



Original Article

Characterization and mass balance of trace elements in an iron ore sinter plant



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ABSTRACT

Environmental legislation is becoming more restrictive in several industrial sectors, especially in the steel industry, which is well known for its large pollution potential. With the recent growth of interest in effects of trace elements on the environment and health, the inclusion of emission limits on these elements in this legislation has become increasingly popular. This article aims to describe the partitioning of trace elements between the products (sinter) and plant emissions in an iron ore sinter plant, aiming to better understand the behavior of these elements in the sintering process to eventually support interventions to modify these partitions. Chemical characterization of several sintering inputs was initially performed, revealing that the steel-making residues contained large concentrations of trace elements, whereas low concentrations were observed in the flux. Based on the trace element concentrations, we analyzed the injection of trace elements in a sintering pilot using a sintering mixture. Mass balance was then used to determine the theoretical partitioning of trace elements in the sinter and emissions; cadmium, nickel, lead, mercury, and copper exhibited greater tendencies to concentrate in atmospheric emissions.

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1. Introduction

The steel industry is known for its large pollution potential. With the new stricter environmental legislation, new studies have been conducted, and more precise emission controls have been implemented. The European Union, which has a very strict environmental legislation when compared to the

rest of the world, has, for the steel industry, restrictive limits for a large number of pollutants; in addition, the legislation defines specific values for each process, operational condition, and abatement technology. Moreover, the limits for the concentration of SO₂, NO₂ and PM₁₀ are more restrictive when compared to other countries [1]. The European legislation is also noteworthy for its efforts to introduce restrictions on the concentration of PM_{2.5} in the air and for including restrictive

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limits for some trace elements such as lead, arsenic, cadmium and nickel [1–3].

Mirroring the European Union, the remainder of the world has adopted new environmental laws and revised current ones, generating greater environmental pressure on the mining and metallurgy industry. This practice is evident in China, which has shown signs of progress in their legislation [4]. For example, recently, the limits of Chinese emission were reduced drastically, from 150 mg/Nm³ to 50 mg/Nm³ in the case of particulate matter, and 2000 mg/Nm³ to 200 mg/Nm³ for SO_x [5].

With the recent growth of interest in the effect of trace elements on the environment and health, the inclusion of certain emission limits for these elements has been increasingly observed as laws have evolved. From the viewpoint of environmental impacts, 14 elements are considered to have potentially higher impact: arsenic, cadmium, chlorine, copper, chromium, manganese, mercury, lead, nickel, vanadium, zinc, polonium, uranium, and thorium [6]. These elements are associated with the main inputs of the steel industry, and, when present in the sinter, can affect (positively or negatively) the steel chain and final product [7].

The gaseous emissions from a sinter plant significantly contribute toward the total emissions of an integrated steel mill and are considered the leading emitter of particulates [8]. Sintering accounts for approximately 45% of all particulate emissions of an integrated steel plant and emerges as the leading emitter of trace elements [9]. The input of these elements in the process occurs through the raw materials, which consist of iron ore, fuels, fluxes, and steel-making residues.

In this paper, for the first time, chemical characterization of trace elements in various sintering inputs was performed, and the intake of these elements in a sintering pilot was then analyzed using a sintering mixture. The mass balance was then considered to determine the theoretical partitioning of trace elements in the products (sinter) and emissions. Therefore, this study describes the partitioning of trace elements between the products and plant emissions, with the aim of better understanding the behavior of these elements in the sintering process to eventually support interventions to modify these partitions.

2. Methods

2.1. Chemical characterization of inputs

In the sintering process, a mixture of raw materials composed of fine ore (sinter feed), solid fuel (coke), flux, returned fines, and steel-making residues is arranged on a conveyor belt and then heated to temperatures close to 1300 °C to achieve reductive-oxidizing semifusion. The product of this process is a mass called sinter [10], which is then crushed; its particle size is adjusted through screening to meet the requirements of the next stages of steel production, and the thin material is reused in the process.

In this study, chemical characterization of various sintering inputs was conducted. These inputs were divided into 11 categories (sinter feed, pellet feed, lump, concentrate, pellet, pellet fine, lump and sinter fines, returned fines, fuel, fluxes,

Table 1 – Description of sintering input samples characterized.

