SPECIATION OF IRON, ZINC, LEAD AND CALCIUM IN BLAST FURNACE TOP-GAS FILTER DUST BY SEQUENTIAL LEACHING

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Abstract

Top-gas dedusting at blast furnaces (BF) is usually done with venturi scrubbers. However, in recent years, the total dry dedusting of BF top-gas has become a common technology. In this case, a fabric filter is used instead of the venturi scrubber. For recycling, the dry dust from a fabric filter is preferable to the sludge from a scrubber. The main constituents of BF dedusting residues, Fe, C and Ca are of some value, while tramp elements, particularly Zn, can cause problems in the process. Results from leaching of the sludge obtained in wet BF dedusting are available. In contrast, data from leaching of dry filter dust from BF dedusting are not available. However, it has to be assumed that the behavior of a dust from dry dedusting deviates somewhat from that of a sludge due to the prolonged residence time of the sludge in the scrubber system under varying pH. In this study the filter dust of a BF top-gas dry dedusting filter was investigated, applying sequential leaching and X-ray diffraction analysis for the investigation of the distribution of Fe, Ca, Zn and Pb in various compounds with a focus on the tramp element Zn.

Keywords: Blast furnace, filter dust, zinc, leaching

1.   INTRODUCTION

In an integrated steel mill the dedusting system for the blast furnace (BF) top-gas normally consists of two stages, a dry pre-separator (dust catcher or cyclone) as the first stage and a venturi scrubber for the final dedusting [1]. In recent years, the total dry dedusting of the top-gas has become a common technology [2-4]. In this case, a fabric filter is used in the second dedusting stage instead of the venturi scrubber. Thereby, the BF sludge from the scrubber system is replaced by dry dust, which facilitates handling of the residue. The main constituents of the BF dedusting residues, Fe, C and Ca are of some value, which supports recycling, e.g. via the sinter plant [5,6]. However, some tramp elements, particularly Zn, are limited in the recycling stream, as they can cause operational problems in the BF. Zn contained in the BF charge is easily reduced to metallic Zn and volatilized when the material moves downwards in the shaft and reaches a temperature higher than 1173 K [7]. The Zn vapour moves upwards with the gas stream and at lower temperature the Zn is re-oxidized forming fine particles, which are partly discharged with the top-gas.

The leaching of Zn from the dust separated in the first dedusting stage (BF dust) has been investigated [8-10]. There is also some information available on the distribution of Zn in this dust. X-ray diffraction patterns of such dusts show that beside ZnO [9-12] and $ZnFe_2O_4$ [9,10] it also contains ZnS [11,12] and $ZnCO_3$ [12]. In contrast to the Zn concentration in the dust from the first dedusting stage the Zn concentration in the residue from the second dedusting stage is usually considerably higher [1,13] Likewise, leaching of the sludge obtained in wet second-stage dedusting (BF sludge) was also investigated [14-18]. In the BF sludge Zn is found as ZnO [15] and as $ZnFe_2O_4$ [16,17].

For the dust from a second stage dry dedusting system (BF filter dus) it is likely that the composition deviates somewhat from that of a BF sludge as well as from a BF dust. In comparison to the BF dust, the particle size of the BF filter dust separated in the second dedusting stage is smaller and the concentrations of the tramp

elements are higher. Due to the prolonged residence time of the BF sludge in the scrubber water system under varying pH conditions, the composition may change and therefore be different to the BF filter dust.

In this study the BF filter dust from a second-stage dry dedusting filter for BF top-gas dedusting was investigated for the distribution of Fe, Ca, Zn and Pb in various compounds, with a focus on the tramp element Zn.

2.   MATERIALS AND METHODS

The BF filter dust sample was obtained from the dust discharge of the second-stage dedusting filter of an industrial BF top-gas cleaning system. Detailed information on the dust sample has been published previously [19].

The leaching experiment was carried out in a sequence of five steps, the residue being treated from a leaching step in the next step. The leaching process was adapted from a leaching procedure for BOF dust [20]. In the first step, the exchangeable, slightly water-soluble fraction (L1) was extracted. In the subsequent steps, the carbonated fraction (L2), the oxides (L3), the reduced fraction (L4) and the residual fraction (L5) were obtained. Details of the leaching process can be found elsewhere [21]. An ICP-OES system (iCAP 7000 Plus Series) was used to measure the concentrations of Fe, Ca, Zn and Pb in the leachates.

Microscopic images of the BF filter dust were produced with a scanning electron microscope TESCAN, type VEGA LM.

For Zn and Pb the thermodynamic equilibrium composition under BF top-gas conditions (50% N_2, 25% CO, 23% CO_2 and 2% H_2O by volume) was calculated as a function of the temperature using the HSC Chemistry® 5.1 program.

