research studies already focus on the recovery of Zn from the blast furnace flue dust e.g. refs 4 and 12. However, it would be of particular interest if this concentrated fraction would allow an economic viable recycling of heavy metals.

Sludge particles  $>40\ \mu\text{m}$  may be internally recycled at the sinter plant since their mean Zn concentration amounts to less than 2,000 mg/kg, Pb concentration to 380 mg/kg, and the Cd content to about 7 mg/kg. Although these concentrations are still higher than in most of the other input materials of the furnace, the total Zn load in this recyclable fraction of the blast furnace sludge is well below the maximum value recommended. According to Remus et al.<sup>37</sup> the maximum Zn load of dusts and sludge recycled at the sinter plant should not exceed 100 g Zn/t HM, which translates into maximum Zn contents in dust and sludge of about 10,000 mg/kg (assuming that 10 kg of dust and blast furnace sludge is recycled per ton of hot metal produced).

In general, it should be noted that the mechanical separation and thus also the quality of separation is not only influenced by the particle sizes themselves but also by the density of the particles. For C carrying particles (abrasion of coke) the density is significantly smaller than for other particles consisting mainly of Fe (or other main elements such as, e.g., Si). Thus, despite differences in the size of iron and carbon carrying particles, some of them show the same sedimentation rate and may hence not be separated from each other by physical processes. In this case chemical separation might be favorable. However, in order to evaluate the pros and cons of mechanical and chemical processes, further research on the separation efficiency and factors influencing this efficiency (such as, e.g., chemicals utilized) is needed.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b00617.

Concentration of input materials, input amount of Zn, Pb, Cd, Cr, Ni, Fe, and C in the blast furnace, digestion parameters, microwave oven program utilized, calculation of surface to volume ration for measurement data and data from the literature, detailed measurement results (PDF)

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### Notes

The authors declare no competing financial interest.

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## Supporting Information

### Characterization of blast furnace sludge with respect to heavy metal distribution

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**Table S 1: Concentration of Input Materials**

	Fe	C	Cr	Ni	Zn	Pb	Cd
	[%]		[mg/kg]				
Sinter	51 - 53	0.05 - 0.2	200 - 233	33 - 43	163 - 177	6 - 7	<0.5
Lump iron ore	64 - 65	0.06	80 - 220	10 - 20	2 - 10	4 - 8	<0.5
Pellets	62 - 63	0.02 – 0.08	50 - 340	10	1 - 21	1 - 8	<0.5
Alternative input materials	47 - 54	0.1 - 5	80 - 560	10	2 - 111	4 - 7	<0.5
Coke	n.d.	97 - 98 <sup>1</sup>	29 - 30	16 - 17	9 - 11	7	<0.5
Alternative reducing agents	n.d.	n.d.	3 - 80	7 - 140	41 – 1,000	4 - 250	2 - 7

**Table S 2: Input amount of Zn, Pb, Cd, Cr, Ni, Fe, C**

	Zn	Pb	Cd <sup>2</sup>	Cr	Ni	Fe	C
	[g/t HM]				[kg/t HM]		
Sinter	110	4	-	136	24	351	5
Lump iron ore	0.93	0.89	-	37	4	124	0.1
Pellets	7.4	1.5	-	152	6	502	0.4
Alternative input materials	2.4	0.2	-	38	0	32	2
Coke	1.9	2.3	-	6	4	-	207
Alternative reducing agents	8.6	4.4	-	1	1	-	-
<i>SUM</i>	<i>131</i>	<i>14</i>	<i>-</i>	<i>370</i>	<i>39</i>	<i>1008</i>	<i>214</i>

**Table S 3: Digestion parameters – Microwave oven program**

Step	Time	Power	Temperature
[-]	[min:ss]	[W]	[K]
1	04:30	1000	413
2	03:30	1000	473
3	04:00	1000	513
4	48:00	1000	513
5	30:00		Ventilation

**Table S 4: Calculation of surface to volume ratio and mean Zn, Pb and Cd concentration for measurement data**

Mean diameter	Mesh size	Surface	Volume	Surface/Volume	Mean Zn content	Mean Pb content	Mean Cd content
[μm]		μm <sup>2</sup>	μm <sup>3</sup>	[1/μm]	[mg/kg]		
13	<20	531	9203	0.058	8326	4368	51.2
30	20 - 40	2827	113097	0.025	3756	1668	19.0
51.5	40 - 63	8332	572151	0.015	2473	856	10.4
81.5	63 - 100	20867	2267574	0.009	1847	566	6.3
175	100 - 250	96211	22449298	0.004	821	207	2.1
300	>250	282743	113097336	0.003	698	300	3.5

<sup>1</sup> waf (water and ash free)

<sup>2</sup> Cd contents < Limit of Quantification for the sampling period

Table S 5: Calculation of surface to volume ratio and mean Zn, Pb and Cd concentration based on measurement data from Heijwegen, et al. <sup>[21]</sup>

Mean diameter	Mesh size	Surface	Volume	Surface/Volume	Mean Zn content	Mean Pb content
[ $\mu\text{m}$ ]		$\mu\text{m}^2$	$\mu\text{m}^3$	[ $1/\mu\text{m}$ ]	[mg/kg]	
2.5	<5	20	65	0.300	35500	11500
7.5	5 - 10	177	1767	0.100	6800	1700
15	10 - 20	707	14137	0.050	3200	1100
25	20 - 30	1963	65450	0.030	2300	500
45	30 - 60	6362	381704	0.017	2200	500
100	>60	31416	4188790	0.008	1600	400

Table S 6: Measurement results for samples S1, S2, S3 for Cd, Cr, Fe, Ni, Pb, Zn and C

	Cd	Cr	Fe	Ni	Pb	Zn	C
	[mg/kg]		[g/kg]	[mg/kg]			[g/kg]
S1							
<20 $\mu\text{m}$	42.5	70.9	463.7	12.2	3083	6072	103
20 $\mu\text{m}$ - 40 $\mu\text{m}$	14.9	65.0	484.5	9.9	1060	2668	110
40 $\mu\text{m}$ - 63 $\mu\text{m}$	6.9	63.6	389.8	11.3	481	1706	245
63 $\mu\text{m}$ - 100 $\mu\text{m}$	3.4	63.7	279.1	12.5	230	1314	453
100 $\mu\text{m}$ - 250 $\mu\text{m}$	2.5	43.8	144.7	10.0	191	843	719
>250 $\mu\text{m}$	0.0	0.0		0.0	0	0	
S2							
<20 $\mu\text{m}$	54.4	89.0	479.5	15.1	3835	8005	94
20 $\mu\text{m}$ - 40 $\mu\text{m}$	19.2	85.1	365.0	10.1	1334	3396	90
40 $\mu\text{m}$ - 63 $\mu\text{m}$	15.4	83.0	399.7	12.6	1143	3101	166
63 $\mu\text{m}$ - 100 $\mu\text{m}$	8.1	73.9	244.0	13.3	607	1901	373
100 $\mu\text{m}$ - 250 $\mu\text{m}$	2.0	36.8	79.7	6.9	187	718	732
>250 $\mu\text{m}$	3.5	6.9	42.2	0.0	300	698	835
S3							
<20 $\mu\text{m}$	56.6	89.1	398.5	19.6	6187	10900	109
20 $\mu\text{m}$ - 40 $\mu\text{m}$	22.8	81.2	402.2	13.4	2608	5205	110
40 $\mu\text{m}$ - 63 $\mu\text{m}$	8.8	74.5	331.1	13.1	945	2614	204
63 $\mu\text{m}$ - 100 $\mu\text{m}$	7.4	78.7	275.4	13.3	860	2327	477
100 $\mu\text{m}$ - 250 $\mu\text{m}$	2.0	48.6	121.8	8.4	242	901	613
>250 $\mu\text{m}$							

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## Herausforderungen für die Umweltüberwachung von Industrieprozessen – Fallstudie: Pb im Hochofenprozess

**Abstract:** Die Stoffflussanalyse stellt ein geeignetes Instrument zur Umweltüberwachung von Industrieprozessen dar. Allerdings müssen bei der Anwendung Faktoren wie beispielsweise repräsentative Probenahme oder der Einsatz geeigneter analytischer Methoden berücksichtigt werden. Letzteres ist insofern von Bedeutung da umweltrelevante Stoffe zumeist nur in sehr geringen Konzentrationen auftreten. Am Beispiel der Stoffflussanalyse des Hochofenprozesses für Blei werden Kriterien, die die Qualität der Ergebnisse dieser Methode beeinflussen, diskutiert und mögliche Verbesserungspotentiale aufgezeigt.

### 1 Einleitung

Der Hochofenprozess stellt eine der wichtigsten Verfahrensrouten für die Roheisenerzeugung dar. Im Jahr 2014 wurden rund 95 Mt (EU28) an Roheisen mittels des Hochofenprozesses hergestellt [1]. Die Einsatzstoffe, die für die Produktion benötigt werden, bestehen dabei hauptsächlich aus Eisen oder Kohlenstoff. Allerdings werden durch die verschiedenen Inputmaterialien auch weitere Elemente in den Hochofen eingebracht, die sich entweder negativ auf die Prozessführung (z.B. Blei, Zink), die Produktqualität beeinflussen können (z.B. Chrom, Schwefel) und/ oder umweltrelevant (z.B. Cadmium, Quecksilber) sind.

Zur Überwachung dieser prozess-, produkt- und umweltrelevanten Elemente stellt die Stoffflussanalyse (SFA) ein geeignetes Instrument dar. Diese erlaubt das Verhalten der betrachteten Elemente zu analysieren und deren Transferkoeffizienten für den betrachteten Prozess zu bestimmen, welche nach ihrer Validierung herangezogen werden um den Probenahme- und Messaufwand in Industrieprozessen zu reduzieren [2, 3].

Allerdings werden für die Durchführung der SFA oft Messwerte herangezogen, die standardmäßig (z.B. auf Grund von Qualitätskontrollen der verschiedenen Input- und Outputmaterialien) erhoben werden. Die Vorgehensweisen, die für die Probenahme und chemische Analytik für diese Fragestellungen gewählt wurden, sind daher meistens nicht für das Monitoring von Elementen geeignet, die nur in Spuren in den verschiedenen Materialien vorkommen. Probenahme von heterogenen und/oder prozessbedingt variierenden Input- und/oder Outputflüssen, Matrixeffekte und Konzentrationen im Spurenbereich stellen eine Herausforderung dar und beeinflussen das Ergebnis der SFA auf Industrieprozesse [4].

Im Folgenden werden am Beispiel von Blei im Hochofenprozess einige Schlüsselfaktoren hinsichtlich der Anwendung der SFA zur Umweltüberwachung von Industrieprozessen diskutiert und das mögliche Verbesserungspotential aufgezeigt.

## 2 Material und Methoden

Die Herausforderungen der Anwendung der SFA werden anhand des Hochofenprozesses demonstriert. Dafür sind Mittelwerte basierend auf Messwerten, die innerhalb eines Jahres vom Anlagenbetreiber regelmäßig bestimmt werden, für alle Input und Outputflüsse verfügbar. Diese Werte umfassen sowohl Massen-, Volumenstrommessungen als auch Konzentrationsmessungen (u.a. für Pb, Zn, Cr, Ni, Cd, Hg) und werden zur Erstellung einer SFA für Blei herangezogen. Der Bilanzzeitraum erstreckt sich dabei über 9 Jahre (von 2005 bis 2013).

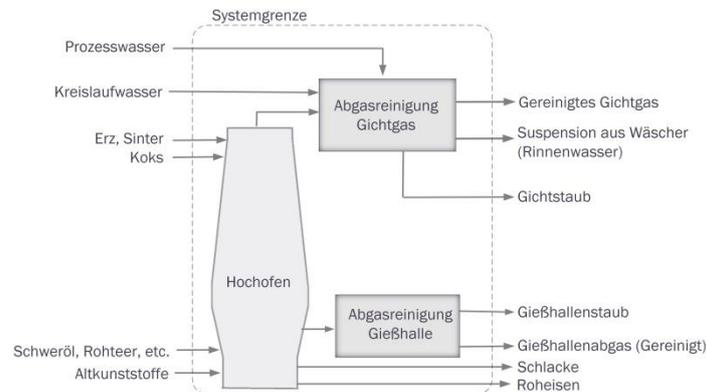


Abb. 1: Modell Hochofenprozess für SFA (basierend auf Trinkel, Cencic [4])

Des Weiteren wurden 35 Roheisenproben in einer zusätzlichen Messreihe analysiert. Dabei wurden die Proben mithilfe unterschiedlicher Messverfahren (Röntgenfluoreszenzanalyse (RFA) und die Funkenemissionsspektrometrie (OES)) auf ihren Pb-Gehalt analysiert. Zusätzlich wurden mittels der RFA beide Probenoberflächen analysiert.

## 3 Ergebnisse und Diskussion

### 3.1 Ergebnisse der SFA für Blei für den Hochofenprozess

Die Blei-SFA für den Hochofenprozess wurde für die Jahre 2005 bis 2013 durchgeführt. Anhand der dabei erhaltenen Ergebnisse wurde ersichtlich, dass die Bilanzdifferenz zwischen Gesamtinput und -output an Blei vor 2007 relativ gering (<10 %) ist und ab 2007 kontinuierlich zunimmt (Max. > 45 %) (siehe Abb. 2).

