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CHARACTERIZATION OF A WEATHERED STEELMAKING FLUE DUST

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RESUMO

Lama de aciaria é um resíduo que pode ser obtido no processo de fabricação de aço empregando um conversor LD, bem como um forno elétrico a arco. Vários elementos úteis como Fe e Zn podem ser encontrados neste tipo de resíduo. Encontrar a melhor tecnologia para o processamento desse tipo de material passa pelo conhecimento detalhado de como esses elementos estão combinados. Este estudo teve como objetivo investigar as características físicas e químicas de uma amostra de pó de aciaria, após intemperismo devido ao armazenamento ao tempo. A investigação foi realizada por meio de difração de raios X, microscopia eletrônica de varredura, espectroscopia de energia dispersiva, análise química multielementar, análise granulométrica, picnometria e medição de área superficial (BET). Os resíduos estudados, apresentaram predominância de wustita, magnetita, hematita, franklinita, grafita, calcita e quartzo. A análise química apontou para 49,33 % de Fe, 9,17 % de CaO, 1,94 % de MgO, 1,06 % de conteúdo de Al_2O_3. O diâmetro médio (d_{50}) foi de 44,04 µm, a densidade foi de 2.990,0 kg/m³ e a área de superfície foi calculada em 15.010,0 m²/kg. Nos difratogramas sobreposição de pico foi observada, que foi minimizada, empregando previamente dupla lixiviação por solução com 16 % de ácido clorídrico, em massa.

PALAVRAS-CHAVE: lama de aciaria, rejeito metalúrgico, caracterização, resíduo siderúrgico.

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ABSTRACT

Flue dust is as waste that can be obtained in the steelmaking process employing a LD converter as well an electric arc furnace. Several useful elements such as Fe and Zn can be found in this type of waste. Finding the best technology for processing this kind of material pass by knowing detailed how these elements are formed and combined. This study aimed to investigate the physical and chemical characteristics of a flue dust steelmaking sample, after weathering. The investigation was carried out by using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, chemical analysis, particle size analysis, pycnometry and surface area measurement (BET). The waste studied, showed the predominance of wustite, magnetite, hematite, franklinite, graphite, calcite and quartz. Chemical analysis has pointed to 49.33 % Fe, 9.17 % CaO, 1.94 % MgO, 1.06 % Al_2O_3 contents. The median diameter (d_{50}) was 44.04 µm, density was 2,990.0 kg/m³ and surface area was calculated to be 15,010.0 m²/kg. In the XRD pattern was observed peak overlapping, which was minimize employing previously a double leaching with 16.8 % mass concentration of hydrochloric acid solution.

KEYWORDS: Flue dust; characterization; steelmaking waste; steelmaking sludge.

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1 INTRODUCTION

Furnace dust is a solid waste generated during the steelmaking process that can be obtained either using Linz-Donawitz converter or electric arc furnace. Steelmaking process by oxygen or electric arc furnace usually produces around 10 to 20 kg of dust per metric ton of steel, generating a significant environmental passive (Nyrenda, 1991).

Flue dust in Brazil is classified by the ABNT 10004/2004 regulation as a dangerous solid-waste class I, since it may have elements as Pb and Cd, which might be leached by weathering waters. Hence it follows this type of material is usually disposed in landfill protected from the rain (ABNT, 2004).

Among the solid residues that are generated during the steel production process, it is remarkable that steelmaking dust has a great potential for recycling. Recovery of the metallic values contained in the waste becomes attractive both from an economic point of view, as it contributes to the reduction of operation costs, and from an environmental point of view, meeting specifications imposed by current legislation (Machado et al., 2006).

Characterization of these residues is often difficult and might take several steps. As expected, this operation has as main objective to determine the physical-chemical characteristics of the material in question, establishing characteristics of it as raw material for different industries (Sarkar & Mazumber, 2015; Vieira et al., 2006; Laforest & Duchesne, 2006).