Type of sample	Origin	Number of samples
Sinter feed	Brazil	17
	South Africa	2
	Australia	13
	China	2
	India	2
Pellet feed	Brazil	5
	Canada	1
Lump	China	17
	Brazil	6
Concentrate	China	9
Pellet	Brazil	1
Pellet fines	Brazil	1
Lump and sinter fines	Brazil	1
Returned fines	Brazil	1
Fuels	Brazil	2
	China	1
Fluxes	Brazil	2
	China	5
Steel-making residues	Brazil	9
Total		97

and steel-making residues), and the average concentrations of each trace element in each of these categories were evaluated. We then studied the concentration distribution of each trace element in each of these categories using column charts. Table 1 provides a description of the samples.

It is not possible to include further details of the chemical analysis method since this work was conducted by two different global laboratories, ALS and SGS Geosol.

For the characterization of arsenic, cadmium, chlorine, copper, chromium, lead, nickel, vanadium, and zinc, 0.25 g samples were prepared and then digested in perchloric, nitric, and hydrofluoric acid. The obtained residue was diluted after being leached with dilute hydrochloric acid. The prepared sample was then analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) using Agilent instruments; the results were corrected for spectral interferences.

For the characterization of mercury, 0.50 g samples were prepared, which were digested in aqua regia for 45 min in a graphite heating block. After cooling, the resulting solution was diluted to 12.5 ml in demineralized water. A portion of the sample was treated with stannous chloride to reduce the mercury, which was then volatilized by purging with argon before being analyzed using atomic absorption spectrometry (AAS).

2.2. Mass balance

In the sintering pilot, a test using the mixture described in Table 2 was conducted. The sintering pilot consisted of a conical pot, with the smallest diameter being 270 mm and the largest diameter being 300 mm, a bed height ranging from 400 to 700 mm, and a volume ranging from 25.4 to 43.9 L. The sintering temperature was approximately 1250 °C with the air flow ranging between 100 and 160 Nm³/h. The same process adopted for the inputs was used to chemically characterize

Table 2 – Standard sinter mix adopted to mass balance.

Input	Mix %
Sinter feed 10	7.86
Sinter feed 11	13.1
Sinter feed 12	2.62
Sinter feed 14	7.86
Sinter feed 15	3.06
Sinter feed 16	4.81
Pellet fines 1	3.49
Pellet feed 5	0.87
Dolomitic limestone	9.03
Quicklime	0.67
Area cleaning material	1.10
Mill scale from operations	0.48
Steel sludge	1.08
Slag of KR process	0.25
Lump and sinter fines	7.80
Carbonaceous dust of coke plant	0.14
Steel slag	0.47
Thin limestone generated by calcination	0.35
Coke breeze	3.30
Returned fines	30.3

the products of this test (sinter, returned fines, and windbox powder).

Using the humidity and loss on ignition data, the actual entry mass of each input in the process was calculated. Understanding the input characterization data enabled the mass values of injection for each trace element to be determined. Thus, it was possible to identify the key inputs responsible for the injection of each of the elements in the sintering mixture.

Based on the characterization data and obtained mass of the products, the output masses and partition of each element were calculated. The mass emissions of trace elements were determined by subtracting the overall entry mass and masses present in the sinter, return fines, and windbox powder.

3. Results and discussion

3.1. Chemical characterization of inputs

3.1.1. Arsenic

The arsenic concentrations in the different categories of inputs are plotted in Fig. 1. The highest arsenic concentrations

were observed in the ferrous products, especially in the concentrate, for which a concentration of 19.88 ppm was observed.

When analyzing the individual samples in each category, high arsenic concentrations of 100.0 ppm and 37.7 ppm were observed in the Chinese concentrate samples 4 and 7, respectively, whereas the concentrations of the seven other Chinese concentrate samples ranged between 0.6 and 13.2 ppm. The Brazilian sinter feed contained a low arsenic concentration with only 1 of 17 samples having a higher concentration than the mean (19.0 ppm); two Chinese, two South African, and nine Australian samples contained higher arsenic concentrations. In the pellet feeds, the Chinese samples again contained the highest arsenic concentrations, with values of 65.1 and 50.8 ppm, whereas the higher index for non-Chinese samples contained more than 10 times less, 4.8 ppm for the Brazilian pellet feed 4.

