CHARACTERIZATION OF DUST FROM PIG IRON DESULPHURIZATION UNITS

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Abstract

In integrated steel mills, the desulphurization of pig iron from the blast furnace is a crucial pretreatment step before the hot metal is converted into steel in the basic oxygen converter. During this process, significant dust emissions can occur, reaching up to 1 kg per tonne of liquid steel, with dust concentrations in the off-gas reported as high as 10 g/m³. The exhaust air from the desulphurization facility is typically cleaned using dry dedusting systems, most commonly electrostatic precipitators or bag filters. The separated dust is often recycled to the sinter plant, closing material loops within the steelworks. In contrast to other residues generated in steel-plant off-gas cleaning systems, comparatively little information is available on the physical properties and chemical composition of dust originating from pig-iron desulphurization. To address this gap, dust samples from desulphurization units at two different steel mills were systematically investigated. Physical and flow properties were determined alongside detailed chemical analyses. The results reveal substantial differences between the two dust samples, particularly in their carbon content, but also in the concentrations of sulphur, zinc, and alkali metals. Substantial variations were likewise observed in key physical properties, including bulk density and particle-size distribution. These parameters strongly influence both the handling behaviour of the material and its recycling. Taken together, the findings underscore the importance of plant-specific characterization when assessing utilization strategies for desulphurization dust.

Keywords: Steel mill, desulphurization unit dedusting, dust composition, physical properties

1. INTRODUCTION

In integrated steelworks, hot metal produced in the blast furnace typically contains sulphur concentrations that are incompatible with the quality requirements of most modern steel grades. Elevated sulphur levels adversely affect physical and flow properties, weldability, and surface quality, making an efficient desulphurization of pig iron a crucial pretreatment step before charging the hot metal into the basic oxygen furnace (BOF). Consequently, hot metal desulphurization has become standard practice in virtually all integrated steel plants worldwide [1-3].

Several industrially established methods are available for pig iron desulphurization, which primarily differ in reactor configuration, injection technique, and desulphurizing agent. Commonly applied processes include magnesium mono-injection, lime or calcium carbide injection, and magnesium-lime co-injection [4,5]. Magnesium-based reagents provide rapid sulphur removal owing to favourable thermodynamics and fast reaction kinetics, whereas lime and calcium carbide enable deeper desulphurization and suppression of resulphurization through the formation of stable calcium sulphide phases [6,7]. As a result, co-injection of magnesium with lime or calcium carbide is widely regarded as the most versatile and cost-effective solution, allowing both fast and deep sulphur removal depending on steel grade requirements [8,9].

During pig iron desulphurization, intensive gas flow, reagent injection, and slag handling lead to the formation of dust-laden off-gas streams. Dust generation rates of up to approximately 1.0 kg per tonne of liquid steel have been reported, with dust concentrations in the off-gas reaching several grams per cubic meter [1,10]. To comply with environmental emission limits, off-gas cleaning systems such as electrostatic precipitators or fabric

filters are employed [1]. The collected dust is typically fine-grained and often contains carbon [11], unreacted or partially reacted desulphurizing agents, sulphides, oxides, and various metallic elements originating from the hot metal or reagents. In many steel plants, desulphurization dust is recycled internally, most commonly via return to the sinter plant as part of the raw mix [1]. This approach allows partial recovery of iron-bearing components, thereby contributing to material loop closure and resource efficiency. However, recycling is constrained by the chemical composition of the dust [12-14], particularly by its sulphur, zinc, chlorine, and alkali metal contents, which may lead to accumulation effects, process disturbances, or increased emissions in downstream units. Consequently, in some plants desulphurization dust is discharged to landfill sites, representing both an economic burden and a loss of valuable secondary raw material.

While numerous studies have focused on the chemistry and kinetics of pig iron desulphurization and on the optimization of injection processes [15-17], comparatively little information is available on the physical properties and detailed material characteristics of dust originating from pig iron desulphurization facilities. In contrast, dusts from other processes in steel mills such as basic oxygen furnaces, electric arc furnaces, or blast furnaces have been extensively characterized with respect to particle size distribution, bulk density, flowability, and chemical composition, as these properties strongly influence handling, storage, transport, and recycling behaviour [18,19]. The importance of dust properties extends beyond chemical composition alone. Mechanical properties such as particle size distribution, bulk density, flowability, angle of repose, and wall friction behaviour are critical parameters for the design and operation of silos, hoppers, and conveying systems. Poor flowability or high cohesiveness may cause arching, ratholing, or segregation, leading to operational problems and limiting recycling options [20].