The most common destination of recycling these wastes is in civil construction, it can be used in cement production, in the paving sector and in the ceramics production (Takano et al., 2000). The material has appreciable amounts of oxide iron in their composition that could be useful in sintering plants.

In this line, this study aimed at investigating the physical and chemical characteristics of steelmaking's flue dust sample (from a stockpile heavily weathered) as basics work to help to form the foundations to find the right technology to produce a raw material to the industry.

2 MATERIALS AND METHODS

2.1 Sample

The sample studied came from a recycling plant located in Sarzedo Municipality (in Minas Gerais State, Brazil). This company is characterized by recycling steelmaking solid waste.

2.2 Particle size analysis and density determination

Experimental particle size distribution was determined by vibrating sieving followed by laser diffraction size analysis for the fraction below 37 µm (using a SILAS–1064 Model analyzer). In sequence, particle size distribution was investigated employing usual theoretical distributions, namely Rosin–Rammler (Equation (1)), Harris (Equation (2)) and Hill equations (Equation (3)), as showed below.

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$$Y(x) = 1 - Exp\left[\ln\left(\frac{1}{2}\right) \times \left(\frac{x}{x_{50}}\right)^{n}\right] \qquad \text{[Rosin– Rammler]} \qquad (1)$$

Where: ***n*** — sharpness coefficient [–]; ***x_{50}*** — median diameter [m].

$$Y(x) = 1 - \left[1 - \left(\frac{x}{x_{max}}\right)^{a}\right]^{b} \qquad \text{[Harris]} \qquad (2)$$

Where: ***a*** — Gaudin–Meloy's exponent [–]; ***b*** — Harris' exponent [–]; ***x_{max}*** — distribution top size [m] (if ***a*** = 1, then the Gates–Gaudin–Schumann distribution results; and if ***b*** = 1, then the Gaudin–Meloy distribution results).

$$Y(x) = \frac{x^{k}}{x^{k} + x_{50}^{k}} = \frac{\left(\frac{x}{x_{50}}\right)^{k}}{\left(\frac{x}{x_{50}}\right)^{k} + 1} \qquad \text{[Hill]} \qquad (3)$$

Where: ***k*** — sharpness coefficient [–]; ***x_{50}*** — median diameter [–].

The regression parameters were estimated using a non-linear algorithm from EasyPlot© software package. This algorithm uses a Marquardt-Levenberg filter (which, unlike the descending simplex search algorithm, allows estimating the uncertainty associated with the regression values) (Karon, 2014).

As sample's density is concerned, its determination was carried out using a helium ultrapycnometer (model 1200e from Quantachrome Instruments), following the conventional approach.

2.3 Surface area measurements

The sample's specific surface area was estimated by nitrogen adsorption at 77 K (BET technique), using a surface area analyzer NOVA 1200e from Quantachrome Instruments (and employing NovaWin2 software for calculation). The procedure was in accordance with that one described by Pereira et al., 2014.

2.4 Chemical characterization

The chemical characterization was focused in determine the metallic fraction of the sample. The analysis was carried out by inductively coupled plasma atomic emission spectroscopy (ICP – OES). As related by Brehm et al. (2002) the acid attack it is the main technique for the digestion of steelmaking solid waste because of their basic matrix elements. The partial digestion occurred on electric plate (110 ± 5 ºC) and the acid addition were like exposed by Figure 1. This procedure was performed twice.

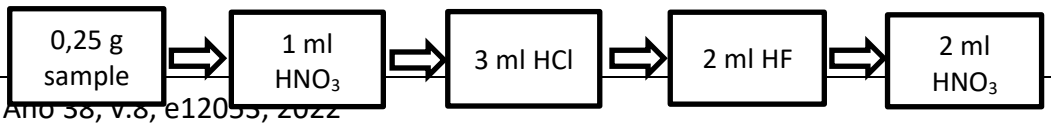

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Figure 1. ***Methodological scheme used for sample acid digestion*****.**

2.5 X-Ray diffraction

The crystalline phases identification was carried out by the total powder method (using particles below 37 µm) employing a PANanalytical's X'Pert3 Powder diffractometer. A monochromatic Cu-Kα radiation was used (λ = 0.1542 nm), with a nickel filter in the 2$\boldsymbol{\theta}$-range from 5º to 90º. As the first scan has exhibited overlapping peaks in some extent, a revised analysis has been performed with an extra leaching step. The process consisted in an open digestion the sample with a mixture of HCl 1:1 (initial mass concentration about 18.6 % HCl) at 100 °C.