3.1.2. Cadmium

Fig. 2 shows the cadmium concentration in the different categories of inputs. The high cadmium concentration in the steel-making residues (1.8 ppm) is evident, with a level at least 10 times greater than that of all the other categories. This value is easily explained by the concentration of cadmium in the mill scale from operations, 12.0 ppm.

3.1.3. Chlorine

In the comparison of the chlorine concentration among the different categories of raw materials, the steel-making residues contained 424.4 ppm. The fuels (6.7 ppm), pellets (20.0 ppm), and pellet fines (20.0 ppm) contained low concentrations compared with the other inputs, as observed in Fig. 3.

Among the steel-making residues, the main chlorine concentrators were the carbonaceous dust of the coke plant (2542.0 ppm), windbox powder (690.0 ppm), and blast furnace dust catcher powder (437.0 ppm). All the other steel-making residues contained concentrations of chlorine lower or equal to 50.0 ppm.

Among the Chinese concentrate samples, similar to the arsenic results, samples 4 and 7 had chlorine concentrations of 430.0 and 530.0 ppm, respectively.

In the pellet feeds, all the samples with chlorine concentrations above the mean originated from China (13 samples).

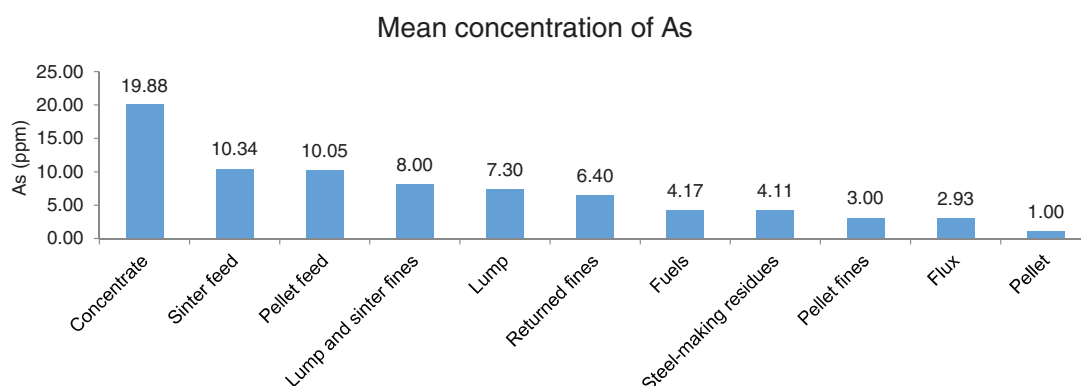


Fig. 1 – Mean concentration of arsenic in the different classes of inputs.

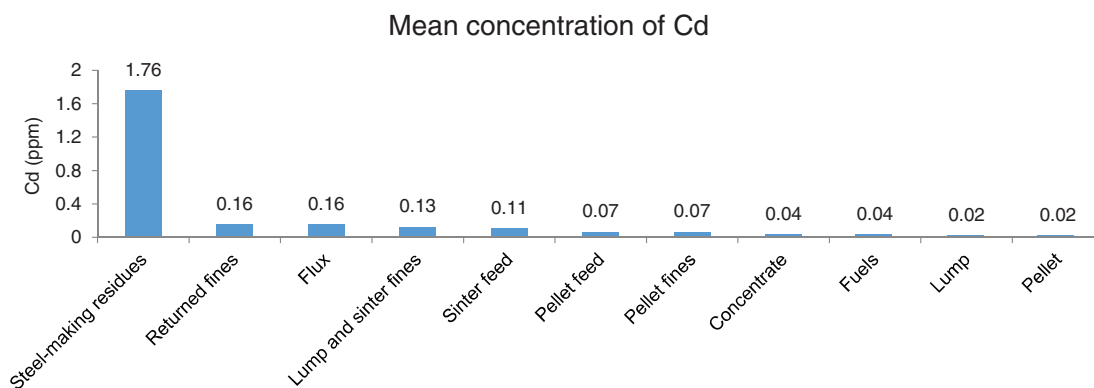


Fig. 2 – Mean concentration of cadmium in the different classes of inputs.