Against this background, the present work aims to contribute to closing the knowledge gap regarding dust from pig iron desulphurization facilities. Dust samples collected from two industrial desulphurization installations were investigated with respect to their mechanical and chemical properties. In addition, sequential dry air classification was applied to assess the potential for size-dependent separation as a means of improving handling behaviour and recycling potential. The results provide insight into the variability of desulphurization dust properties and underline the importance of comprehensive characterization when evaluating utilization and recycling strategies.

2. MATERIALS AND METHODS

2.1. Materials

Dust samples were collected as single grab samples from the dust discharge of the off-gas filters of two pig iron desulphurization facilities. Approximately 2 kg of dust material was collected for each sample. The samples were dried at 105 °C until constant mass was achieved. After drying, the bulk sample was reduced to a representative quantity suitable for the various laboratory analyses by repeated sample splitting using mechanical sample dividers (Haver & Boecker HAVER RT, Quantachrome Micro Riffler).

2.2. Measurement of physical properties and chemical analysis

For particle size analyses, the dust samples were first sieved with a Fritsch Analysette 3 PRO vibratory sieve shaker using a sieve stack with mesh sizes of 500 µm, 800 µm, 1,250 µm, 2,000 µm, and 3,150 µm. In a second step, the particle size distribution of the material passing the 500 µm sieve was determined by laser diffraction using a HELOS/RODOS system with dry dispersion (Sympatec). Instrument performance was verified using a Sympatec SiC P600’06 reference standard. The width of the particle size distribution was expressed as the ratio of d_{90} to d_{10} following the definition proposed by Rumpf [21]. The bulk density of the dust samples was measured in accordance with ÖNORM EN ISO 60 [22] while the angle of repose was determined following ISO 4324 [23].

The flow behaviour of the dust was characterized using an annular shear tester (Schulze RST-XS). The tests were carried out according to ASTM D6773 [24] at four normal stress levels (600 Pa, 2,000 Pa, 6,000 Pa, and 20,000 Pa). Quantitative assessment of flowability was based on the flow factor ff_c, calculated as the ratio of the major consolidation stress to the unconfined yield strength. Flow behaviour was classified into five categories, from not flowing ($ff_c < 1$) to free-flowing ($ff_c > 10$) [25]. In addition, the wall yield locus of the dust samples was determined using the ring shear tester [26]. In the wall shear cell, the bottom ring consisted of the investigated wall material (structural steel S235JR, 1.0038). Measurements were performed at wall normal stresses of 600 Pa, 2,000 Pa, 6,000 Pa, and 20,000 Pa.

The total carbon (TC) content of the dust samples was determined using a varioTOC analyser (Elementar Analysensysteme). Calibration of the instrument was performed using a certified soil reference material from Elementar Analysensysteme with a TC/TOC content of 7.7%. The concentrations of S, P, Cl and selected metals were measured by X-ray fluorescence spectroscopy (XRF) using a SPECTRO XEPOS spectrometer (AMETEK). Powder samples were analysed using the TurboQuant method. Instrument calibration was carried out using an MCA fusion tablet, and performance was verified with the certified reference material BCR®-176R (incineration ash; European Commission, Community Bureau of Reference).

Micromorphological examination of the dust samples was performed using a scanning electron microscope (SEM; TESCAN MIRA3). Elemental composition of individual particles was determined by energy-dispersive X-ray spectroscopy (SEM-EDX).

2.3. Size separation

Sequential dry classification of dust sample A was carried out using a laboratory air classifier (Hosokawa Alpine 100 MZR). Dust A was selected for classification because of its wider particle size distribution. Prior to air classification, the size fraction > 500 µm was separated by sieving. Subsequently, in the first classification step, the finest particle fraction was separated from the bulk material < 500 µm. The remaining coarse fraction was subsequently used as feed material for the second classification step, during which the classifier was operated at a reduced rotational speed. In this step, the material was separated into the second fines size fraction and a newly generated coarse fraction. This procedure was repeated twice to obtain further size fractions. The principle and methodology of the sequential air classification approach are described in detail in the literature [27]. The classifier rotational speeds applied in the four classification steps were 21,000 rpm, 11,000 rpm, 6,000 rpm, and 3,000 rpm, respectively. In the air-classified samples, the concentrations of Cr and Ni are not reliable because of some erosion of the classifier wheel [28].