2.6 Scanning electron microscopy and micro-analysis

Any recycling method by sorting is influenced by particle's morphology and structure, as well by their chemical composition. In view of this, scanning electron microscopy (SEM) with X-ray energy dispersive spectrometry (EDS) were performed to investigate the sample's microstructure. The equipment used was a bench-scale Phenom© and did not require any special sample preparation.

3 RESULTS AND DISCUSSION

3.1 Particle size analysis and density determination

The sample's particle size distribution is plotted in Figure 2 as experimental accumulated passing-through fraction against particle size (circles in Figure 2). The distribution has a good correlation with Hill distribution (solid line in Figure 2). The parameters $\boldsymbol{x_{50}}$ and exponent $\boldsymbol{k}$ had a value of 74.5 µm and 0.499 respectively. It is possible to verify somewhat poor goodness-to-fit in some fine size classes, for all theoretical distributions tested. This would be probably due to the agglomerated state of the fine particles reported by several authors (as Cruells et al., 1992). Nevertheless, it is more likely that this is just an indication that the sample studied is actually formed by mixture of more than one population. It also possible to verify that aggregates/particles are smaller than 10,000 µm and goes by until get smaller than 1 µm representing a very heterogeneous distribution of the hydrodynamic point of view (Takano et al., 2000). Xia e Pickles (2000) also have pointed out the extreme variability in apparent size distribution of flue dust and its proneness to aggregation.

The aberrantly high value of the top size is actually due to weathering processes, with probable sinter-feed class contamination, in addition to particle cementation by carbonates, for example, due to the longtime of outdoor storage of such metallurgical residue. This points to the use of prior attrition step, in the case of industrial use of this raw material.

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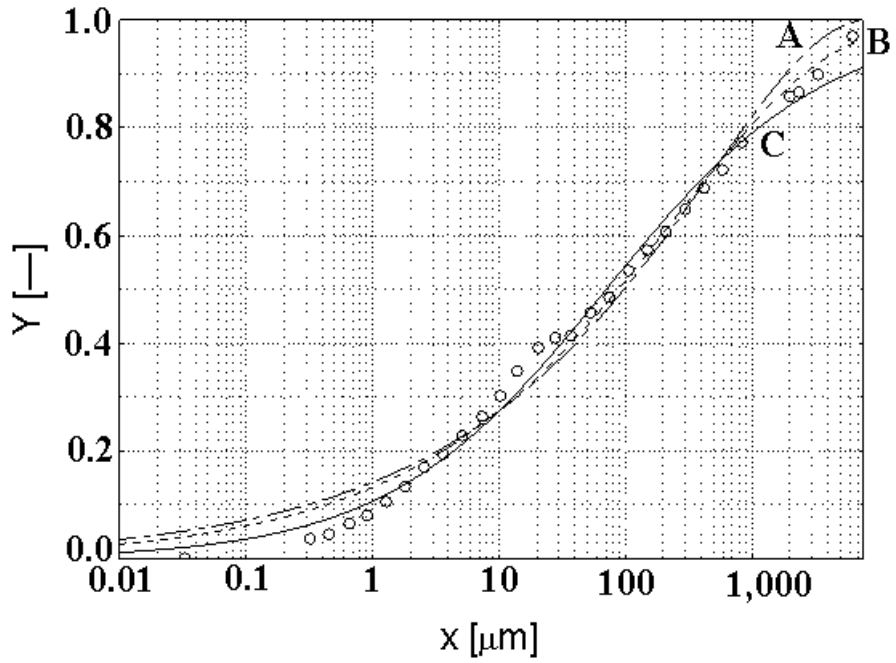

Figure 2. Experimental accumulated passing-through fraction against size (circles) of particle size distribution and regression tries (A — Harris; B — Rosin–Rammler; C — Hill).