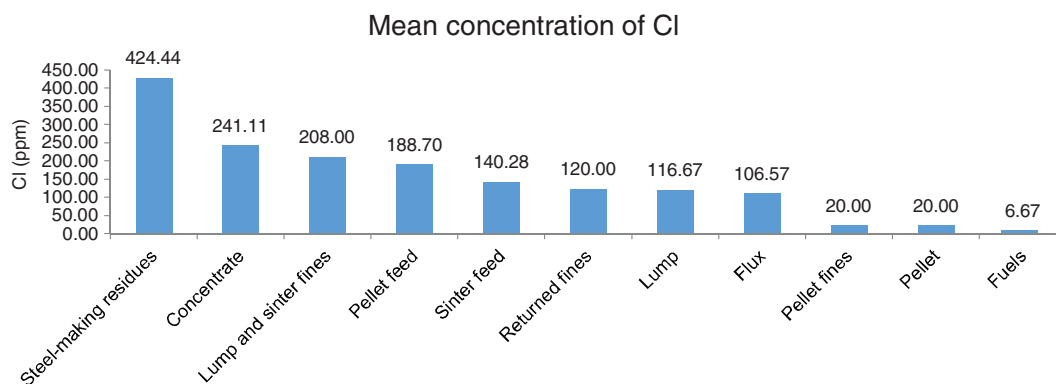


Fig. 3 – Mean concentration of chlorine in the different classes of inputs.

In the sinter feeds, the highlight was the low concentration of chlorine in the Brazilian samples, with only 1 of 17 samples having a higher value than the mean (200 ppm).

3.1.4. Chromium

Analyzing the chromium concentration in the different categories of inputs it was noted that the ores, especially the lump (40.7 ppm) and sinter feed (45.1 ppm), along with the fluxes (45.3 ppm), had a low average concentration compared with the other inputs. The highest concentration was again observed for the steel-making residues, 220.1 ppm, as observed in Fig. 4.

3.1.5. Copper

The copper concentration results for each of the categories of inputs are presented in Fig. 5. The steel-making residues had the highest copper concentration, 67.7 ppm, which was almost twice as high as the second highest copper content of 37.0 ppm.

The main component responsible for increasing the mean concentration of copper in the steel-making residues was the carbonaceous dust of the coke plant, with 360.9 ppm. All the other steel-making residues had concentrations below 50.0 ppm. In the Chinese concentrate, one sample was responsible for the high mean, concentrate 9, which

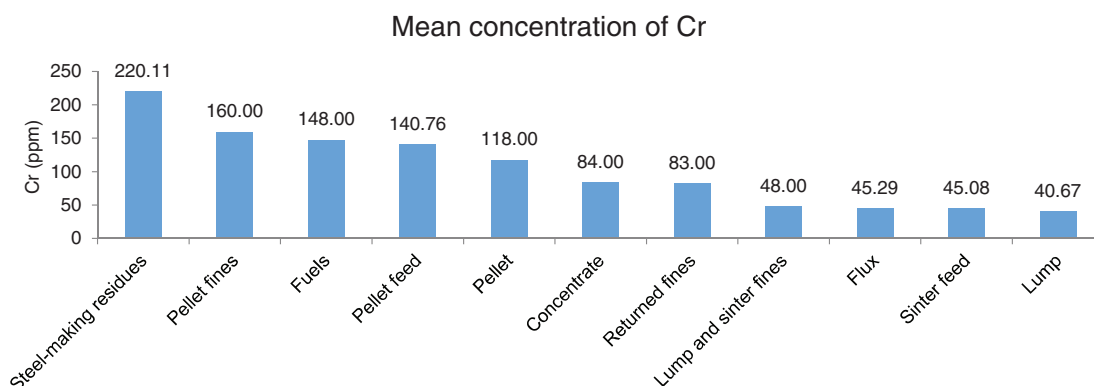


Fig. 4 – Mean concentration of chromium in the different classes of inputs.