3.   RESULTS AND DISCUSSIONS

The concentrations of Fe, Ca, Zn and Pb in the dust were 13.6%, 5.2%, 1.88% and 0.29%, respectively. **Figure 1** shows a microscope image of the BF dust.
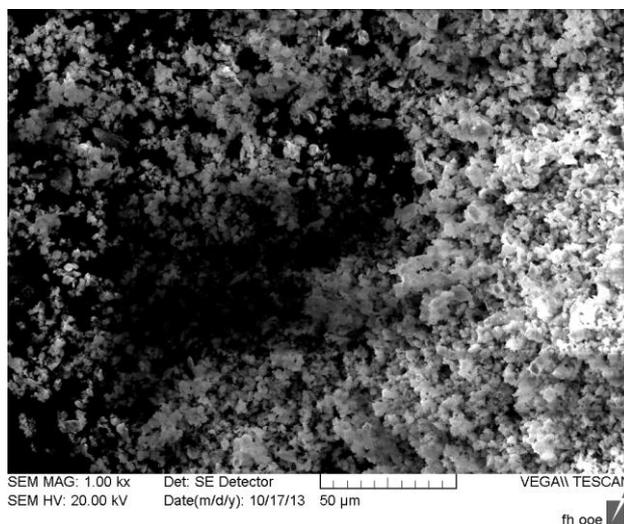
Figure 1 Microscope image of the BF dust

The results of the sequential leaching test are shown in **Figure 2**. Fe was found mainly in the residual fraction (81%) and to a lesser extent in the carbonated fraction. This corresponds to reported qualitative data [16]. In

contrast, Ca was found in all fractions L1 to L4 to a noticeable extent with two thirds of the amount in L1 and L2 to approximately similar parts.

Zn was found mainly in the carbonate fraction (60%) and in the oxide fraction (27%), while a lower amount of Zn was found in the reduced fraction (11%). The amount in the residual fraction was 3%, indicating that the amount of $ZnFe_2O_4$ in the dust was small. The distribution of Zn in the BF filter dust is therefore more similar to that in the BF dust [9-12] than to the distribution in BF sludge [15-17].
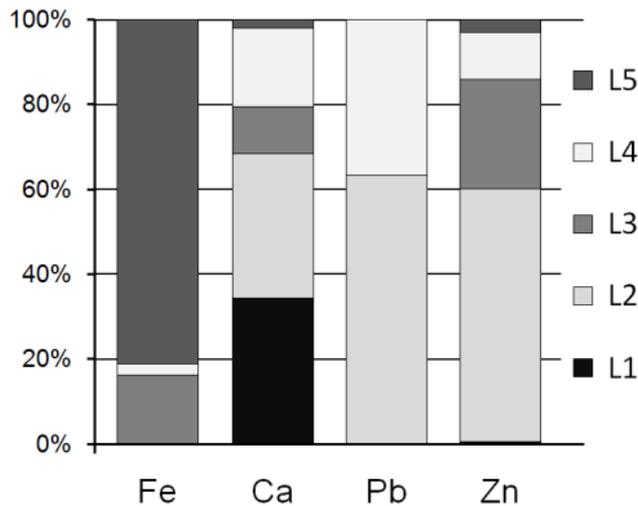
Figure 2 Fe, Ca, Pb and Zn in various fractions

The results of the thermodynamic equilibrium calculations for the distribution of Zn as a function of the temperature are shown in **Figure 3**.
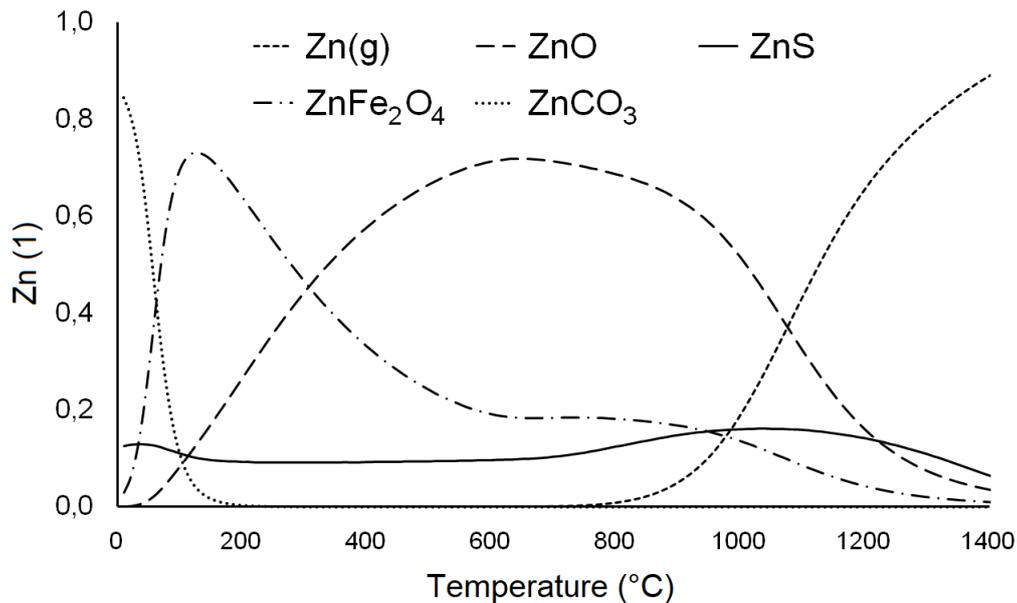
Figure 3 Distribution of Zn at thermodynamic equilibrium