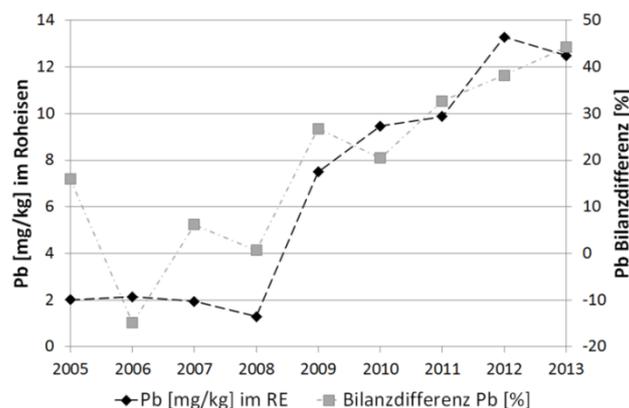


Abb. 2: Pb Gehälter im Roheisen (RE) und Bilanzdifferenzen 2005 - 2013 (erweitert auf Basis von Trinkel et. al. [5])

Eine positive Bilanzdifferenz bedeutet, dass mehr Blei im Output des Hochofens gefunden wird als über sämtliche Inputmaterialien zugeführt wird. Für den gegenständlichen Fall (ab 2008) suggerieren die Ergebnisse der SFA, dass der Input an Blei in den Hochofen signifikant unterschätzt wird. Des Weiteren wurde aus den durchgeführten SFA ersichtlich, dass der Blei-Output über das Roheisen (RE) einen ähnlichen zeitlichen Verlauf aufweist wie die Bilanzdifferenz. Dies spiegelt sich auch im Konzentrationsverlauf für Blei im RE wieder.

Die Jahresmittelwerte der Blei-Gehälter im Roheisen weisen nach dem Jahr 2008 einen deutlichen Sprung auf (von rund 2 mg/kg bis 2008 auf bis zu über 12 mg/kg nach 2008) (siehe Abb. 2). Eine derart signifikante Erhöhung des Gehaltes an Blei im Roheisen kann nicht mit dem Verhalten dieses Elements im Hochofen bzw. einer Änderung der Prozessführung erklärt werden. Blei ist im flüssigen Eisen nicht löslich und neigt auf Grund seiner höheren Dichte dazu sich unter dem Roheisen anzusammeln [6].

### 3.2 Vergleich RFA- und Funkenemissionsspektrometer-Messungen der Roheisenproben

Auf Basis der Ergebnisse der SFA wurden für den Outputfluss Roheisen Konzentrationsmessungen mit zwei verschiedenen Analysemethoden durchgeführt. Dafür wurde der Blei-Gehalt der Proben mittels RFA (Standardmethode für Roheisenproben im regulären Betrieb) sowie mittels Funkenemissionsspektrometer analysiert. Dabei wurde ersichtlich, dass die Messergebnisse der beiden Methoden sich deutlich unterscheiden (siehe Abb. 3) und die Messergebnisse der RFA stets über den Ergebnissen der Funkenemissionsspektrometer liegen. Über die 35 Proben wurde im Mittel ein Blei-Gehalt von 5,2 mg/kg mittels der OES ermittelt, wohingegen die RFA Messungen einen Mittelwert von 20,3 mg/kg aufwiesen. Somit liegen die RFA Gehälter für Blei um Faktor 4 über den Werten des Funkenemissionsspektrometers.

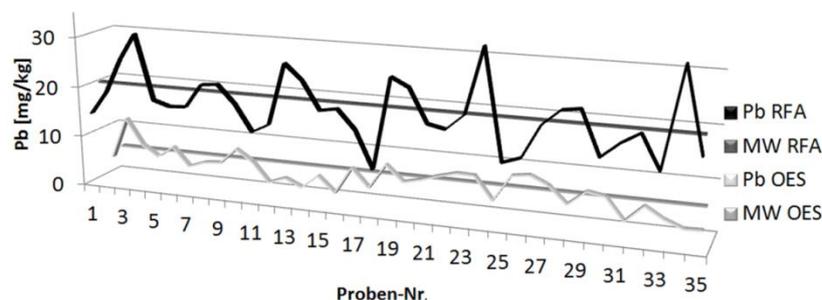


Abb. 3: Vergleichsmessungen der Roheisenproben mittels RFA und OES

Zu den Messungen muss angemerkt werden, dass die Analysen der Roheisenproben mittels RFA hinsichtlich der Produktqualität (z.B. Eisen, Phosphor) optimiert wurden und für Blei an der unteren Grenze des Messbereichs analysiert wird. Daher sind die RFA Messwerte mit einer sehr hohen Wahrscheinlichkeit mit einem großen Fehler behaftet.

### 3.3 Verteilung von Blei in den Roheisenproben

Zur Kontrolle ob Blei in den Roheisenproben gleichmäßig verteilt vorliegt, wurden 6 Proben, die wie auch im regulären Probennahmefall eine zylindrische Form aufweisen, von beiden Seiten hinsichtlich des Blei-Gehaltes analysiert. Dabei wurde festgestellt, dass obwohl die Probenvorbereitung und auch die Messung auf beiden Seiten identisch durchgeführt wurden, unterschiedliche Blei-Gehalte festgestellt wurden (siehe Abb. 4)

Auf Grund dieser Ergebnisse kann darauf geschlossen werden, dass Blei in den Roheisenproben nicht gleichmäßig verteilt vorliegt. Hinzu kommt, dass die Probenahme händisch erfolgt und somit die Probenahmeparameter variieren können (z.B. Eintauchtiefe der Probenahmeverrichtung in den flüssigen Roheisenstrom), was zusätzlich zur ungleichen Verteilung von Blei in der Roheisenprobe, eine weitere Herausforderung bei der Bestimmung eines repräsentativen Blei Gehaltes im Roheisen darstellt.

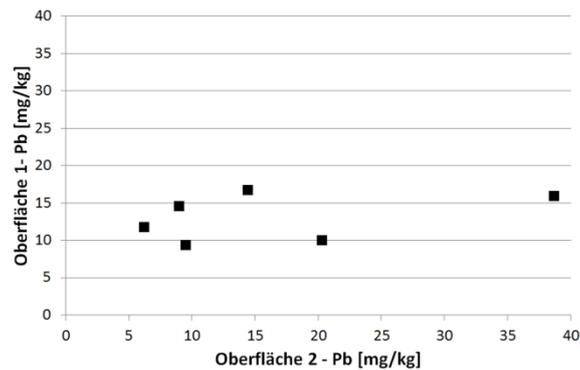


Abb. 4: Vergleich Pb - Gehalt der beiden Probenoberflächen in [mg/kg]

## 4 Zusammenfassung und Ausblick

Die SFA für Blei im Hochofenprozess auf Basis von standardmäßig erhobenen Daten zeigte, dass der Outputfluss RE ein signifikanter Fluss für die Güte des Ergebnisses der Methode ist. Bei genauerer Betrachtung der Bilanzdifferenzen, der Blei-Gehälter im RE sowie unter Berücksichtigung des chemisch-thermodynamischen Verhaltens zeigte sich, dass die gewählte analytische Vorgehensweise zur Blei Bestimmung im Roheisen ein Verbesserungspotential aufweist. Anhand von Vergleichsmessungen für Roheisenproben mittels RFA und Funkenemissionsspektrometer wurde festgestellt, dass die RFA (aktuelles Messverfahren im regulären Betrieb) einen um Faktor 4 höheren Blei-Gehalt liefert. Durch Messungen an der Proben Ober- und Unterseite konnte gezeigt werden, dass Blei in den Roheisenproben mit nicht gleichmäßig verteilt vorliegt. Auf Grund dieser Ergebnisse kann geschlussfolgert werden, dass für die Verbesserung der Ergebnisse der SFA stets die Probenahme und die Analytik, die zur Charakterisierung des Materials herangezogen wird, hinterfragt werden muss. Im vorliegenden Fall bedeutet dies, dass in weiterer Folge eine genaue Charakterisierung der Verteilung von Blei in der Roheisenprobe erfolgen muss. Zusätzlich ist die Evaluierung der Repräsentativität der Probenahme von Roheisenproben von Interesse. Darüber hinaus ist zu evaluieren in wie weit die Schnellanalytik zur Bestimmung von Spurenelementen geeignet ist und optimiert werden kann.

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**Distribution of Zn, Pb, K and Cl in blast furnace lining**

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The furnace campaign of a blast furnace represents an important factor for the iron-making industry due to the fact that maintenance such as relining is not only costly but also time consuming. The furnace campaign is largely determined by the functionality of the lining, which is influenced by wear mechanisms and the damaging behavior of certain elements. To these unwanted elements that may attack the lining belong, for example, Zinc (Zn), Lead (Pb), Potassium (K) and Chlorine (Cl). In this paper the distribution of Zn, Pb, K and Cl within the lining of a blast furnace at the end of its furnace campaign is investigated and discussed. The results demonstrate that the content of some elements (Zn, Cl, Pb) in the lining and also their penetration depth significantly varies over the blast furnace height. For Zn and Pb, the highest contents (43 g Zn kg<sup>-1</sup> and 0.14 g Pb kg<sup>-1</sup>) are observed in the inner lining stones (adjacent to the hot metal), whereas for Cl, a contrary distribution pattern is observed. The highest contents are detected in the outer stones of the lining at the top of the blast furnace.

## 1. Introduction

For blast furnaces, the furnace campaign is of crucial importance. It strongly influences not only the overall costs but also represents an important factor with respect to the loss of production since maintenance work is time consuming and connected with a production stop. In the case of blast furnaces, the furnace campaign strongly depends on the lining material<sup>[1]</sup>. For this reason, improvements in the properties and variety diversification of refractories remain a focus of current research<sup>[2]</sup>.

In blast furnaces two basic types of refractories are utilized. In the shaft (upper part of the blast furnace) mainly high alumina products are used, which consist of more than 45 % of  $\text{Al}_2\text{O}_3$ , whereas in the lower part (towards the tuyeres) carbon based products are attached<sup>[3]</sup>. These materials are damaged by various mechanisms. On the one hand, the durability of the blast furnace lining is negatively influenced by mechanical abrasion of the material (e.g., during charging and downward sliding of the burden).<sup>[1, 4, 5]</sup> On the other hand, the durability is also influenced chemically and physically by different elements unintentionally fed into the process via the different input materials utilized. To these unwanted elements belong, for example, Zinc (Zn), Lead (Pb), Potassium (K) and Chlorine (Cl).

Zn leads, for example, to an increased wear of the lining and tends to form accretions in the blast furnace, which show Zn concentrations of up to 60 %<sup>[6]</sup>. The increased wear results from vaporized Zn, which penetrates into the pores of the refractory linings. There Zn tends to condensate and solidify, resulting in an increased volume of Zn due to change in the state of aggregation. This in turn causes internal stress and subsequently damages the lining<sup>[7, 8]</sup>. In contrast, Zn leads to an increase of Carbon (C) depositions at temperatures below 450 K.<sup>[7]</sup> This can be traced back to the fact that ZnO, and to a minor extent also ZnS and  $\text{ZnOAl}_2\text{O}_3$ , act as a catalyst for the decomposition of CO to form C and  $\text{CO}_2$ .<sup>[9]</sup> Like Zn and ZnO, the newly formed C also penetrates and deposits in the pores. Thereby it can lead to the formation or extension of cracks initially existing in the lining.<sup>[7, 9]</sup> Pb also actively penetrates into the

fine pores and the gaps of the lining, which are located at the bottom as well as in the hearth of the furnace, thereby destroying the linings.<sup>[10, 11]</sup> Additionally, metallic Pb vapor is able to attack the shaft lining or condenses around the cooling plates.<sup>[11]</sup> Like Zn and Pb, K is able to destroy the lining in the lower part of the blast furnace as well as in the shaft region.<sup>[12]</sup> In the bosh area (area above the blast furnace tuyeres) K can penetrate into monolithic aluminosilicate. This leads to the rearrangement of the crystalline lattice, which goes along with a reduction in the mechanical strength of the refractory lining.<sup>[13]</sup> The K steams enter the lining due to the open porosity of the refractory. In the lining K can be reoxidized and thus may condensate within the lining in the form of Kaliophilite ( $K_2OAl_2O_3SiO_2$ ) and Leucite ( $K_2OAl_2O_3SiO_2$ ).<sup>[14, 15]</sup> Thereby a significant increase in the volume of the reaction product relative to the source materials, which leads to the mechanical destruction of the lining material, can be observed.<sup>[14]</sup> In the investigations of Narita, et al.<sup>[16]</sup> K was also found in the middle part of the shaft as Kaliophilite, which was mainly detected at the surface of the fireclay brick.

The effect of Cl on the blast furnace process is mainly discussed in connection with its corrosive behavior towards metals and a decrease in coke reactivity.<sup>[17, 18]</sup> To the knowledge of the authors, the effect of Cl on the linings has hardly been investigated so far. Dana, et al.<sup>[19]</sup>, for example, mentioned that Cl is able to infiltrate into aluminosilicate bricks and cause corrosion. Grambalova, et al.<sup>[20]</sup> described the interaction of molten salts in the system of  $SiO_2-Al_2O_3$ . In their investigations they described corrosion caused by molten NaCl and KCl salts. Furthermore, Binsheng, et al.<sup>[21]</sup> argued that HCl gas may increase the porosity of the lining bricks, which further promotes the erosion of the lining.

All elements under investigation are able to reduce the furnace campaign of blast furnace linings. However, their concentrations within the linings have hardly been investigated so far. Besta, et al.<sup>[22], [23]</sup> and Konopicky, et al.<sup>[24]</sup> are, to the knowledge of the authors, the only ones who have analyzed the distribution of Zn, K and Na in the blast furnace lining over the height

of the blast furnace before a relining. Nevertheless, their investigations are lacking detailed information about sampling and/or the chemical analysis conducted. Furthermore, the work from Konopicky, et al.<sup>[24]</sup> was carried out in the 1950s. Since that time operating conditions and limits for unwanted elements in the different input materials have changed significantly. Thus, the objective of the present work was to close these gaps in the research by determining the contents of Zn, Pb, K and Cl in the blast furnace lining. Thereby the spatial distribution of these elements in the lining over the height of the blast furnace and over the depth of the lining was investigated.