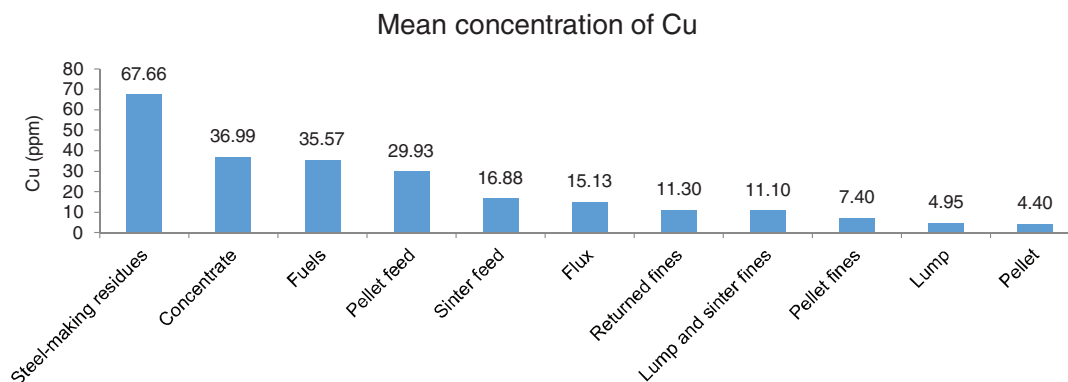


Fig. 5 – Mean concentration of copper in the different classes of inputs.

had a copper concentration of 235.0 ppm, whereas the concentrations for all the other samples only reached as high as 34.2 ppm.

Analyzing the pellet feed samples, the copper concentrations varied widely, ranging from 1.6 to 155.3 ppm. Among these samples, the Brazilian sample 1, with 103.5 ppm, and Chinese sample 9, with 155.3 ppm, had the highest concentrations.

In the sinter feed, however, two samples showed great prominence, the Brazilian sample 1, with 107.5 ppm, and the Australian sample 7, with 176.3 ppm. All the other sinter feed samples had copper concentrations below 27.3 ppm.

3.1.6. Mercury

The mercury concentration in the sintering inputs was low compared with that of the other trace elements, always below 1.0 ppm. In this context, the highest concentrators of mercury were the ferrous inputs, either as sinter feed (0.08 ppm) or pellet feed (0.07 ppm), as observed in Fig. 6.

The results of two samples stood out, the Australian sample 7, with 0.54 ppm, and the Brazilian sample 12 with 0.30 ppm. The mercury concentrations of all the other samples were below 0.15 ppm.

For the pellet feeds, all 5 Brazilian samples as well as the Canadians samples had values below the mean of 0.07 ppm, whereas the 6 Chinese samples had values between 0.10 and 0.36 ppm.

3.1.7. Nickel

Fig. 7 plots the mean nickel concentration in the different categories of sintering inputs. Among these categories, the fuel and steel-making residues stood out, with average concentrations of 135.9 and 87.3 ppm, respectively.

Analyzing the concentration of nickel in the steel-making residues, high values were observed in the carbonaceous dust of the coke plant and in the area cleaning material, with 361.1 and 200.0 ppm, respectively. The remaining residues fluctuated with nickel concentrations ranging from 10.3 to 62.0 ppm.

Among the pellet feeds, the Chinese sample 13 stood out with a nickel concentration of 349.5 ppm, a value that was approximately four times greater than that of the Chinese sample 6, which was the sample with the second highest concentration (93.3 ppm). For the sinter feeds, the highlight was the Australian sample 7, with 161.0 ppm, whereas the other samples contained concentrations at least five times smaller (less than 30.0 ppm).

3.1.8. Lead

Analyzing Fig. 8, high average lead concentrations in the fuel and steel-making residues of 273.5 ppm and 132.7 ppm, respectively, were observed compared with those in the other categories; these values are at least five times larger than those in the other categories.