3. RESULTS AND DISCUSSION

3.1. Physical properties and chemical composition of the dusts

The particle size distributions of dust samples A and B are shown in **Figure 1** (left side). The size distributions differ substantially. The mass median diameter (d_{50}) was 55 µm for dust A and 150 µm for dust B. Dust A exhibited a broad particle size distribution with a spread of 350, whereas dust B showed a considerably narrower distribution with a spread of 11. An atypical feature of both samples is the presence of a fraction of particles larger than 500 µm, accounting for more than 5% of the dust. Such coarse particles are uncommon in filter dust, as particles of this size typically settle within the off-gas system before reaching the filter. The occurrence of these large particles in the filter dust therefore suggests a relatively low particle density, resulting in only moderate settling velocities.

The bulk density was 570 kg/m³ for dust A and 435 kg/m³ for dust B. The right side of **Figure 1** illustrates the stress dependence of the bulk density. Despite its coarser particle size, dust B exhibits a lower bulk density, which is atypical. This behaviour may be related to a comparatively lower particle density of the coarse particles.

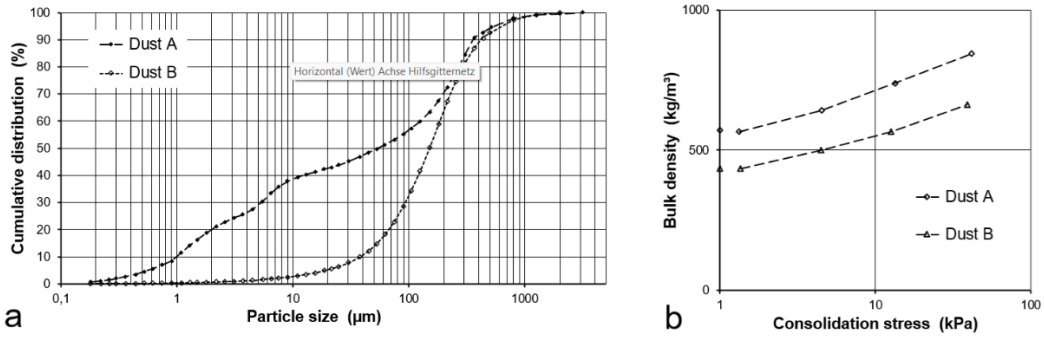

Figure 1 Particle size distribution of the dusts (a) and bulk density as a function of applied stress (b)

The angle of repose is commonly used as a simple measure to characterize the flowability of powders [29]. The measured angles of repose were very similar for both dust samples, amounting to 50° for dust A and 53° for dust B. According to the corresponding classification [30], both materials fall into the flowability class “cohesive”. The shear test results (**Figure 2**) suggest an even worse flowability classification. The left panel presents the flowability ff_c of the dusts as a function of the applied consolidation stress. Flowability increases slightly with increasing consolidation stress; however, the material remains within the “very cohesive” category over the entire stress range. The wall friction angle of dust A is largely independent of the wall normal stress and remains at approximately 30° or slightly below (right panel). In contrast, the wall friction angle of dust B decreases significantly with increasing wall normal stress, from about 32° to 20°.

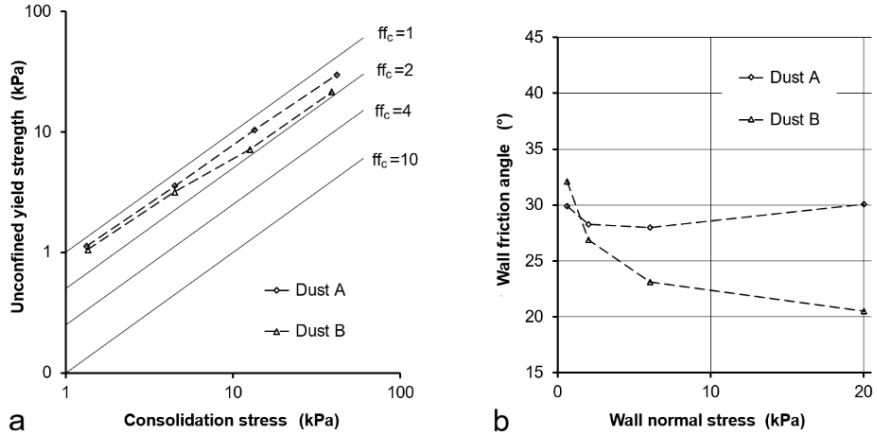

Figure 2 Flowability ff_c (a) and wall friction angle (b) as a function of applied stress

Table 1 summarizes the chemical composition of the dusts. As iron and carbon are the predominant components, recycling the dust within the steel production process is suitable. The high Mg concentrations observed reflect the desulphurization processes, which were both based on magnesium injection.