## 2. Materials and Methods

The investigations have been conducted at a blast furnace with a hearth diameter of 8 m and a daily production rate of 2,500 t hot metal (HM). The pressure at the tuyere level of the furnace is around 1.5 bar and the total height of the furnace amounts to 32.5 m. The operation period since the last relining is about 5 years.

Furthermore, virgin lining bricks were chemically analyzed for their content of the respective elements to determine the background concentration. This was necessary in order to assess which fraction of the element contents observed in the linings can be attributed to the operation of the furnace.

### 2.1. Sampling of lining

In total 18 samples from the lining were taken over the height of the blast furnace before the relining. Before the sampling took place, the cooling elements in the blast furnace shaft had been removed. The first sample was taken from the height 32 m, the last sample (sample number 18) was obtained at a height 12 m, which is around 2 m above the tuyeres. The vertical distance between each sampling point was around 1 m (see **Figure 1**). Each sample represents one lining brick (dimension of new lining brick approximately 450 mm x 200 mm

x 98 mm), whereby the depth of the bricks varied due to the different degree of wear (minimum was around 25 cm).

Each of the 18 samples was subsequently manually split into three parts which were approximately equal in size (with a maximum of 15 cm – in the case that hardly any wear was observed). Thereby, subsample 1 is representative for the part of the lining brick that is turned towards the inside of the blast furnace (hot side). Subsample 2 represents the middle part of the lining, while the third subsample is representative for the outer side of the lining which faces the blast furnace wall (cold side).

## **2.2. Chemical analysis**

All 54 subsamples were milled to a grain size of 250  $\mu\text{m}$  using a vibratory disc mill (Fritsch Pulverisette 9 with an agate stone inset). For the chemical characterization of the samples regarding their contents of Zn and Pb, a mass of 1 g was digested in Teflon vessels (HPR 1000) with 2 ml  $\text{H}_2\text{O}$ , 1 ml  $\text{HNO}_3$  and 7 ml  $\text{HCl}$  in a microwave oven (MLS Start 1500). The digestion parameters applied are available in the Supporting Information Table S2. The analytical characterization of Zn and Pb was done using an inductively coupled plasma optical emission spectrometer (Horiba Jobin Yvon ULTIMA 2). A customized multi-element standard containing all analyzed elements was used for calibration. For the measurement the following wavelengths were used: Pb: 220.353 nm, Zn: 213.856 nm. The results were determined using a max-mode function and were averaged over a triplicate determination.

The Cl and K contents were quantified by a mobile XRF handheld device on a portable test stand (Thermo Niton XL3t Air).

## **3. Results and Discussion**

In a first step, virgin lining material (prior its utilization) was chemically analyzed in order to determine the background concentration for the elements under investigation. The results for

the two different lining materials used at the blast furnace investigated, fireclay and andalusite, are summarized in **Table 1**. The Zn and Pb concentrations were smaller than the limit of quantification (LOQ). Considerable background concentrations were only detected for K.

Afterwards the contents of Zn, Pb, K and Cl in all 54 subsamples were analyzed. The results of the analysis demonstrate that the Zn concentration is always higher for the subsample set 1 (hot side) than for the subsample sets 2 (middle part) and 3 (cold side) (**Figure 2**). The Zn concentrations for the subsample sets 2 and 3 were very low or sometimes even below the LOQ. Thus, it can be concluded that Zn penetration into the lining bricks is limited to the innermost 15 cm of the brick.

Depending on the blast furnace height, the highest Zn content were observed in the lower zones of the blast furnace (Samples 13-16, subsample set 1, which are located approximately 10 to 5 m above the tuyeres). Thus, Zn accumulation occurs at a sufficient distance from the copper tuyeres and thus may not damage them, according to Yang, et al.<sup>[25]</sup> In this area the temperature of the reducing gas is in the range of between 973 and 1173 °K. At these temperatures Zn is most likely present as metallic Zn vapor and thus can penetrate into the pores of the linings. The destruction of the lining material may take place according to the following reactions<sup>[14]</sup>:



The increase of the Zn concentrations depending on the blast furnace height is similar to those reported by Besta, et al.<sup>[22], [23]</sup> and Konopicky, et al.<sup>[24]</sup>. The maximal Zn concentration determined for the subsample set 1 (<4.5 % Zn, sample 16/ subsample 1, ~5 m above the tuyeres) is in the same range as the maximal value reported by Konopicky, et al.<sup>[24]</sup>. They determined a maximal Zn concentration of less than 5 % for the part of the lining brick turned towards the hot side for a blast furnace with a hearth diameter of 5.5 m and a working period

of 12 years. This concentration was detected at a height between 13 and 14 m above the tuyeres. The second highest Zn concentration, with around 2 %, was detected 8 m and 17 m above the tuyeres<sup>[24]</sup>. In contrast, Besta, et al.<sup>[22]</sup> reported Zn concentrations of more than 40 wt % at a height of around 7 m and 19 to 22 m, whereby the height of 0 m referred to the blast furnace top. In another study conducted by Besta, et al.<sup>[23]</sup>, Zn concentrations of up to 25 % in the lining material were observed. The highest concentrations were again detected at around 9 m and between 21 to 25 m (height of 0 m referred to the blast furnace top). Due to the fact that they did not provide further information on the working conditions (e.g., counter pressure on the blast furnace top), no conclusion can be drawn regarding their impact on the penetration behavior. However, it is most likely that if the furnace is operated under higher pressure, then the Zn concentration in the lining bricks might be higher (if the input amount with regard to Zn is similar). Nevertheless, the concentrations reported by Besta, et al.<sup>[22], [23]</sup> seem unrealistically high and may only occur at accretions in the blast furnace shaft, which may show Zn contents of up to 60 %, according to Deike, et al.<sup>[6]</sup>. Since there is no information available about the sampling, it cannot be ruled out that the samples may contain not only the lining material but also the accretions.

To evaluate whether the inserted amount of Zn has a significant effect on the concentration of the lining bricks, the Zn input from the different studies was compared. Thereby it turned out that the amount of Zn entering the blast furnace in the study of Besta, et al.<sup>[22]</sup> (116 g t<sup>-1</sup> HM) is quite similar to that of our investigations (108 g t<sup>-1</sup> HM, see Supporting Information Table S1). Konopicky, et al.<sup>[24]</sup> did not report the input amount of Zn inserted.

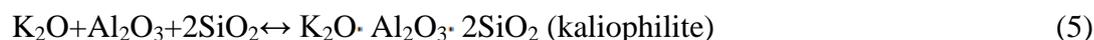
In comparison to Zn, the Pb concentrations determined are much smaller (two orders of magnitude difference) (see **Figure 3**). The highest concentrations were, as was the case for Zn, detected in the subsample set 1, facing the hot side. The other subsamples sets (2 and 3) contained hardly any Pb. Only for sample 4 could a significant Pb concentration be detected in subsample 3. However, this result seems to be unrealistic and might be traced back to

contamination during the sampling. With respect to the distribution of Pb in the lining over the blast furnace, it can be stated that the highest concentrations were determined for sample 3, subsample 1 (around 21 m above the tuyeres) and sample 14 and 16, subsample 1 (around 7 to 10 m above the tuyeres). The concentrations measured at these heights ( $<0.15 \text{ g kg}^{-1}$ ) are higher compared to Pb concentrations of the input materials (sinter and iron ores show Pb concentrations between  $0.001 - 0.01 \text{ g kg}^{-1}$ ). Thus, a small accumulation may take place at these heights. However, it must be noted that due to the physico-chemical behavior Pb tends to accumulate below the liquid HM (in the blast furnace hearth) due to its higher density <sup>[10]</sup> Thus, it is also most likely that Pb will accumulate in the refractories below the tuyeres.

For K the highest contents have been determined in the subsample set 1. The data utilized in **Figure 4** have already been corrected for the background concentration of K, which amounts to  $3.5 \text{ g kg}^{-1}$  and  $4.2 \text{ g kg}^{-1}$ , respectively (see Table 1). The K concentration in the subsample sets 2 and 3 is significantly smaller. The highest K concentrations (up to  $24 \text{ g kg}^{-1}$ ) were detected for samples number 13 and 14, subsample 1, which are located around 10 m above the blast furnace tuyeres. At this level gas temperatures reach up to  $1073^\circ\text{K}$  and the following reaction may occur (between  $1073^\circ\text{K}$  <sup>[14]</sup> and  $1273^\circ\text{K}$  <sup>[15]</sup>):



The K oxides may further react with Al and Si and increase the wear according to:



The maximal K concentration measured was  $24 \text{ g kg}^{-1}$  (2.4 %) for sample 13 (subsample 1), which is slightly above the area in which the highest Zn contents were determined. This concentration is, compared to the literature, still quite low. Besta, et al. <sup>[23]</sup> reported K concentrations in the lining of up to 7 % between a height of 13 to 17 m (measured from the blast furnace top) (gas temperature range of about  $1073$  and  $1673^\circ\text{K}$ ). Konopicky, et al. <sup>[24]</sup>

reported even higher concentration of up to 20 %. However, the concentration pattern over the blast furnace height of both studies is similar to our findings.

Cl shows a different distribution pattern compared to the other elements investigated (see **Figure 5**). The concentration of Cl increases from the bottom of the blast furnace to the top, where the top gas leaves the furnace. This distribution pattern appears to be reasonable since Cl is highly volatile under blast furnace conditions. All in all, the subsample set 1 still show the highest Cl concentrations. However, almost the same accumulation of Cl was detected within the subsample set 3. Thereby, the concentration in these outer lining samples significantly increased towards the upper part of the blast furnace shaft. Cl concentrations detected within the subsample set 2, which represent the middle part of the lining bricks, were comparatively smaller. Looking at the Cl content of the lining over the blast furnace height, it became obvious that larger concentrations are observed in the upper zones of the shaft.

Cl enters the blast furnace together with iron ores and coke mainly as alkali chlorides (NaCl, KCl).<sup>[13, 26]</sup> Within the process highly volatile compounds such as hydrochloric acid (HCl) are formed, which are to a large extent carried out of the blast furnace via the top gas.<sup>[26]</sup> This behavior of Cl in the process supports our findings that Cl is found to a large extent in the upper part of the blast furnace shaft. However, knowledge about which Cl compounds will condensate and/or react with the lining material in the upper part of the furnace is, to the knowledge of the authors, not available so far.

### **3. Conclusion**

In the study presented the lining of a blast furnace was characterized for its contents of Zn, Pb, K and Cl after a furnace campaign of 5 years. Thereby the concentrations of these elements were determined depending on the blast furnace height and the penetration depth in the lining bricks.

The distribution pattern for Zn over the blast furnace height is similar to the results reported in the literature. The maximal detected Zn concentration, with around 4 %, is still smaller than the content reported in the literature. Our observations show the highest concentration at about 5 to 10 m above the tuyeres. Thus, there is hardly any potential of Zn damaging the blast furnace tuyeres. In practice, however, damage to the copper tuyeres due to the presence of Zn is sometimes observed. Furthermore, Zn was mainly detected in subsample 1, facing the hot side. Thus it can be concluded that Zn penetration into the lining is limited to a maximum of 15 cm.

The highest Pb concentrations were determined at around 21 m and between 7 to 16 m above the tuyeres. In this region a slight accumulation of Pb in the lining material takes place. However, due to the physico-chemical behavior of Pb in the blast furnace, Pb tends to accumulate below the liquid iron. Thus further investigations into the distribution of Pb in the carbon refractories and its potential damaging mechanism would be of interest.

The behavior of K is comparable to Zn. The highest K concentration (2.4 %) was determined at around 10 m above the tuyeres. The observed distribution of K over the blast furnace height corresponds to results of other studies reported in the literature. Nevertheless, the maximum K concentration of 2.4 % analyzed in our investigation is significantly lower than the concentrations given in the literature (maximum K concentration in the blast furnace lining of 20 % reported by Konopicky, et al.<sup>[24]</sup>).

The pattern of Cl is different compared to K and Zn. The Cl concentration increases with the blast furnace height. Moreover, Cl was not only detected in the subsample set 1 (facing towards hot side of the blast furnace), but also in the subsample set 3 facing the cold side. The maximal Cl concentration detected was around 0.5 %. Although, this concentration is rather small, further investigations regarding the behavior and the potential damage mechanism for the blast furnace linings is needed since Cl may increase lining porosity according to Binsheng, et al.<sup>[21]</sup>.

Finally, it has to be noted that further research should focus on the relevance of the process conditions (e.g. different counter pressure at the blast furnace top) and on the relevance of the input composition with respect to the damage mechanism of the elements considered on the blast furnace lining. Such information would probably allow limits for these elements in the blast furnace input to be set. This information, however, could lead to an improved internal recycling strategy (e.g., better knowledge about the maximum chargeable Zn content could improve the amount of top gas dust which is internally recycled at the sinter plant).