In the steel-making residues, high lead concentrations of 400.0 ppm were observed in the carbonaceous dust of the

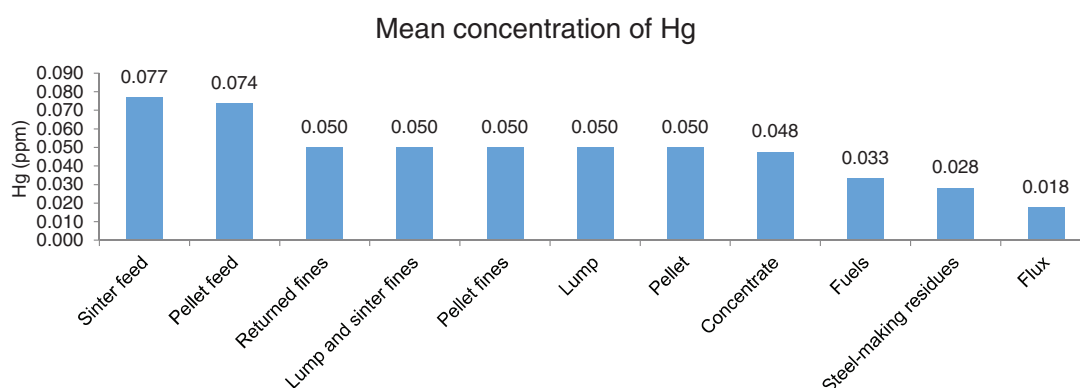


Fig. 6 – Mean concentration of mercury in the different classes of inputs.

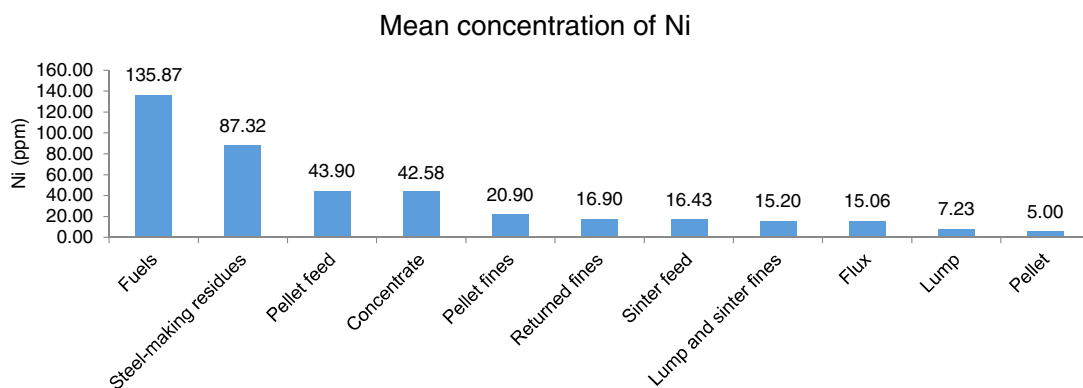


Fig. 7 – Mean concentration of nickel in the different classes of inputs.

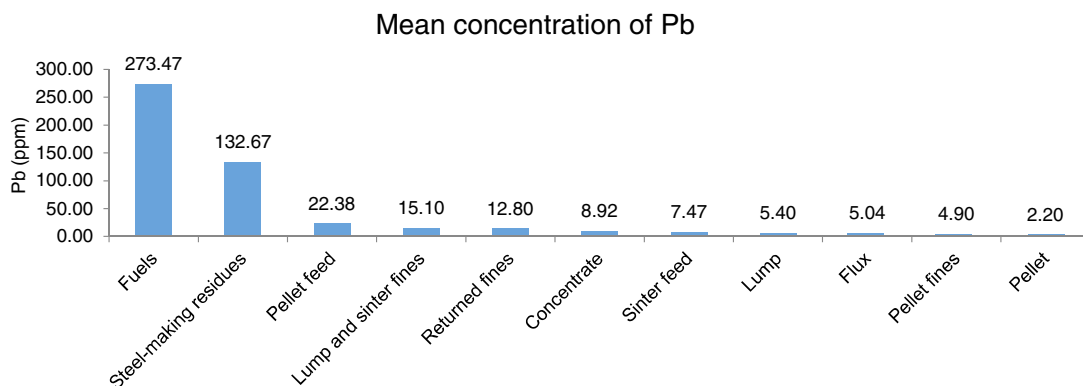


Fig. 8 – Mean concentration of lead in the different classes of inputs.

coke plant and the area cleaning material. The steel sludge and mill scale from operations also contained relatively high concentrations of 178.0 and 125.0 ppm, respectively, whereas the remaining residues had lead concentrations of less than 56.0 ppm.