Regression analysis was performed for the previously selected equations. Table 1 systematizes the results of statistical adherence in relation to the cloud of experimental points for the three distributions. The Hill equation performed better.

Table 1. Regression analysis for the particle size distribution.

Distribution	Standard error	Coefficient of determination (R^2)	Regression parameters
Rosin–Rammler	0.0302	0.98945	x_{50} = 87.99 μm; n = 0.3540
Harris	0.0405	0.980958	x_{max} = 9,000.0 μm; a = 0.3056; b = 2.3979
Hill	0.0249	0.99284	x_{50} = 70.54 μm; k = 0.4986

As density (or specific mass) is concerned, the helium pycnometry essays have resulted a typical mean value, as can be seen in Table 2.

Table 2. Density determination by gas pycnometry.

Characteristics	Value
Average sample volume:	1.33463×10^{-4} m³
Volume standard deviation:	1.83×10^{-7} m³
Average density:	2,922.9 m³/kg
Density Standard deviation:	4.0 m³/kg
Coefficient of variation:	0.1374 %

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3.2 Surface area measurement

As expected by the small size of the particles it can be seen a large surface area and others surface characteristics in Table 3. The specific surface area determined for the sample was close to that recorded by Wu (1999), who reported 14,650 m^2/kg for steelmaking flue dust.

Table 3. Surface characteristics.

Characteristics	Value
Specific surface Area BET:	15,010.0 m^2/kg
Pore volume density:	7.0 x 10^{-5} m^3/kg
Pore diameter:	17,1 x 10^{-10} m

3.3 Chemical characterization

The results expressed in the Table 4 are the data obtained by the ICP multielemental analysis.

Table 4. Chemical characterization.

Element	Mass content [%]
Fe	49.33
Ca	9.17
Mg	1.94
Al	1.06
Mn	0.86
Zn	0.44
K, S, Ti, Pb, Na	0.94

In ICP analysis it is usual to express conventionally the results as the most stable oxides; but using the other characterization techniques in the present study it was possible to identify that the elements are not only in these crystalline phases.

As expected by previously works (Majuste & Mansur, 2008; Sofili, 2004), iron is the major component of the material. The low content of Zn indicates it occurs rather as spinels like $ZnFe_2O_4$ and $ZnFe_3O_4$ (Silva, 2006). This feature points towards a lack of availability of galvanized scrap iron in the steelmaking process. Calcium may be present due to the use of calcite as flux and addition for control of the slag basicity (Apocalypse, 2016).

3.4 X-ray diffraction

The Figure 3 shows the X-ray diffraction pattern of the original sample.

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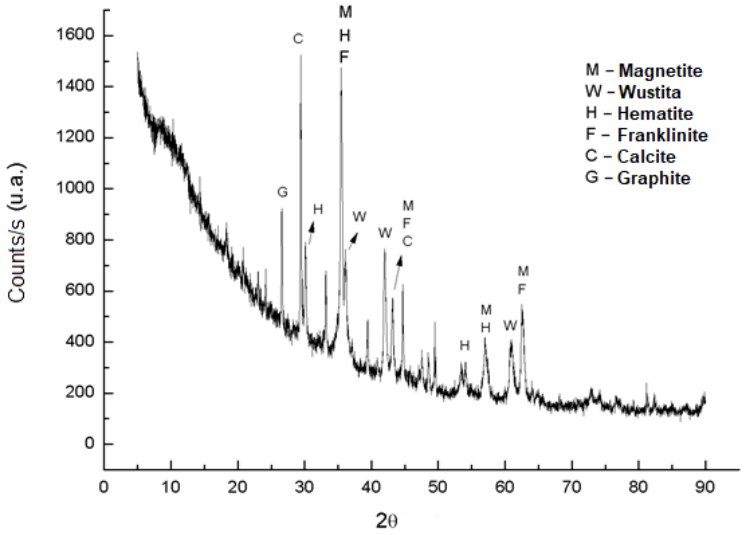

Figure 3. X-ray diffraction pattern of original sample.