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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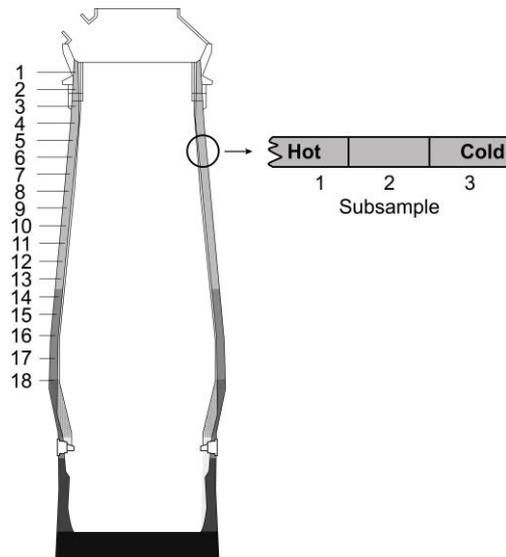
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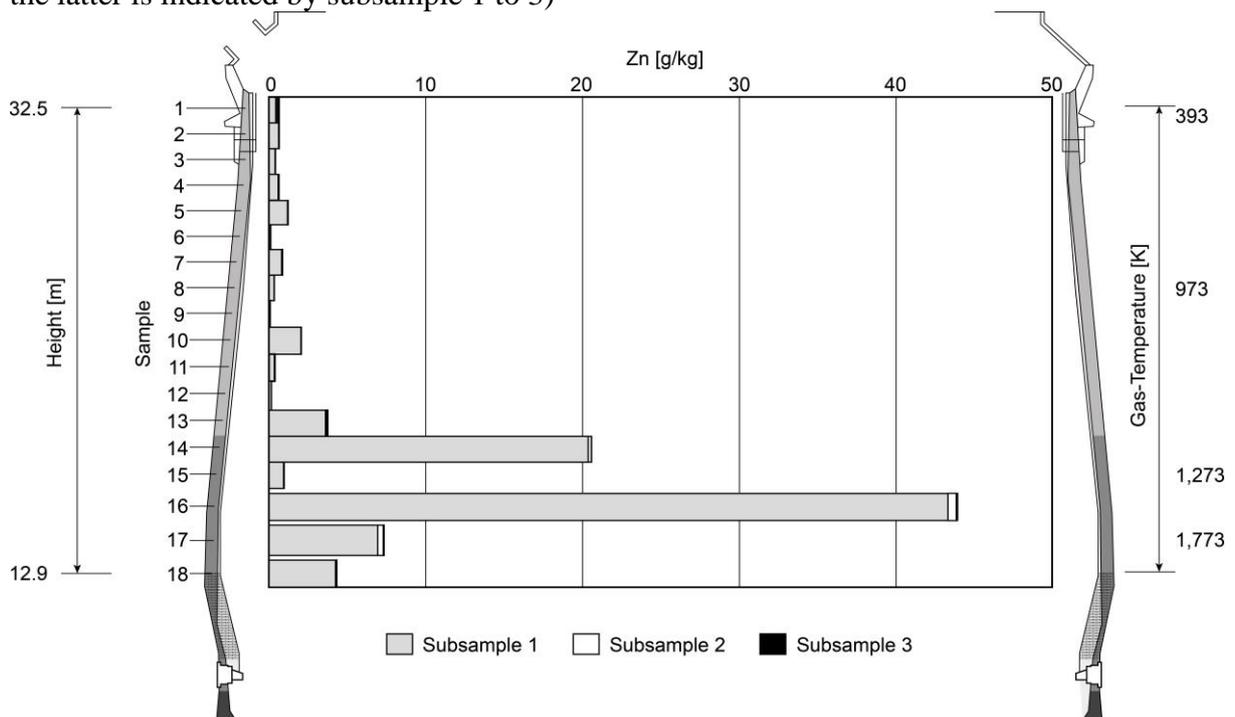
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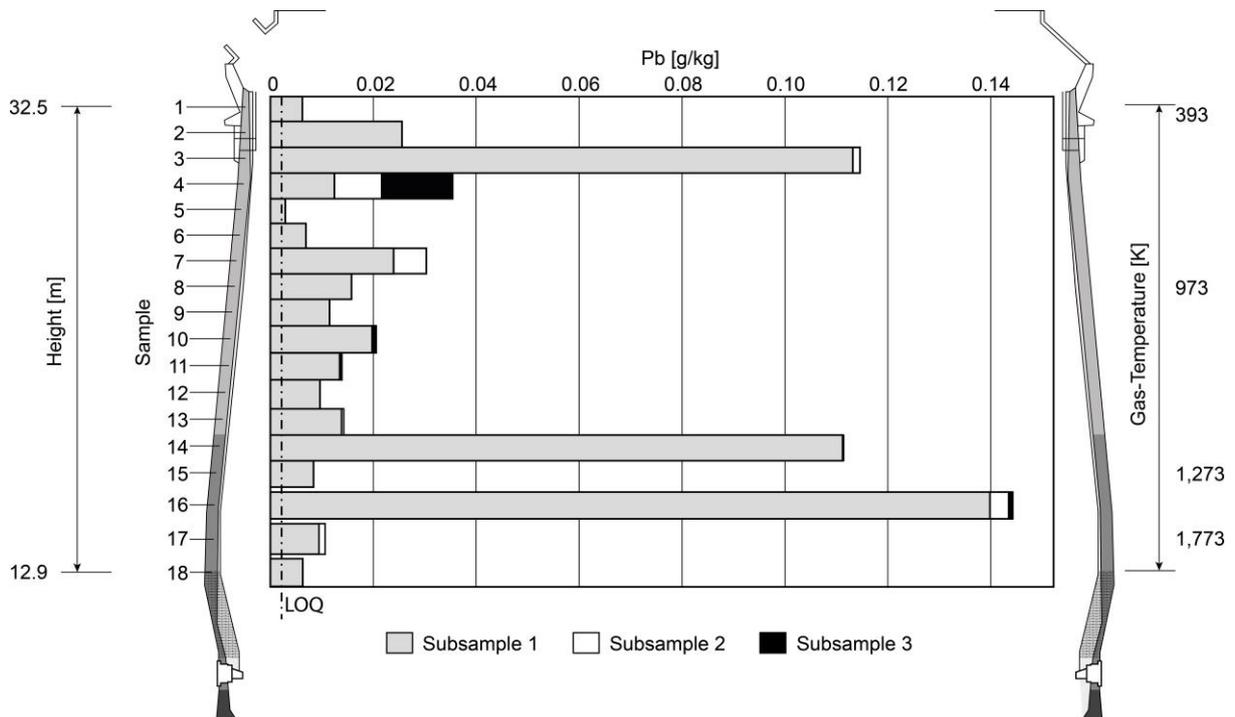
**Figure 1:** Sampling points for the lining over the blast furnace's height



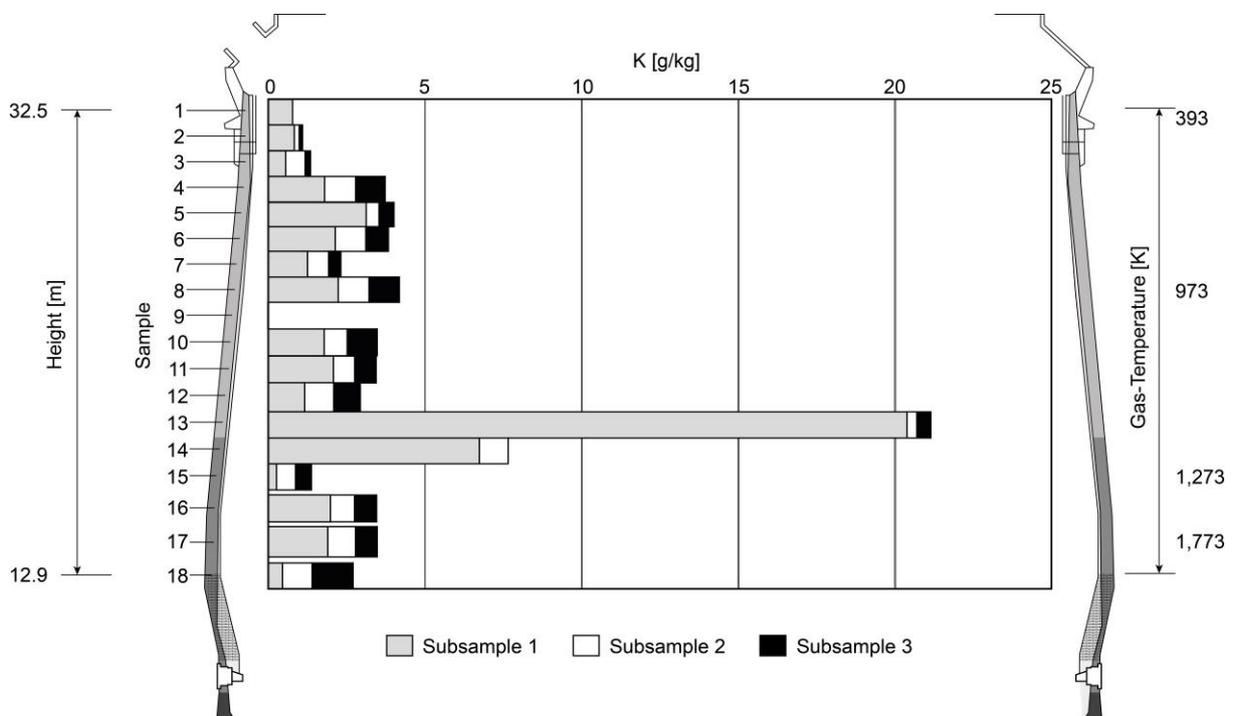
**Figure 2:** Zn contents [g/kg] in blast furnace lining (distribution over height and brick depths, the latter is indicated by subsample 1 to 3)



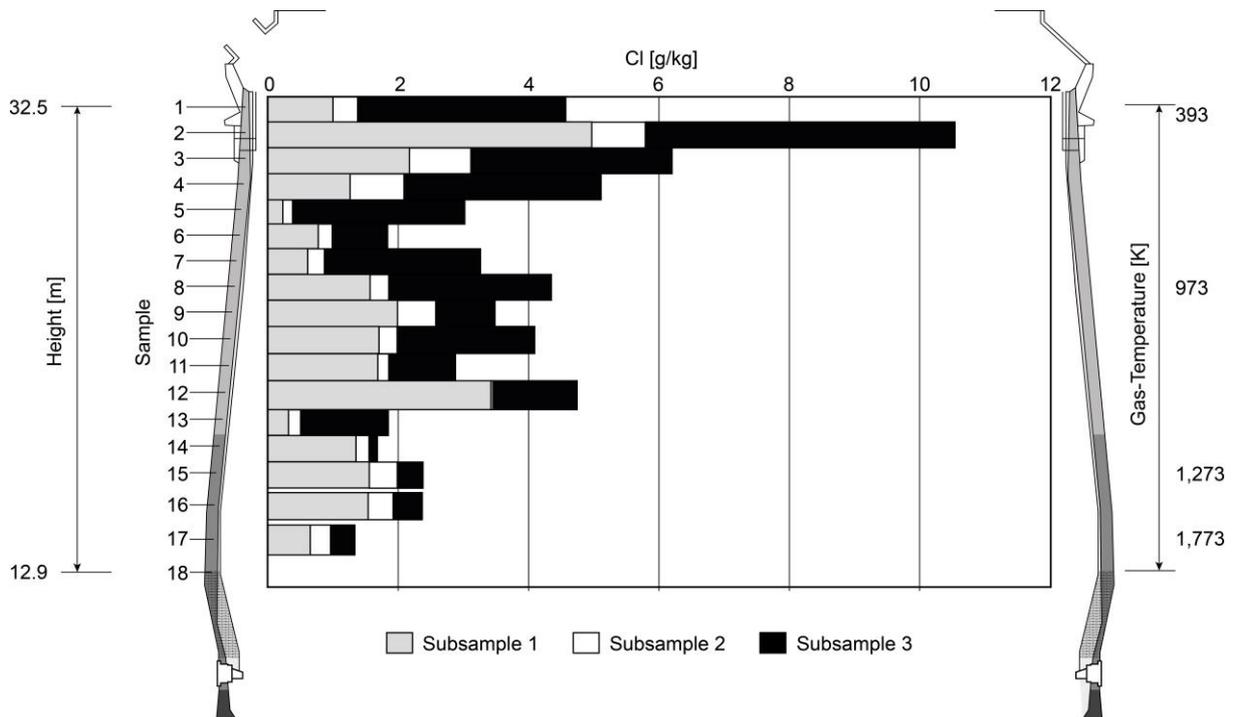
**Figure 3:** Pb contents [g/kg] in blast furnace lining (distribution over height and brick depths, the latter is indicated by subsample 1 to 3)



**Figure 4:** K contents [g/kg] in blast furnace lining (distribution over height and brick depths, the latter is indicated by subsample 1 to 3)



**Figure 5:** Cl contents [g/kg] in blast furnace lining (distribution over height and brick depths, the latter is indicated by subsample 1 to 3)



**Table 1:** Background concentration for virgin lining material

Material	Sample	Zn	Pb	K	Cl
		[g/kg]			
Fireclay	1 - 13	<0.0007	<0.0024	3.5	0.1
Andalusite	14 - 18	<0.0007	<0.0024	4.2	<LOQ

## Supporting Information

**Distribution of Zn, Pb, K and Cl in blast furnace lining**

Verena Trinkel\*, Philipp Aschenbrenner, Christoph Thaler, Helmut Rechberger, Ole Mallow and Johann Fellner

**Table S 1: Input balance for Zn for the working period of five years**

<b>Zn - Input</b>	Year 1	Year 2	Year 3	Year 4	Year 5
	[g/t HM]				
Iron Ores (including Pellets, lump ores, etc.)	12	11	33	14	15
Sinter	96	86	84	45	48
Alternative input materials	-	-	-	1.2	1.2
Coke	6.0	6	6	7.1	6.6
Alternative reducing agents	33	28	3	0.03	0.03
<b><i>SUM</i></b>	<b><i>147</i></b>	<b><i>131</i></b>	<b><i>125</i></b>	<b><i>68</i></b>	<b><i>71</i></b>