3.1.9. Vanadium

Among the classes of sintering inputs, the pellet feed exhibited the highest mean concentration of vanadium (384.7 ppm), followed by concentrate (292.9 ppm) and steel-making residues (155.0 ppm). Fig. 9 shows that the fluxes and fuel contained very low levels of vanadium compared with the other inputs.

The vanadium concentrations in the pellet feeds varied widely, ranging from 0 to 2710 ppm. A large difference was also observed between the mean of the 17 Chinese samples, 500 ppm, and that of the 5 Brazilian samples, 62.6 ppm.

Among the Chinese concentrate samples, the vanadium concentration stood out in sample 1 at 1500.0 ppm. This value was almost four times higher than the second highest concentration observed for sample 7 (379.0 ppm).

Regarding the vanadium concentration in the steel-making residues, two samples exhibited significantly higher values than the others. These were the mill scale from operations (625.0 ppm) and the steel slag (470.0 ppm). All the other samples had vanadium concentrations as high as 111.0 ppm.

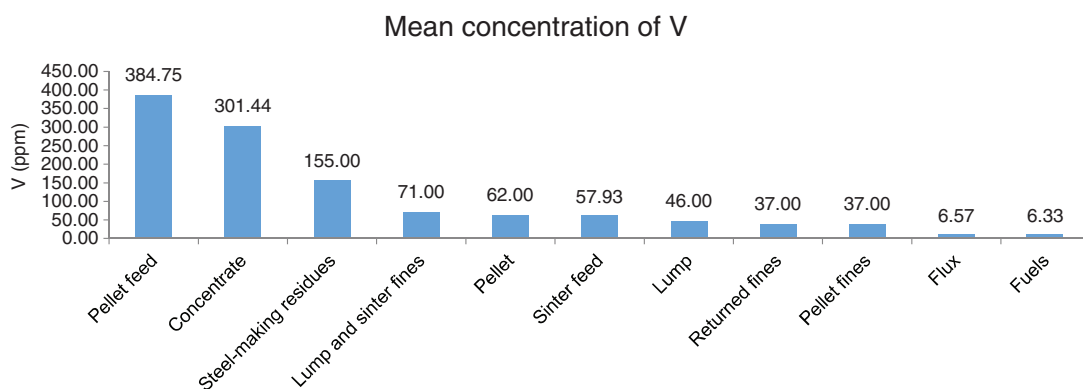


Fig. 9 – Mean concentration of vanadium in the different classes of inputs.

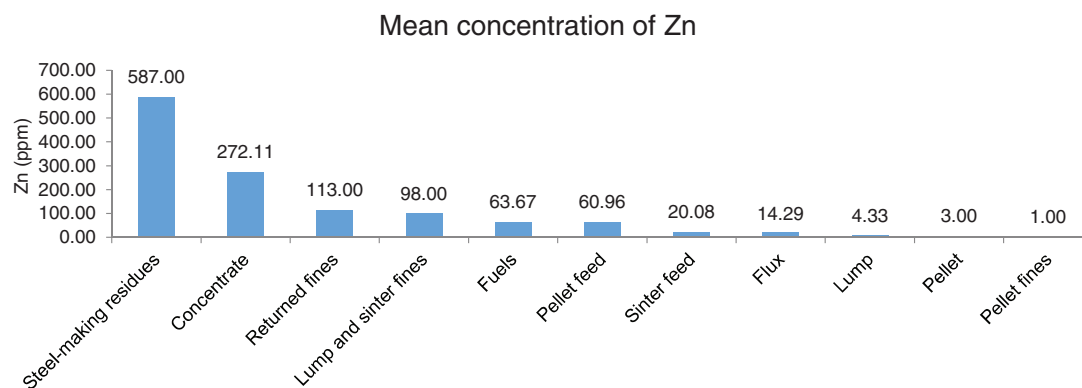


Fig. 10 – Mean concentration of zinc in the different classes of inputs.