In the high temperature zone of the BF, most Zn is present as metallic Zn(g) while some ZnS also exists. Solid ZnO and $ZnFe_2O_4$ are formed when the gas temperature decreases. Below 600°C the ZnO concentration decreases because of the formation of $ZnFe_2O_4$. The comparatively small amount of $ZnFe_2O_4$ found in the leaching experiments might be due to the fact that reaction rates in solid reactions are low. When the dust and

the ZnO particles are separated by the fabric filter, a filter cake is formed on the filter cloth and the top-gas containing CO_2 passes through this filter cake for some time before the filter cake is removed in the pulse-jet cleaning cycle. During this period of time the reaction of ZnO with CO_2 to $ZnCO_3$ might occur.

Pb was found only in the carbonate fraction (63%) and in the reduced fraction. This finding agrees well with the results of the equilibrium calculations shown in **Figure 4.** At a temperature above 1000°C, gaseous Pb(g) and PbS(g) exist parallel to PbO, while below these temperatures the stable form is PbO. At temperatures below 400°C the equilibrium gradually shifts to PbS. Below 200°C $PbCO_3$ is also formed. In the fabric filter the formation of $PbCO_3$ can take place in a similar way, as explained previously for $ZnCO_3$.
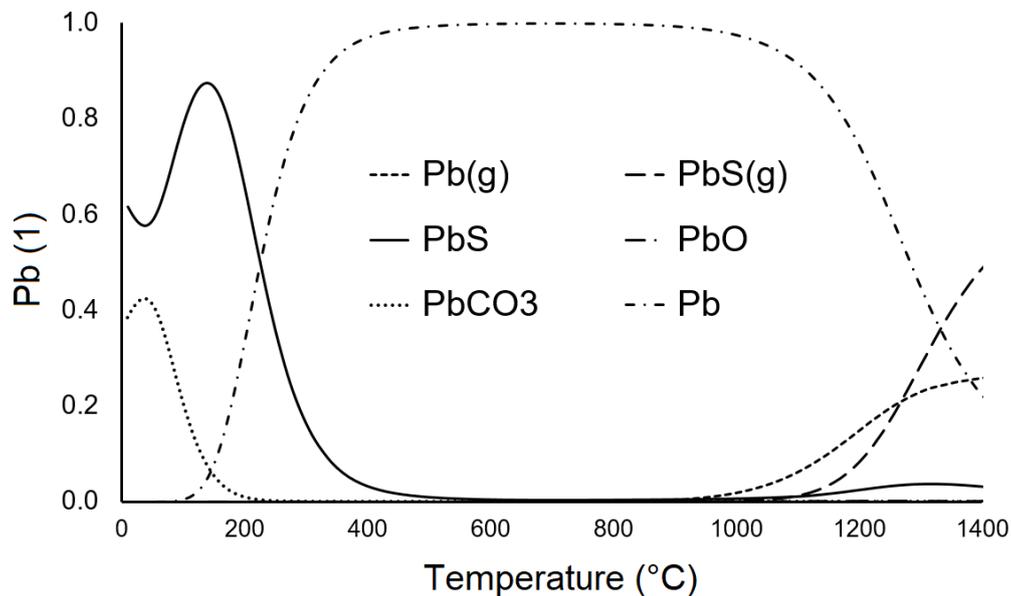
Figure 4 Distribution of Pb at thermodynamic equilibrium

4.   CONCLUSIONS

In the BF filter dust from second-stage BF dedusting Fe was found mainly in the residual fraction and Ca was found mainly in the exchangeable fraction and the carbonated fraction to approximately similar parts. The tramp element Zn is mainly present in the carbonate fraction, in the oxidic fraction and in the reduced fraction. In contrast, Pb is present in the carbonate fraction and in the reduced fraction. The deviations between the measurement results and the results of the thermodynamic equilibrium calculations can be explained by taking into account the conditions in the gas cleaning system. With respect to the distribution of Zn, the BF filter dust obtained in dry second stage dedusting is more similar to the BF dust from first stage dedusting than to the BF sludge obtained in wet second stage dedusting.

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