**Table S 2: Input balance for Pb for the working period of five years**

<b>Pb - Input</b>	Year 1	Year 2	Year 3	Year 4	Year 5
	[g/t HM]				
Iron Ores (including Pellets, lump ores, etc.)	4.4	3.5	6.3	5.4	3.7
Sinter	6.5	4.4	4.2	2.9	2.4
Alternative input materials	-	-	-	0.1	0.1
Coke	3.1	3.1	3.0	3.4	2.5
Alternative reducing agents	2.6	1.7	0.1	0.0	0.0
<b><i>SUM</i></b>	<b><i>16.5</i></b>	<b><i>12.8</i></b>	<b><i>13.6</i></b>	<b><i>11.7</i></b>	<b><i>8.7</i></b>

**Table S 3: Input balance for K for the working period of five years**

<b>K - Input</b>	Year 1	Year 2	Year 3	Year 4	Year 5
	[kg/t HM]				
Iron Ores (including Pellets, lump ores, etc.)	0.69	0.61	0.74	0.58	0.79
Sinter	0.00	0.01	0.00	0.00	0.00
Alternative input materials	-	-	-	-	-
Coke	0.78	0.76	0.77	0.67	0.63
Alternative reducing agents	-	-	-	-	-
<b><i>SUM</i></b>	<b><i>1.48</i></b>	<b><i>1.38</i></b>	<b><i>1.51</i></b>	<b><i>1.25</i></b>	<b><i>1.42</i></b>

**Table S 4: Input balance for Cl for the working period of five years**

Cl - Input	Year 1	Year 2	Year 3	Year 4	Year 5
	[g/t HM]				
Iron Ores (including Pellets, lump ores, etc.)	54	44	63	50	49
Sinter	159	106	77	41	27
Alternative input materials	-	-	-	0	0
Coke	157	153	143	137	114
Alternative reducing agents	17	12	8	6	9
<b>SUM</b>	<b>387</b>	<b>315</b>	<b>291</b>	<b>234</b>	<b>200</b>

**Table S 5: Digestion parameters – Microwave oven program**

Step	Time	Power	Temperature
[-]	[min:ss]	[W]	[K]
1	04:30	1000	413
2	03:30	1000	473
3	04:00	1000	513
4	48:00	1000	513
5	30:00		Ventilation

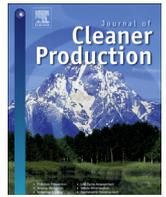
**Table S 6: Measurement results for Zn and Pb (ICP-OES)**

Sample	Zn			Pb		
	Sub-sample 1	Sub-sample 2	Sub-sample 2	Sub-sample 1	Sub-sample 2	Sub-sample 2
	[g/kg]			[g/kg]		
1	0.44	0.09	0.13	0.0062	0.00	0.00
2	0.62	0.02	0.02	0.0256	0.00	0.00
3	0.39	0.01	0.02	0.1132	0.00	0.00
4	0.59	0.02	0.04	0.0124	0.01	0.01
5	1.18	0.03	0.01	0.0029	0.00	0.00
6	0.09	0.00	0.00	0.0069	0.00	0.00
7	0.81	0.05	0.01	0.0239	0.01	0.00
8	0.32	0.00	0.00	0.0158	0.00	0.00
9	0.06	0.01	0.00	0.0115	0.00	0.00
10	2.04	0.02	0.02	0.0198	0.00	0.00
11	0.36	0.00	0.01	0.0135	0.00	0.00
12	0.14	0.00	0.00	0.0096	0.00	0.00
13	3.60	0.08	0.08	0.0138	0.00	0.00
14	20.40	0.21	0.01	0.1112	0.00	0.00
15	0.93	0.02	0.02	0.0084	0.00	0.00
16	43.41	0.53	0.08	0.1399	0.00	0.00
17	6.94	0.35	0.06	0.0095	0.00	0.00
18	4.25	0.07	0.00	0.0063	0.00	0.00

Table S 7: Measurement results for K and Cl (XRF)

Sample	K			Cl		
	Sub-sample 1	Sub-sample 2	Sub-sample 2	Sub-sample 1	Sub-sample 2	Sub-sample 2
	[g/kg]			[g/kg]		
1	0.8	0.2	0.1	1.00	0.38	3.19
2	0.6	0.6	0.2	4.97	0.82	4.75
3	1.8	1.0	0.9	2.17	0.94	3.09
4	3.1	0.4	0.5	1.26	0.83	3.02
5	2.1	1.0	0.7	0.23	0.15	2.64
6	1.2	0.7	0.4	0.77	0.21	0.85
7	2.2	1.0	1.0	0.61	0.26	2.39
8	0.0	0.0	0.0	1.57	0.29	2.49
9	1.8	0.7	1.0	1.99	0.58	0.91
10	2.1	0.7	0.7	1.71	0.28	2.11
11	1.2	0.9	0.9	1.69	0.17	1.02
12	20.4	0.3	0.5	3.42	0.03	1.29
13	6.7	0.9	0.0	0.32	0.19	1.34
14	0.3	0.6	0.5	1.35	0.20	0.13
15	2.0	0.8	0.7	1.56	0.43	0.40
16	1.9	0.9	0.7	1.54	0.38	0.45
17	0.5	0.9	1.3	0.65	0.31	0.37
18	0.8	0.2	0.1	1.00	0.38	3.19





# Influence of waste plastic utilisation in blast furnace on heavy metal emissions



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## ABSTRACT

Waste plastics can be utilised in blast furnaces as an alternative reducing agent. However, the use of waste plastics also implies an additional input of heavy metals into the process. The present paper investigates the extent to which this increased input influences the emissions of heavy metals from blast furnaces. A multitude of measurements characterising the input and output flows of a full-scale blast furnace that utilised waste plastics over a period of 4 years have been analysed with respect to their contents of Mercury (Hg), Cadmium (Cd), Zinc (Zn) and Lead (Pb). The results of the study indicate that despite the fact that waste plastics were utilised only at a maximum rate of 35 kg/t HM (Hot Metal) (during the considered time period), they contribute significantly to the total input of Hg (<44%) and Cd (>54%) into the blast furnace. By contrast, waste plastics are of minor importance (<14%) to the overall input of Zn and Pb. Investigations of the process outputs demonstrate that the heavy metals under investigation are to a large extent transferred into outputs that are subsequently landfilled (Cd 98%, Hg 90%, Pb 62%, and Zn 35%). Significant amounts of only Zn and Pb are internally recycled (Pb 11%, Zn 34%) or end up in the final product, hot metal (Pb 27%, Zn 30%). With the exception of Hg (10%), emissions to air or water account for less than 1.5% of the total output.

The results of further analyses indicate that the emissions of heavy metals to the atmosphere and the hydrosphere are completely independent from their input into the blast furnace. Thus, the usage of transfer coefficients to predict emission levels is (at least for minor flows such as emissions) inadequate. It has been shown that constant emission factors (describing the specific emission load of a heavy metal per unit hot metal), which are independent from the input of heavy metals, describe process emissions at least as well as transfer coefficients, which require detailed information about the input flow to predict emissions. This finding also implies that a certain increased input of heavy metals into a blast furnace does not necessarily increase its emissions, and thus, the usage of transfer coefficients would result in a significant overestimation of environmental burdens associated with plastic utilisation.

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## 1. Introduction

Recycling and the utilisation of waste plastics have received increasing interest in recent decades. In addition to ever stricter legal recovery targets for plastic-containing goods such as WEEE (Waste Electrical and Electronic Equipment) or EoL (End of Life) vehicles (Lazarevic et al., 2010), this development has been mainly

driven by industries looking for alternative energy sources, with plastic waste representing such a source.

Within the European Union, large quantities of waste plastics are thermally utilised in classical incineration plants including cement kilns. Minor amounts undergo material recycling processes to finally end up in re-granulated products, and to some extent, feedstock recycling of waste plastics is also conducted. The latter is an attractive option for difficult-to-recycle plastics (e.g., composite plastics, mixed plastics) by turning them into valuable chemical compounds (e.g., synthesis gas) that can subsequently be used in various applications (Al-Salem et al., 2009; Delgado et al., 2007;

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Feketitsch et al., 2014). An application which somehow combines thermal utilisation (energy content of plastics) and feedstock recycling (generation of reducing gas) is the usage of waste plastics as an alternative reducing agent in the blast furnace process. Actually, this utilisation of plastics is a common practice in several integrated steel plants in Austria, Germany and Japan (Ariyama et al., 1997; Bürgler et al., 2007; Lindenberg et al., 1996).

First investigations regarding technical feasibility of the injection of waste plastics into the blast furnace were carried out, for example, by Ariyama et al. (1997), Janz and Weiss (1996), Lindenberg et al. (1996). Further studies investigated the extent to which waste plastics can replace the commonly used coke as a reducing agent (Heo and Baek, 2002; Jeschar and Dombrowski, 1996), forecasted the energy effects within the blast furnace due to the injection of waste plastics (Ziębik and Stanek, 2001), or aimed at investigating the combustion and gasification behaviour of waste plastics in the blast furnace (Asanuma et al., 2000; Cao et al., 2005; Kim et al., 2002). Most of recent research studies are based on Computational Fluid Dynamics (CFD) simulations for the raceway (Buchwalder et al., 2007; Harasek et al., 2007; Jordan et al., 2010).

Because environmental aspects, such as greenhouse gas reduction (Rynikiewicz, 2008), are getting more and more important in the metal producing industry, a focus of recent studies has also been on the replacement of fossil reducing agents (such as heavy fuel oil) by waste plastics thereby reducing greenhouse gas emissions (Ariyama et al., 2005; Liu and Liu, 2012; Sekine et al., 2009). To assess the environmental impact of the steel industry Life Cycle Assessment (LCA) (Burchart-Korol, 2013; Norgate et al., 2007; Vadenbo et al., 2013) have been carried out and extensive Life Cycle Inventory (LCI) data has been collected (Bieda, 2012; Huang et al., 2010; Jing et al., 2014). Spengler et al. (1998) developed a Multi Criteria Decision Making (MCDM) concept to support environmental assessment of recycling measures in the iron and steel industry. Schultmann et al. (2004) performed a flowsheet-based simulation of recycling concepts in the metal industry. Within their study they also considered the injection of waste plastics in the blast furnace. They focused on the additional input of chlorine and Zinc (Zn) due to the utilisation of waste plastics, because these elements are potentially problematic for the ironmaking process (Schultmann et al., 2004).

However, the extent to which other environmental issues, such as gaseous emissions and/or waste water from blast furnace top gas cleaning, may be influenced by the utilisation of waste plastics has hardly been investigated so far. To our knowledge, Vadenbo et al. (2013), Pilz and Bürgler (2007), and Bürgler et al. (2007) were the only ones who accounted for the additional input of heavy metals into the blast furnace and the emissions induced when utilising waste plastics. Vadenbo et al. (2013) conducted a detailed LCA to investigate the effects on heavy metal distribution of waste plastics utilised in ironmaking. For their LCA model, they assumed a linear relationship between the input of heavy metals and the resulting emission levels based on fixed transfer coefficients (TC) for the blast furnace. (Transfer coefficients describe the partitioning of a substance in a process and its transfer into a certain output, cf. Brunner and Rechberger (2004)). The results of the study indicated a rather significant impact of the utilisation of waste plastics on the heavy metal emissions of the blast furnace and thus an overall environmental burden of this type of waste plastics utilisation. Pilz and Bürgler (2007) compared the utilisation of waste plastics as an alternative reducing agent in a municipal waste incineration plant and in a blast furnace. Within this study, they also evaluated and compared the environmental impacts (e.g., heavy metal emissions) from both modes of utilisation. For their investigations, they also used fixed transfer coefficients, thereby assuming that emission levels are proportional to the input of heavy metals. According to

the results of their evaluation, a major portion of the heavy metals introduced into a blast furnace is discharged and finally ends up at landfills (for Mercury (Hg), approximately 95%, for Lead (Pb) 87%, and 95% of Cadmium (Cd)).

Bürgler et al. (2007) performed a substance flow analysis and determined fixed TC for the blast furnace process for some heavy metals (Hg, Zn, Cd, and Pb). Their analysis was performed with data available for a measurement period of 3 months. From their investigations, they concluded that the input of the heavy metals under consideration influences the gaseous and particle-bound emissions and the performance of the gas cleaning system. However, after some modifications of the scrubber parameters, the concentration of heavy metals in the cleaned top gas of the blast furnace could be kept in the same range as during standard operation (without plastics utilisation).

All three studies evaluated the impact of waste plastics utilisation on the heavy metal flows and emissions of blast furnaces based on fixed transfer coefficients, thereby assuming a linear relationship between the total input and the different output flows of heavy metals. However, this assumption has never been tested.

Thus, the aim of the present paper is to investigate the extent to which the utilisation of waste plastics actually influences heavy metal flows (in particular, heavy metal emissions) in the blast furnace process. Special emphasis is given to testing the so far commonly used assumption of a linear relationship (fixed transfer coefficients) between input and output flows of heavy metals (Bürgler et al. (2007), Pilz and Bürgler (2007), Vadenbo et al. (2013)). As an alternative to fixed transfer coefficients, the usage of so-called emission factors (EF) is evaluated. In contrast to TC, EF assume that the overall quantity of emissions is proportional to the amount of the final product (in this case, hot metal); in other words, each unit of product is characterised by a constant emission load (EEA, 2013).

For these investigations, emissions and monitoring data recorded at an Austrian blast furnace (Voestalpine Stahl GmbH) as well as information about the amount and composition of different burden materials are evaluated over a period of 4 years. During this time, different amounts and qualities (with respect to the content of heavy metals) of waste plastics were utilised. The analyses with respect to heavy metal flows and how they are influenced by utilising waste plastics focused on the following elements: Zn, Pb, Hg, and Cd.