As it can be seen, there are phases exhibiting peak overlapping so their presence cannot be unequivocally assured. As the expected, there are several crystalline phases related to iron, it was possible to detect Fe_3O_4, FeO and Fe_2O_3 (Cruells et al., 1992; Laforest & Duchesne, 2006). As the citation in item 3.3, the phase $ZnFe_2O_4$ might be the main phase contributing for Zn content in the sample.

In order to improve the phase identification, it was proposed a digestion of carbonates and iron oxides by the addition of HCl 1:1 mixture and another diffraction pattern has been obtained as Figure 4. It was possible to find a SiO_2 pattern, but that was also detect the peaks overlapping phenom again indicating that it is necessary complementary techniques for crystalline phases identification.

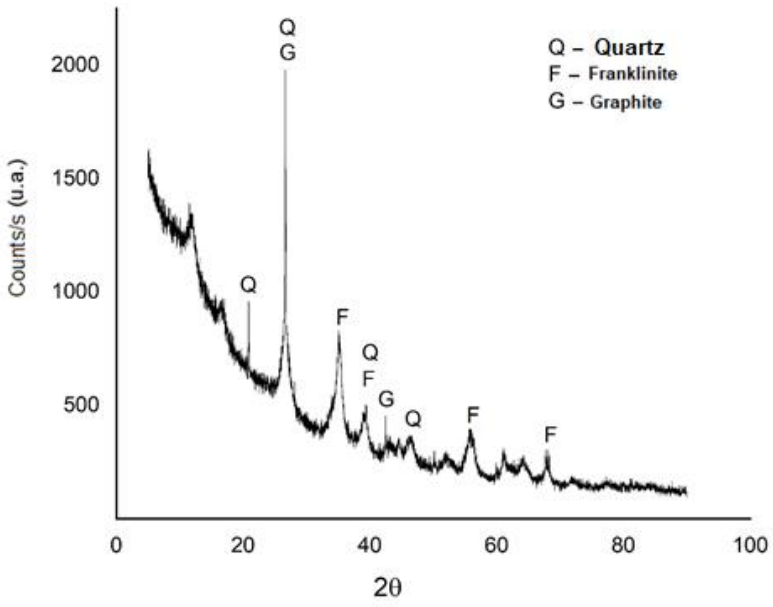

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Figure 4. X-ray diffraction pattern of leached sample.

3.5 Scanning electron microscopy and micro-analysis

In Figure 5 it is possible to see a general image for the sample's structures, most of them are fine grained. Irregular or elongated structures are observed, at the same time there are some spherical. It is also possible to verify particles agglomeration related by Sofili (2004) as well.