Table 1 Chemical composition of the dusts in mg/kg d.b. (* not determined)

Element	Dust A	Dust B	Element	Dust A	Dust B	Element	Dust A	Dust B
Fe	622,000	420,000	S	3,240	608	Cr	84	101
TC	63,000	507,000	P	169	101	Cu	169	182
Mg	85,500	56,900	Cl	122,000	4,480	Ni	118	12
Ca	1,010	1,280	Na	14,900	1,220	Pb	236	8
Al	1,600	3,240	K	38,600	851	Zn	10,800	1,080
Si	1,830	- *	Mn	9,940	689			

The exceptionally high total carbon (TC) content of dust B explains the atypical physical behaviour of this material compared with dust A. Specifically, dust B exhibits (i) a lower bulk density and very poor flowability, remaining in the “very cohesive” class despite its relatively coarse particle size distribution, and (ii) a pronounced decrease in wall friction angle with increasing wall normal stress. Dust A contains comparatively high concentrations of volatile components, including alkali chlorides as well as Zn and Pb, whereas these constituents are present at much lower levels in dust B.

3.2. Size separated dust

Dust A was separated into six size fractions by sequential air classification. The mass median diameters of these size fractions were 1.2, 2.9, 8.3, 57, 170, and 800 µm. **Figure 3** shows micrographs illustrating the morphology of the different size fractions.

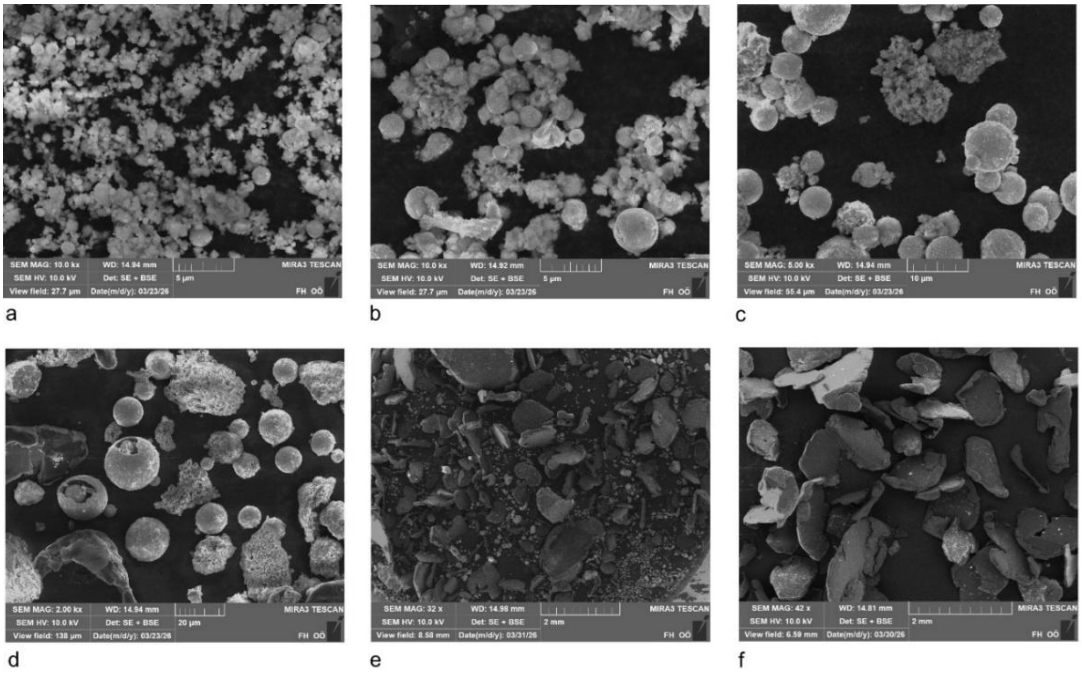

Figure 3 Micrographs of the different size fractions, from the finest (a) to the coarsest (f)

Figure 4 presents the relative concentrations of various elements in the different size fractions. The TC content was strongly enriched in the coarsest fraction, whereas all other elements were strongly depleted, as this fraction consisted almost exclusively of TC. For many components, the concentrations varied only slightly among the five finer fractions.