These heavy metals were chosen because they are either environmentally relevant or relevant for process stability. Process stability refers in this context to the ability of Zn and Pb to form circulation processes within the blast furnace. Zn, for example, is transferred to the gaseous form in the lower (high temperature) zones of the blast furnace and ascends to the low temperature zones where it condenses on the surface of burden and coke. Subsequently, it descends with the charge materials to higher temperature zones where it is reduced, melted and again transferred to the gaseous phase. Together with the gas stream within the furnace, it ascends to the upper zone and condenses again (Babich et al., 2008). The accumulation of Zn, for example, can lead to clogging of the pores from sinter and coke and cause scaffold formation, which disturbs burden descent (Babich et al., 2008; Deike and Hillmann, 1999). As another example, Pb can accumulate in the hearth bottom and seep through the refractory linings and thereby destroy them (Babich et al., 2008).

## 2. Materials and methods

### 2.1. The investigated blast furnace

The considered blast furnace has a hearth diameter of 12 m and a daily production rate of approximately 8500 t hot metal. The main

input materials are coke and different burden materials (e.g., different iron ores pellets, lump ore and sinter), which are charged from the top of the furnace. Other reducing agents such as heavy fuel and crude tar are injected through the tuyeres in the hearth of the furnace. Additionally, waste plastics are utilised as an alternative reducing agent in the investigated blast furnace. These waste plastics have been mainly derived from processing (mechanical separation) of separately collected packaging and commercial waste. To a minor extent the material utilised represents light-weight fractions generated from shredding end of life vehicles. The grain size of the injected waste plastics is largely in the range of 4–10 mm.

The outputs of the process include solid, liquid and gaseous flows. The main output flows consist of top gas, hot metal and slag. The top gas, which leaves the blast furnace at the top, is first cleaned of coarse particles using a dust bag. This dust (top gas dust) is internally recycled via the sinter plant. After this first dedusting step, the top gas is further cleaned by a wet scrubber and is subsequently utilised in a gas turbine for power generation. The scrubber water is processed in a waste water treatment plant that allows recycling of a large portion of the scrubber water (see Fig. 1). The scrubber water is subsequently fed into a thickener to separate the liquid phase from the solid phase (sludge). The latter is further piped into a hydro cyclone, where the larger solid particles are separated from the finer ones. This is done because the small-grained particles are likely to contain higher amounts of heavy metals, whereas the larger particle fraction is enriched in iron. The finer (heavy metal enriched) fraction is further processed in a second thickener. Finally, the small-grained sludge is drained using a chamber filter press and afterwards deposited at a landfill. The coarser-grained (iron enriched) sludge is internally recycled and further processed within the sinter plant together with the top gas

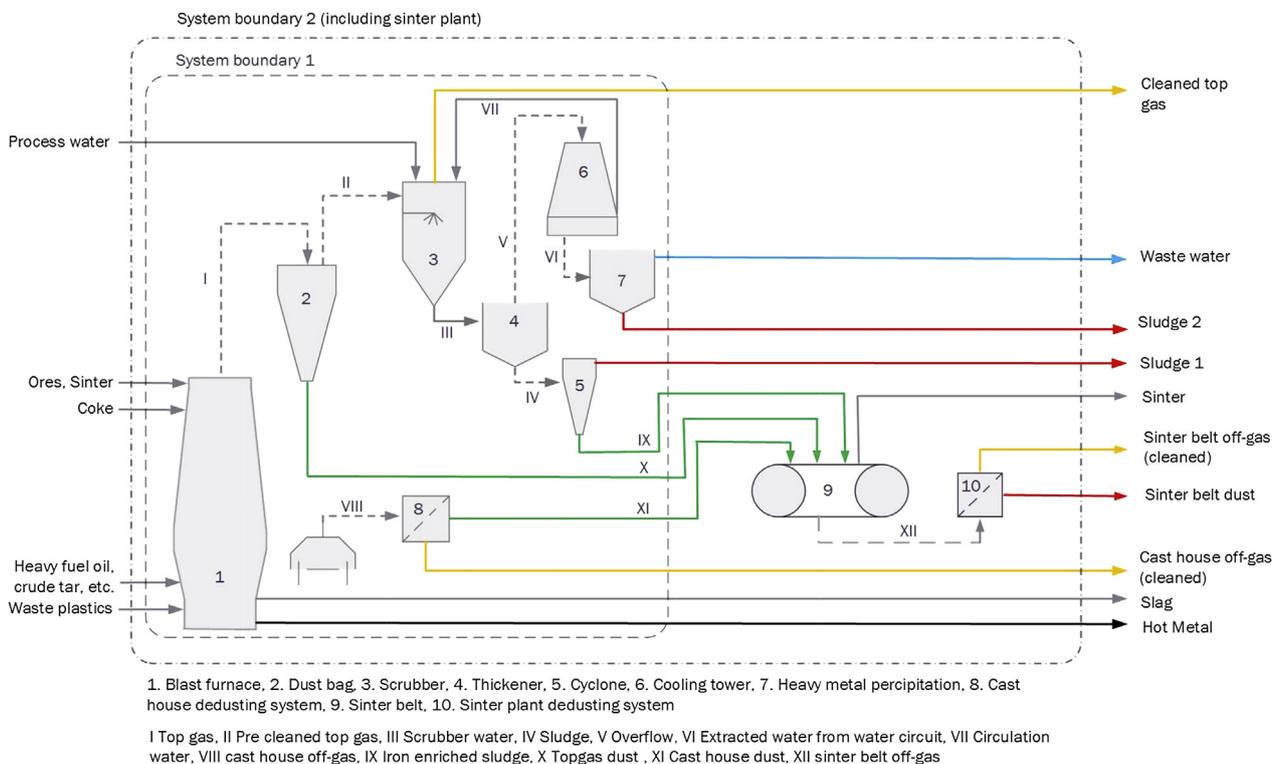
dust and the cast house dust. The off-gas generated at the sinter plant is cleaned using a dry cleaning procedure with a fabric filter (Fleischanderl et al., 2008). The dust that is separated is landfilled and the cleaned off-gas of the sinter plant is released into the atmosphere.

The liquid phase from the scrubber is recirculated in an internal water circulation system. Just a small part ( $\ll 1\%$ ) is deducted from the circulation system and replaced with fresh process water to prevent the accumulation of certain substances, mainly easily soluble salts. The water that is deducted from the internal circulation system is further treated via heavy metal precipitation. After this treatment step, the pre-cleaned waste water is discharged into the nearby municipal waste-water treatment plant.

In the cast house, where the hot metal is tapped, the exhaust air is also collected and cleaned. The cast house dust thereby obtained is recycled within the sinter plant, and the cleaned cast house off-gas is released to the atmosphere.

Thus, for the investigated blast furnace process, the following flows can be identified as the main emission paths: cleaned top gas, cleaned exhaust air from the cast house, heavy metal enriched sludge from both the heavy metal precipitation (sludge 2) and the cyclone (sludge 1), which are both landfilled, and waste water, which is further treated in a waste water treatment plant. The other output flows include hot metal, which is the product of the process, slag as a by-product, iron-rich sludge from the cyclone, top gas dust and cast house dust. The latter three are all internally recycled via the sinter plant (Fig. 1, system boundary 1). As already mentioned above, the off-gas of the sinter plant is cleaned and the separated dust is subsequently landfilled (Fig. 1, system boundary 2). The sinter produced is utilised as input material for the blast furnace.

Due to environmental regulations and process control requirements, numerous measurements must be taken regularly at



**Fig. 1.** Blast furnace process schematic; flows indicated in red are landfilled, green flows are internally recycled, yellow flows represent emissions to the atmosphere, blue flows represent emissions to the hydrosphere; system boundary 1 excludes the sinter plant, system boundary 2 includes the sinter plant. This figure shows the scheme of the considered blast furnace process.

the blast furnace and its satellite processes. Fig. 1 represents a scheme of the described blast furnace process. Flows illustrated by solid lines indicate the ones for which regular qualitative and quantitative (mass, volume and concentration) measurements are conducted; for the flows with the dashed lines, no qualitative measurements are available. The volume flow of the cleaned top gas, however, is based on calculations using information about its N<sub>2</sub> content.

The system boundary defines the production process for which the materials flow analysis is carried out. System boundary 1 includes the blast furnace, the different gas cleaning processes and the waste water treatment. The sinter plant, where some of the residues from the gas cleaning processes are recycled, is excluded here. Thus, the outputs of system boundary 1 include emissions, the product and by-product and internally recycled flows (green flows in Fig. 1). By contrast, system boundary 2 additionally includes the sinter plant to trace heavy metal flows through the entire process.

### 2.1.1. Input materials of the blast furnace

In the blast furnace process, raw materials such as different iron ore pellets and lump ores, sinter, coke and other reducing agents are utilised. In Table 1 the amounts of inserted materials expressed in kg per ton hot metal (HM) are shown for the investigated years. From this table, it is clear that the amount of waste plastics utilised doubled from 17 kg/t HM in 2007 to 35 kg/t HM in 2011.

It must be noted that within the year 2007, the utilisation of waste plastics as an alternative reducing agent had just started. Moreover, within this year the water recycling process was established and, the output flows thus changed significantly. Therefore, this investigation of the impact of plastics utilisation on blast furnace emissions has been limited to the years 2008 through 2011.

### 2.1.2. Measurement points and frequency of analysis

The input and output flows of the blast furnace are characterised with respect to quantity and quality due to environmental and process control considerations. Flow quantities of the flows are usually recorded continuously, whereas the extent and frequency of qualitative analyses may vary considerably. In Fig. 1 all flows that are regularly sampled and analysed regarding their composition are indicated with a solid line. The consistency of the different flows, as well as their contents of heavy metals, may be highly diverse. The consistency ranges from low concentration solids (e.g., iron ore) to liquids with varying particle contents and thus also varying contents of heavy metals.

In Table 2 the regularly sampled flows are listed and information about the measurement frequency is given:

From Table 2, it is obvious that the measurement frequency can range from daily measurements (e.g., hot metal) to once per quarter (crude tar).

The number of analyses is required to determine the uncertainties of the input and output flows (see Eq. (3)).

**Table 1**  
Input materials of the blast furnace expressed in kg/t HM for the years 2007–2011.

Input material	2007	2008	2009	2010	2011
Burden materials	1607	1620	1615	1630	1628
Coke	349	370	401	382	372
Alternative reducing agents (e.g., heavy oil)	89	81	53	70	71
Waste plastics	17	23	24	26	35

## 2.2. Evaluating the impact of plastics utilisation on the emissions of a blast furnace

To evaluate the significance of additional heavy metals input due to utilisation of waste plastics, the amount of the considered heavy metals (Hg, Cd, Pb, and Zn) is determined for each input flow. Then, the annual mean concentration of each of the different heavy metals is multiplied by the annual volume (or mass flow), of its respective input flows. Subsequently, the single input flows of Hg, Cd, Pb and Zn are added to determine the total input of all the heavy metals, which is finally referenced to the amount of hot metal produced in the considered year (Eq. (1)):

$$I_j = \frac{\sum_{i=1}^n m_{\text{Input},i} \cdot c_{i,j}}{m_{\text{HM}}} \quad (1)$$

where  $I_j$  is the input of Hg, Cd, Pb or Zn from “iron ore”, “crude tar, heavy oil, etc.”, “coke”, “waste plastics” [kg/t HM],  $m_{\text{Input},i}$  the mass or volume of the respective input material for a certain year [kg] or [m<sup>3</sup>],  $c$  the mean concentration of the respective heavy metal for a certain year [mg/kg] or [mg/m<sup>3</sup>] and  $m_{\text{HM}}$  the mass hot metal [t/a].

Similar calculations are performed for the different outflows of the blast furnace: internal recycling, landfilling, by-product, hot metal, emissions to water, and emissions to air (Eq. (2)):

$$O_j = \frac{\sum_{i=1}^n m_{\text{Output},i} \cdot c_{i,j}}{m_{\text{HM}}} \quad (2)$$

where  $O_j$  is the output of the respective heavy metal from “internally recycling”, “landfilling”, “by product”, “hot metal”, “emission to water”, “emission to air” [kg/t HM],  $m_{\text{Output}}$  the mass or volume of the output material for a certain year [kg] or [m<sup>3</sup>],  $c$  the mean concentration of the respective heavy metal for a certain year [mg/kg] or [mg/m<sup>3</sup>] and  $m_{\text{HM}}$  the mass hot metal [t/a].

Additionally, uncertainty ranges (see Eq. (3)) for the emissions are determined. These values of heavy metal emissions per quarter are referenced to the quarterly amount of hot metal produced and subsequently compared with the amount of the considered heavy metal introduced into the process (see Section 3.3):

$$u = \frac{s}{\sqrt{n}} \quad (3)$$

where  $u$  is the uncertainty of the mean value,  $s$  the standard deviation and  $n$  the number of measurement values.

TC and EF are used to predict emissions and are defined as follows:

$$TC_{k,j} = \frac{m_{\text{Output},k,j} \cdot c_{k,j}}{\sum_{i=1}^n m_{\text{Input},i} \cdot c_{i,j}} \quad (4)$$

where  $TC_{k,j}$  is the transfer coefficient for the respective heavy metal into a certain output flow (... “cleaned top gas”, “waste water”, “heavy metal enriched sludge 2”, “heavy metal enriched sludge 1”, “iron enriched sludge”, “topgas dust”, “cast house dust”, “cast house off-gas”, “slag” or “hot metal”) [-],  $c_{k,j}$  the mean concentration of the respective heavy metal in a certain output for a certain year [mg/kg] or [mg/m<sup>3</sup>],  $c_{i,j}$  the mean concentration of the respective heavy metal in a certain input for a certain year [mg/kg] or [mg/m<sup>3</sup>],  $m_{\text{Input},i}$  the mass or volume of the input material for a certain year [kg] or [m<sup>3</sup>] and  $m_{\text{Output},k,j}$  the mass or volume of the respective heavy metal for a certain output material for a certain year [kg] or [m<sup>3</sup>].