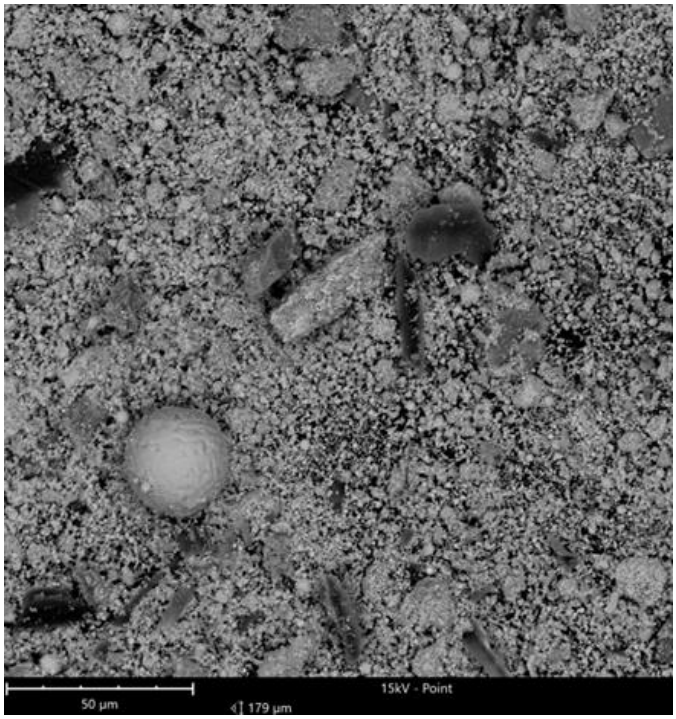

Figure 5. Waste general particles by SEM analysis.

The first structure indicated by (1) in Figure 6 displays an irregular shape and the EDS (Table 5) analysis indicate a high content of Si and O indicating that silicon dioxide might be present in the sample. This condition is in according with the second diffraction pattern.

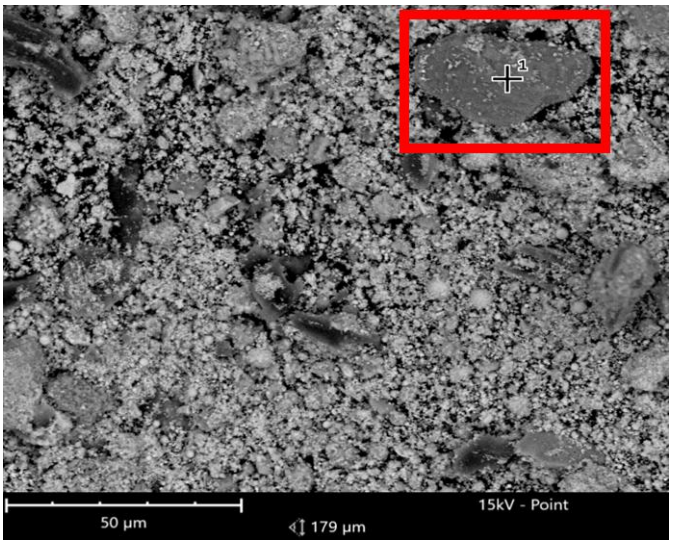

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Figure 6. Particle with an irregular shape with a high content of Si and O.

Table 5. Area 1's energy dispersive spectrometry with a high content of Fe and O.

Element	Mass content [%]
O	60.75
Si	26.12
Fe	12.98
Ca	0.16

The particle indicated by (2) in Figure 7 has also an irregular profile. As one can see in Table 6, the high presence of Al, Ca, in addition to O and Fe, may indicate partial substitution of iron by these two first-mentioned elements. Some metallic cations like Al^{3+} Ca^{2+} had already been reported partially replacing Fe in the magnetite structure. These replacements may form structures like $Ca_{0,15}Fe_{2,85}O_4$ reported by Machado (2006).

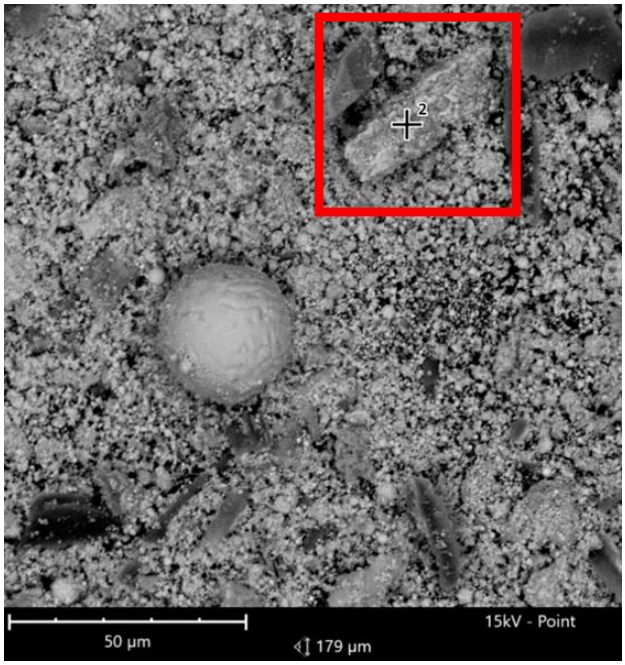

Figure 7. Scanning electron micrograph displaying an irregular particle with a high content of Fe, Al and Ca.