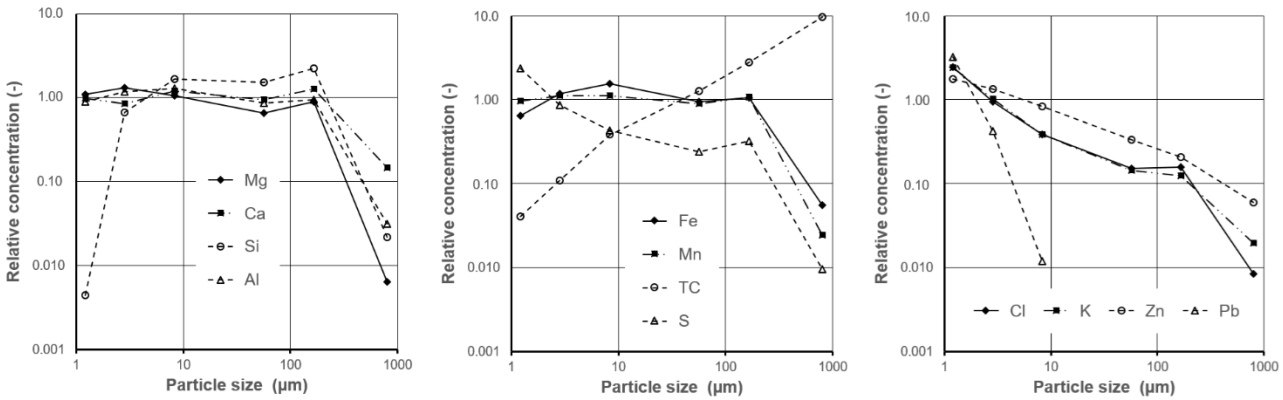

Figure 4 Relative concentration in the various size fractions of dust A

In contrast, the more volatile elements Cl, K, Zn, and Pb exhibited a clear decrease in concentration with increasing particle size which is consistent with trends reported in the literature [27]. The coarsest size fraction is composed almost entirely of carbon, which was confirmed by SEM-EDX analysis as shown in **Figure 5** (left side). The right side of **Figure 5** shows the bulk density of the different size fractions. For the finer fractions, the bulk density increases with particle size, which is a commonly observed behavior. In contrast, for the two coarsest size fractions, the bulk density decreases with increasing particle size, while at the same time the TC content increases substantially.

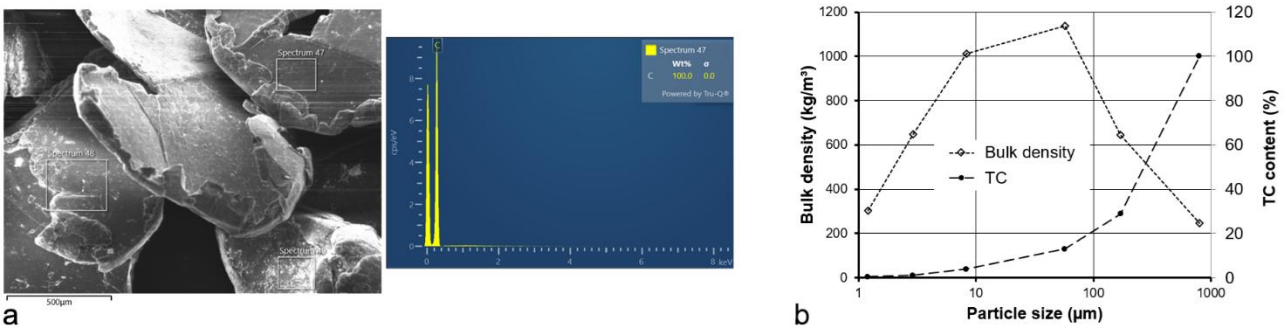

Figure 5 SEM image and EDX spectrum of a particle from the coarsest size fraction of Dust A (a) and bulk density and TC content of the Dust A as a function of the particle size (b)

4. CONCLUSION

The investigated desulphurization dusts contain substantial amounts of iron and carbon and therefore represent potentially valuable secondary materials for internal recycling. The chemical composition of the dusts and their particle size distributions can vary substantially. Despite their compositional differences, both investigated dust samples exhibited poor flowability and were classified as very cohesive. In the investigated materials, a high carbon content was associated with coarser particle sizes and reduced bulk density. These properties must be taken into account in the design of storage and conveying equipment. In addition, the concentrations of volatile elements - particularly alkali chlorides and zinc, which may accumulate through recycling - can be relatively high and should therefore be carefully considered in recycling mass balance calculations.

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