**Table 2**  
Analyses frequency of input and output flows.

Input	Sampling frequency	Frequency of analyses	Number of analysis per year	Output	Sampling frequency	Frequency of analysis	Number of analyses per year
Process Water	24-h composite sample (2 L)	Once a month	12	Cleaned top gas	3 successive half-hour averages per month	Once a month	12
Circulation Water	24-h composite sample (2 L)	Every 8 days	12	Sewage water	24-h composite sample (2 L)	Every 8 days	>40
Iron Ores	Each delivery (approximately 5 kg)	Once a month	12	Top gas dust	Two samples (2–3 kg) a week	Once a month	12
Coke	Continuously (every 6 min) from conveyor belt	Once a month	12	Cast house dust	One sample (2–3 kg) for each delivery	Once a month	12
Sinter	Continuously from sinter band; every 8 min	one time per month for Cd, Hg; every 4 days for Zn, Pb	12	Cast house off-gas	Continuous measurement of dust content (heavy metal emissions based on dust content + average composition of dust)		
Heavy fuel oil	Each day (approximately 0.5 L)	Once a month	12	Hot metal	One sample per pan	Each pan by each tap (approximately 40 samples per day)	>14,000
Crude tar	Each day	Once per quarter	4	Slag	One sample per tapping	Each tap (typically approximately 14 samples per day)	>5000
Waste plastics	Sampling according standard DIN EN 15442 (2011).	each 400 t	>250	Sludge to landfill	One sample a week	Once per month	12

$$EF_{k,j} = \frac{m_{Output, k,j} \cdot c_{k,j}}{m_{HM}} \quad (5)$$

where  $EF_{k,j}$  is the emission factor for the respective heavy metal and a certain output,  $c_{k,j}$  the mean concentration of the respective heavy metal in a certain output for a certain year [mg/kg] or [mg/m<sup>3</sup>],  $m_{Output, k,j}$  the mass or volume of certain output material for a certain year [kg] or [m<sup>3</sup>] and  $m_{HM}$  the mass hot metal [kg/a].

From Eq. (5), it is clear that for EF in comparison with TC, no information about the input and its composition is required.

To compare EF and TC with respect to the validity of their emissions predictions the absolute and relative deviations between the predicted (determined with EF or TC) and observed emissions are calculated and used as a quality measure (Eq. (6) and (7)):

$$d_{abs} = \sqrt{\frac{\sum_{i=1}^n (E_m - E_p)^2}{n}} \quad (6)$$

where  $d_{abs}$  is the absolute deviation,  $E_m$  the measured emissions,  $E_p$  the predicted emissions and  $n$  the number of measured emissions.

$$d_{rel} = \frac{d_{abs}}{\sum_{i=1}^n E_{m_i}} \quad (7)$$

where  $d_{rel}$  is the relative deviation,  $d_{abs}$  the absolute deviation and  $E_m$  the measured emissions.

### 3. Results

#### 3.1. Share of heavy metals from waste plastics to total input of heavy metals

The different raw materials for the blast furnace process contribute in different amounts to the total input of heavy metals. From Fig. 2, it becomes obvious that the main source for Pb and Zn in the input of the blast furnace is the different iron ores and that their entry is thus from “geogenic” origin.

The contribution of the iron ore to the total Zn input (which amounts from 130 to 145 g Zn/t HM) is approximately 80% and ranges from 106 to 119 g Zn/t HM for the years under investigation. Approximately 10–16 g Zn/t HM or less than 11% of the total Zn input is inserted by waste plastics. Other reducing agents such as crude tar and heavy oil play a minor role in the overall Zn input.

Iron ore also represents the major Pb input source (between 59 and 70% of the total Pb input) for the blast furnace and ranges from 13 to 17 g Pb/t HM. In comparison, waste plastics contribute up to 14% (or approximately 3 g Pb/t HM) to the total Pb input, which is quite similar to the share of Pb input due to the utilisation of coke (3 g Pb/t HM).

In contrast to Zn and Pb, for Cd waste plastics, injection represents the main input. The amount of Cd inserted by the utilisation of waste plastics as an alternative reducing agent ranges from 123 mg Cd/t HM to 178 mg Cd/t HM. The share of Cd inserted by waste plastics therefore ranges between 54% (in 2011) and 81% (2008) of the total Cd input. Iron ore contributed up to 21% (60 mg Cd/t HM) to the total input in 2011. However, it must be noted that the contribution of iron ore to the total Cd input represents a low estimate, as the Cd content of the iron ores analysed was often below the limit of quantification, and these non-quantifiable values have been set to zero with the awareness that the “real” Cd content of those ores must be between 0 and the limit of quantification. This method was chosen because the limit of quantification for the chemical analysis was not available, and therefore, no other method (e.g., to use one-half of the limit of quantification instead of 0) could be applied.

In the case of Hg, waste plastics make a relatively high contribution of up to 44% (2009) to the total Hg input. The amount of Hg inserted by waste plastics was almost constant throughout the different years (6–7 mg Hg/t HM), although the amount of waste plastics utilised increased significantly (Table 1). Hence, the average Hg content of the plastics utilised decreased during the years by almost 50%. The main portion of the Hg input into the blast furnace originates from crude oil products (up to 76% in 2011) such as crude tar and heavy oil. Fig. 2 indicates that in 2011, the amount of Hg inserted by crude tar had nearly doubled (from approximately 10 mg Hg/t HM to 25 mg Hg/t HM) compared to the years

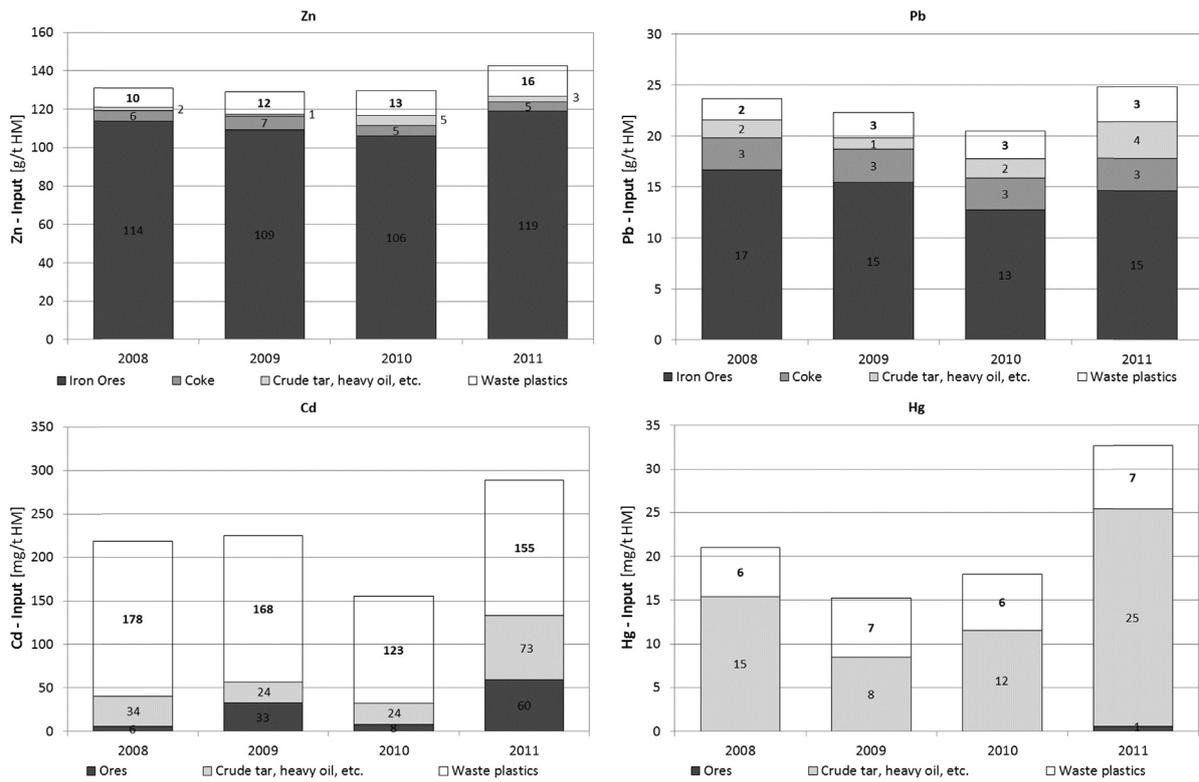


Fig. 2. Sources of the heavy metals Zn, Pb, Cd, and Hg in the blast furnace input.

2008–2010. Coke does not contribute to the total input of Hg at all. The share of Hg inserted through iron ore is almost negligible and amounted to 2% (1 mg/t HM) of the total Hg input in 2011. For the other years investigated ore contributed less than 2% (<0.1 mg Hg/t HM) to the total Hg input and is therefore not visible in Fig. 2.

In general, it can be noted that the amount of injected waste plastics increased during the years under investigation from 23 kg plastics/t HM in 2008 to 35 kg plastics/t HM in 2011. However, the amount of heavy metals introduced by plastics into the blast furnace remained rather constant (Hg, Pb, and Cd) or increased just slightly (Zn) over time. Therefore, it can be concluded that the heavy metal content of waste plastics has decreased significantly over the years.

### 3.2. Distribution of heavy metals in output flows

The distribution of the heavy metals in the different outputs of the blast furnace depends on the respective heavy metal and its physico-chemical characteristics (e.g., melting point, evaporating point). In Fig. 3, the distribution of heavy metals in the various output flows, which are indicated in Fig. 1 is presented for the year 2011. Within Fig. 3, the output flows for both system boundaries (system boundary 1 and system boundary 2 with sinter plant, as indicated in Fig. 1) are shown.

For system boundary 1, “Landfilling” includes the sludge from the heavy metal precipitation and the heavy metal enriched sludge from the cyclone. “Emissions to water” refers to the waste water, which is further processed in the municipal water treatment plant. “Emissions to air” includes the cleaned top gas and the off-gas from the cast house, the former of which is not directly released to the atmosphere but utilised in an electric power plant. Moreover, the flows of heavy metals output through the hot metal and the slag by-product are included in Fig. 3. “Internally recycled (to sinter plant)” consists of the cast house dust, the top gas dust and the sludge from

the cyclone, which are processed in the sinter plant. During the sintering process, the considered heavy metals may evaporate (as temperatures of up to 1350 °C are reached (Babich et al. (2008))) or remain in the sinter material. Hg, for example, does not remain in the sinter material and is transferred into the gas phase because of its low evaporation point of approximately 360 °C (Barin et al. (1973)). For Pb approximately 30% of the total input into the sinter plant remains in the sinter and approximately 70% passes into the gas phase (Kieberger (2013)). Zn mostly remains in the sinter material because it enters the sinter process as zinc oxide (ZnO), which is characterised by a high melting point of approximately 1975 °C (Deike and Hillmann (1999)). Cd most likely passes nearly completely into the gas phase because of its low evaporation

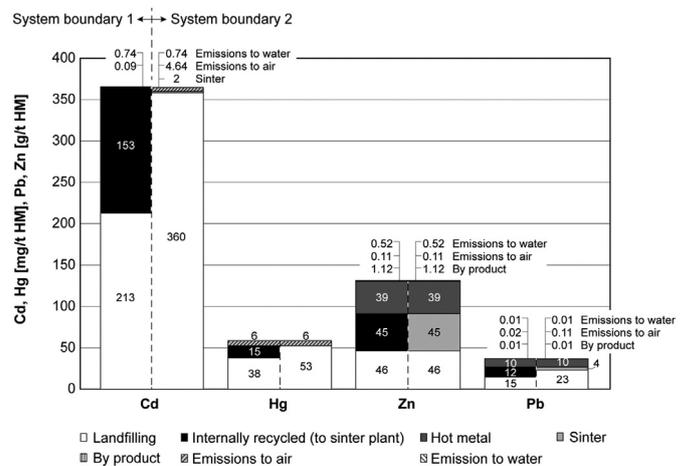


Fig. 3. Distribution of heavy metals in output flows for 2011 (Cd, Hg [mg/t HM]; Zn, Pb [g/t HM]).

point of approximately 770 °C (Barin et al. (1973)). This assumption is also supported by the very low Cd concentrations detected in the sinter product. Most analysis values available were under the quantification limit (only 1 out of 48 Cd analyses delivered quantifiable levels of Cd), demonstrating that hardly any Cd is present in the sinter material.

The off-gas of the sinter plant is cleaned with fabric filters (and some additives such as CaOH<sub>2</sub> or NaHCO<sub>3</sub>), and the dust obtained is subsequently landfilled. This cleaning system reduces gaseous emissions by up to 99% (for Pb, for instance) (Siemens (2010)). Thus, it can be assumed that the Cd and Hg that is internally recycled (input into the sinter plant) is almost completely removed from the system and transferred to the fabric filter dust, which is subsequently landfilled (see Fig. 3). In particular, it was assumed that approximately 1% of the internally recycled Cd remains in the sinter material. This assumption is based on observations of the Cd content of the sinter material. The output flows for system boundary 2 (which includes the sinter plant) are also shown in Fig. 3 (right side of each bar). In this case “landfilling” includes, in addition to the sludge from the heavy metal precipitation and the heavy metal enriched sludge from the cyclone, the off-gas dust of the sinter plant. The emissions to the atmosphere consist of the emission of cleaned top gas (after the top gas scrubber), of cleaned cast house off-gas (after dedusting) and of cleaned off-gas from the sinter plant (after dedusting).