Table 6. EDS from a particle with a high content of Fe, Al and Ca.

Element	Mass content [%]
O	42.03
Fe	36.51
C	11.72
Ca	6.59
Si	1.21
Al	1.03
Mg	0.92

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This spherical shape expressed by (3) in Figure 8 is in agreement with several authors that concluded that this type of particle is formed due the particles ejection from liquid metal and slag as a mass of metallic iron and probably oxidated as magnetite, as it been shown their high content of Fe and O in EDS analysis showed in Table 7.

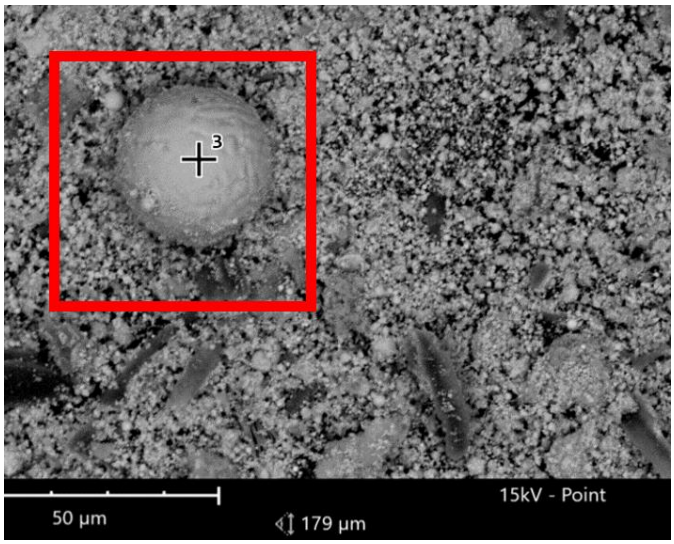

Figure 8. Particle with a spherical shape rich in Fe.

Table 7. Area 3's Energy dispersive spectrometry with a high content of Fe and O.

Element	Mass content [%]
Fe	58.92
O	39.06
Ca	1.11
Si	0.41
Al	0.28
Mg	0.23

The EDS analysis through the structures indicates large amount of oxygen that can be a sign of oxides presence distributed throughout the waste. Concerning the iron oxides, it is possible to describe that they have variable formulae, as some cations are partially substituting Fe atoms in the crystal lattices.

4 CONCLUSION

The characteristics of the studied steelmaking flue dust proved to be typical, despite the natural chemical weathering process suffered by the sample, since it came from outdoor stockpile (with more than two years of storage). As a probable result of such a process, some aggregation of the constituent particles of this metallurgical residue occurred, masking the experimental granulometric distribution. The chemical characterization indicates iron content equal to 49.33 %, in addition to 9.17 % Ca, 1.94 % Mg and 1.06 % Al. Concentration of deleterious elements, like zinc and lead low; only 0.44 % Zn and 0,04 % Pb, pointing to the advantage of its recycling in blast

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furnace or converter operations (especially zinc, due to its low vaporization temperature, tends to be trapped in the circuit, progressively increasing its content in products and/or provoking furnace scaffolding).

The Hill distribution showed to be adequate descriptor for size distribution of sample, with median size of 70.5 µm and a small sharpness index (***k*** = 0.499), resulting a large size range (amplitude). The density and specific surface area of the studied sludge were typical for this kind of granular material. The main identified crystalline phases were: FeO, Fe_2O_3, Fe_3O_4, Fe_2ZnO, CaO, C_x and SiO_2.

Regarding its industrial beneficiation, in the light of the properties raised, this bulk material insinuates itself amenable to sorting. As a result of this study, customized routes for its physical and physical-chemical processing are being studied and will be the subject of a future article.

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