ET	Main supplier	Partition, %			Total (g/t of sinter)
		Sinter	RFin	Emissions +	
As	Sinter feed	89%	41%	-30%	7.18
Cd	Mill scale from operations	41%	25%	35%	0.30
Cl	Fines of lump and sinter	48%	53%	0%	105.21
Cr	Sinter feed	52%	37%	11%	104.02
Cu	Sinter feed/Dolomitic limestone	51%	24%	25%	21.97
Hg	Sinter feed	50%	23%	27%	0.10
Ni	Sinter feed	42%	24%	34%	32.51
Pb	Area cleaning material/Steel sludge	48%	23%	29%	25.97
V	Fines of lump and sinter/Sinter feed	71%	30%	-1%	57.51
Zn	Steel sludge	92%	42%	-33%	125.31

Fig. 11 – Mass balance results. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

In the sinter feeds, the vanadium concentration in the Chinese 1 sample was high (823.0 ppm), a value three times higher than that of the second highest vanadium concentrator, the Australian sample 7, with 271.0 ppm. All the other samples had concentrations below 74.0 ppm.

3.1.10. Zinc

Among the sintering input categories, zinc was concentrated primarily in the steel-making residues, as observed in Fig. 10. In the steel-making residues, the mean zinc concentration was 587.0 ppm, whereas the next highest value was approximately half this value, 272.1 ppm, for the concentrate.

Among the steel-making residues, zinc appeared in higher concentrations in the steel sludge at 2568.0 ppm, blast furnace dust catcher powder at 1562.0 ppm, and area cleaning material at 624.0 ppm. All the other residues contained zinc concentrations below 210.0 ppm.

The zinc concentration in the Chinese concentrate sample 4 stood out at 1910 ppm. This value was almost seven times higher than the second highest concentration for sample 9 (282 ppm).

3.2. Mass balance

The mass balance results are presented in Fig. 11. The large intake of zinc (125.31 g/t sinter), chlorine (105.21 g/t sinter), and lead (104.02 g/t sinter) is notable.

Regarding the partitions, the elements more likely to concentrate in air emissions were cadmium (35%), nickel (34%), lead (29%), mercury (27%), and copper (25%).

Note that for arsenic, vanadium, and zinc, the mass observed in the sum of the sinter and returned fines was greater than the mass input of these elements, as indicated by the negative red bars in the table. This result can be explained by the heterogeneity of the sinter and returned fines studied.

4. Conclusions

In this study, chemical characterization of several sintering inputs in an iron ore sinter plant was performed. The steel-making residues contained the highest concentrations of trace elements (1680.1 ppm), reaching more than twice the concentration of the second highest inputs, the concentrates (772.7 ppm). Samples with high concentrations of one specific trace element showed a tendency to also contain high concentrations of other elements; for example, the carbonaceous dust from a coke plant contained high concentrations of chlorine, lead, nickel, and copper. Regarding the intake of trace elements, the elements with the highest entry masses in the sintering were zinc (125.31 g/t sinter), chlorine (105.21 g/t sinter), and lead (104.02 g/t sinter). It was not possible to achieve mass balance for some elements, indicating the presence of measurement error; the chemical characterization of each of the inputs and outputs is being performed again to mitigate such errors. Furthermore, the element partitioning suggests the manner in which their mass is distributed between the sinter, returned fines, and emissions. Because the masses of the sinter and returned fines generated in the process are much larger than the emissions mass, an element that is directed mainly for products may still be present at a higher

concentration in the emissions because of the low dilution. We also observed that the trace elements behaved in three ways during the sintering. The elements and compounds with lower vaporization temperatures volatilized and concentrated in the emissions, whereas the elements that did not volatilize during the process remained in the mixture and formed the sinter or the particles were dragged into the emissions. To understand this mechanism, future studies will be performed in a radiant furnace (with heating rates and temperature similar to the sintering process) to determine the behavior of each trace element.

Conflicts of interest

The authors declare no conflicts of interest.

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