Consequently, total amounts of approximately 360 mg Cd/t HM and 53 mg Hg/t HM are discharged from the system and subsequently landfilled. Thus, approximately 90% of the total Hg output and approximately 98% of the total Cd output are transferred to an appropriate sink. The total amount of Pb (including the off-gas dust from the sinter plant) that is landfilled is approximately 23 g Pb/t HM (equals to 63% of the total Pb output).

Approximately 42% (153 mg Cd/t HM) of the total Cd output is found in the top gas dust, the cast house dust and the sludge. All of these outputs are utilised in the sinter plant. During the sintering process, the major part of Cd (>99%) is transferred into the off-gas filter dust and subsequently landfilled. Approximately 98% (360 mg Cd/t HM) of the total Cd output is finally landfilled. Considering the system without the sinter plant (system boundary 1), Cd emissions to the atmosphere amount to around 0.3% (0.09 mg Cd/kg HM) of the total output. For system boundary 2 (including the sinter plant), the overall gaseous Cd emissions increase to approximately 1.2% (4.6 mg/kg HM), assuming that the off-gas dedusting system of the sinter plant retains approximately 97% of the total Cd in the filter dust. Approximately 0.2% (0.74 mg Cd/kg HM) of the total Cd output is emitted into the hydrosphere.

About two-thirds of the Hg is transferred within the blast furnace and its satellite processes to products that are landfilled. Around 26% (15 mg Hg/t HM) of the total Hg output is discharged via dust and sludge and subsequently introduced to the sinter plant. There, the majority of the Hg is transferred to the filter dust, which is landfilled. Altogether approximately 10% (6 mg Hg/g HM) of the total Hg output leaves the process through the exhaust air from the cast house and the cleaned top gas.

More than 34% (45 g Zn/t HM) of the total Zn output accumulates in dust and sludge, that are utilised in the sinter plant. It can be assumed that all of the Zn remains within the sinter material and is thus recirculated into the blast furnace. Approximately 29% (39 g Zn/t HM) of the total Zn leaves the process with the hot metal, and approximately 1% (1.1 g Zn/t HM) is transferred into the by product. Around 35% (46 g/t HM) of the total Zn output enters the landfill. Gaseous emissions of Zn account for approximately 0.1% (0.11 g Zn/t HM), and almost four times as much (0.4% or 0.52 g Zn/t HM) is emitted into the hydrosphere (to the waste water treatment plant).

The share of Pb that is internally recycled (33%) and transferred into the product (27%) is comparable to the results for Zn. However, a larger fraction of Pb (approximately 39% of the total lead output) ends up in the landfill (considering system boundary 1). When including the sinter, the share of Pb finally transferred to the landfill increases to approximately 63% (23 mg Pb/t HM).

The results of the investigations demonstrate that only a minor share of the heavy metal output occurs in the form of emissions to the environment (atmosphere and hydrosphere). Only Hg emissions into the atmosphere represent a significant flow among the total output flows. The majority of the heavy metals from the blast furnace and its satellite processes are transferred to landfills, which represent a sink for these heavy metals.

### 3.3. Heavy metal emissions as a function of total input load

To investigate the validity of the transfer coefficients, gaseous and liquid emissions of Cd, Hg, Pb and Zn are investigated and referenced to the specific inputs of the heavy metals. According to previous works (Bürgler et al., 2007; Pilz and Bürgler, 2007; Vadenbo et al., 2013), that applied transfer coefficients to assess emissions, a clear dependency between emission levels of heavy metals and their respective inputs into the blast furnace should be expected.

In Fig. 4, quarterly mean values of Zn, Pb, Cd and Hg emissions and their input flows are illustrated for the period 2008 to 2011. It is clear that no correlation exists between the total inputs of the different heavy metals and their emissions. The quarterly emissions of Zn, Pb, Cd and Hg seem to be independent of the total inputs of those heavy metals into the blast furnace. Moreover, the Hg content of the waste water and the Cd content of the cleaned top gas are predominantly below the limit of quantification (more than 13 (Cd, Hg) out of 16 quarterly values are below the quantification limit). Therefore, these measurement values are indicated with <<0.01 mg/t HM in Fig. 4.

Because no correlation between input and emissions of the considered heavy metals can be detected, transfer coefficients seem to be inappropriate for describing heavy metal emissions from the blast furnace process. To verify this statement, the quarterly mean transfer coefficients for the cleaned top gas and the waste water were calculated. As an example, the transfer coefficients for Cd into the waste water are shown in Fig. 5. The results indicate that the TC for Cd into waste water is far from being constant. It varies between 0.2% and 2%.

To compare the two different concepts for predicting/describing emissions, namely EF and TC, the absolute and relative deviation between predicted (applying EF or TC) and observed emissions of heavy metals have been determined. This investigation has been limited to the elements Hg, Zn and Pb because for Cd, too many observations were below the limit of quantification. To predict emissions into the atmosphere, the TC published by Bürgler et al. (2007) (TC<sub>Hg</sub> = 5%, TC<sub>Zn</sub> = 1.4%, TC<sub>Pb</sub> = 1.2%), the mean TC calculated in the present study (TC<sub>Hg</sub> = 13%, TC<sub>Zn</sub> = 0.03%, TC<sub>Pb</sub> = 0.07%) and the mean EF derived from the present study (EF<sub>Hg</sub> = 4.3 mg/t HM, EF<sub>Zn</sub> = 0.041 mg/t HM, EF<sub>Pb</sub> = 0.014 mg/t HM) were used. From Table 3, it can be observed that the values predicted using the EF show the lowest relative deviation. In comparison, the mean relative deviation when applying the TC of Bürgler et al. (2007) is quite high except for Hg.

## 4. Conclusions

Detailed analysis of heavy metal input indicates that in most cases, “geogenic” resources such as iron ores dominate the input of heavy metals into the blast furnace process. The contribution of

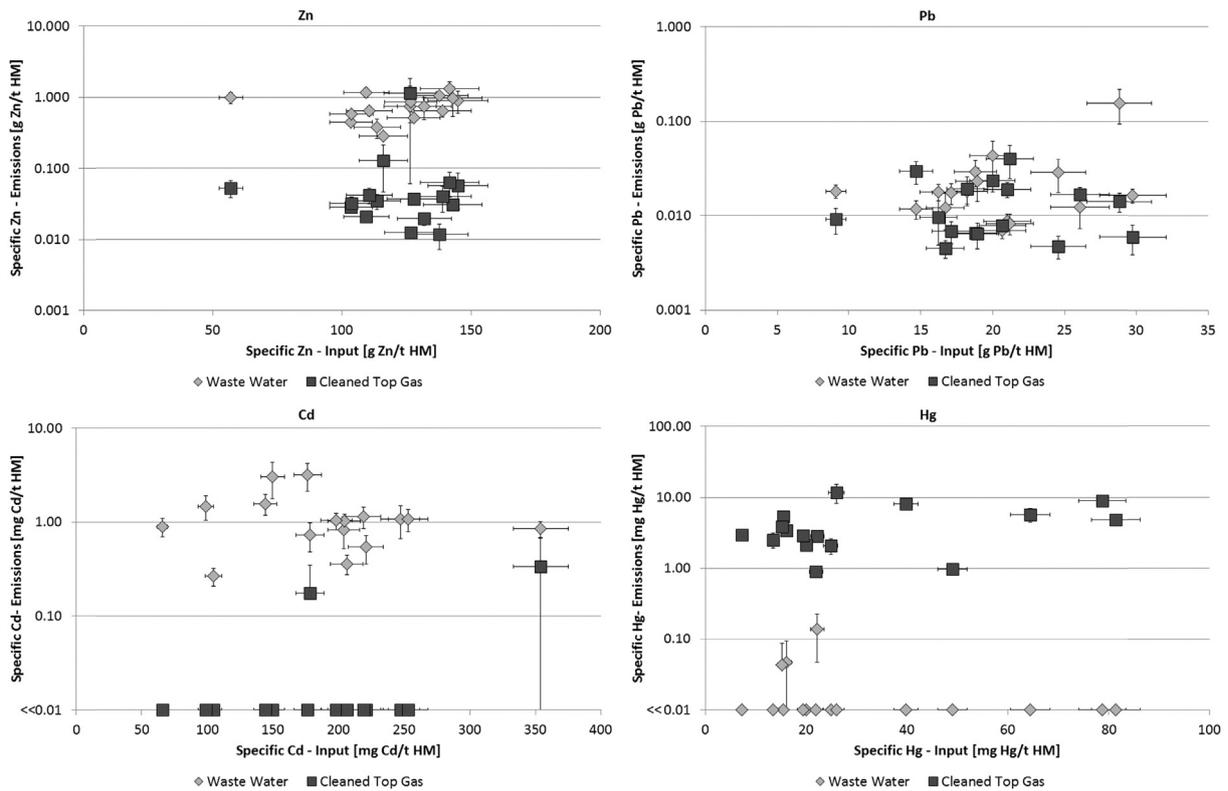


Fig. 4. Specific heavy metal emissions versus specific heavy metal input (expressed in g/t HM or mg/t HM).

waste plastics is only significant for Cd and Hg. For Cd, waste plastics contribute to approximately 81% of the total input, whereas for Hg almost half of the input (up to 44%) can be attributed to the utilisation of plastics. The figures for Hg and Cd represent an upper limit of the contribution of waste plastics to the total input, as their levels in iron ore, for instance, are often below the limit of quantification. For the metals Zn and Pb waste plastics contribute less than 14% to the total input. For these two elements, the iron ore could have been determined as the main input source.

Major amounts of the heavy metals introduced into the process are finally landfilled (for Cd, more than 95%, for Hg 90%, for Pb 60% and for Zn around 34%).

The shares of these heavy metals emitted to the hydrosphere are well below 1% of the total (approximately 0.3% for Cd,

approximately 0.4% for Zn and not detectable for Hg and Pb). However, it must be noted that these figures represent the very upper limit, as the cleaned waste water from the blast furnace is further cleaned off-site in a municipal waste water treatment plant. Similar results are also observable for the gaseous emissions. Only minor amounts of Zn (<0.1%), Pb (<0.2%) and Cd (approximately 1%) with respect to the total output flows are emitted into the atmosphere. Between 4 and 10% of the total Hg output can be found in the cleaned top gas. For the cleaned top gas, it has to be noted that the values given represent an upper limit of emissions because prior to its release into the atmosphere, it is used for electricity production and is further cleaned (Selective Catalytic Reduction).

Based on detailed investigations of temporal heavy metal emissions and their respective input into the blast furnace, it can be concluded that the common assumption of a constant TC (suggesting a linear correlation between input and output flows) for assessing heavy metal emissions with respect to the overall input of heavy metals into the blast furnace might not be valid. This is especially the case for the emission paths of minor heavy metal flows. According to the monitoring data of the plant, it may be concluded that the input loads of heavy metals (in the time period 2008–2011) can be efficiently retained by the filter and cleaning devices in place. However, knowledge regarding the

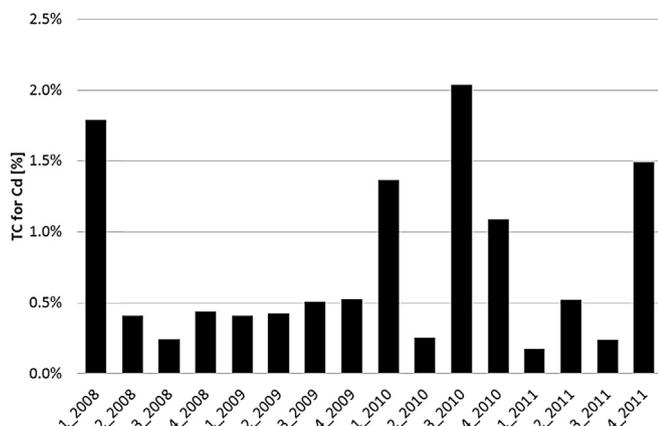


Fig. 5. Quarterly mean TC for Cd to waste water (before municipal waste water treatment).

Table 3  
Mean absolute ( $d_{abs}$ ) and relative deviation ( $d_{rel}$ ) between the observed and predicted emissions of Hg, Zn, and Pb.

	Hg		Zn		Pb	
	$d_{abs}$ [mg/t HM]	$d_{rel}$ [%]	$d_{abs}$ [mg/t HM]	$d_{rel}$ [%]	$d_{abs}$ [mg/t HM]	$d_{rel}$ [%]
TC Bürgler et al. (2007)	2.6	87	1199.6	4254	175.5	1802
Mean TC (calculated)	2.3	77	19.1	68	7.0	72
Mean EF	2.0	68	18.5	66	6.8	70

extent to which these devices are capable of coping with higher loadings of heavy metals is so far lacking. Based on the current knowledge, the concentrations of heavy metals in the cleaned top gas and the waste water are unaffected by utilisation of waste plastics at a rate up to 35 kg/t HM. Thus, further investigations into the linkage between input and output flows and processes are necessary to reliably predict emissions from blast furnaces.

Based on these results it can generally be concluded that the utilisation of waste plastics does not influence the heavy metals emissions of a blast furnace under actual process conditions and loadings. It was clearly demonstrated that the majority of the heavy metals are transferred into the landfill, which can be regarded as a sink for the heavy metals investigated. Because of the absence of a clear correlation between the inserted amount of heavy metals and the emissions to the environment, EF should rather be utilised instead of TC for predicting gaseous and liquid emissions from blast furnaces.

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### Glossary

- CFD: Computational Fluid Dynamics  
 EF: Emission factor  
 EoL: End of Life  
 HM: Hot Metal  
 LCA: Life Cycle Assessment  
 LCI: Life Cycle Inventory  
 MCDM: Multi Criteria Decision Making  
 MFA: Material Flow Analysis  
 TC: Transfer coefficient  
 WEEE: Waste Electrical and Electronic Equipment