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Characterization of metallic particles extracted from fly ash of a thermoelectric plant in Boyacá-Colombia

Caracterización de partículas metálicas extraídas de cenizas volantes de una planta termoeléctrica de Boyacá-Colombia

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Abstract

In this work, it was studied the by-products of fly ashes, obtained from a thermoelectric power station in Boyacá, Colombia, through magnetic separation. The morphological characterization of the particles was performed by a scanning electron microscopy. Its elemental composition and crystalline structure were studied through energy dispersive spectroscopy and an X-ray diffraction, respectively. The results obtained show the presence of ferrospheres and cenospheres, which are irregular and rough compounds with a high iron content. The mineralogical phases present in the samples are mainly magnetite and hematite, with some traces of mullite. These phases can provide magnetic properties and extend the range of applications of these particles using a simple separation process in fly ashes.

Keywords: fly ash; cenospheres; ferrospheres; magnetite; hematite; mullite; morphological characterization.

Resumen

En este trabajo se estudiaron muestras de hierro, obtenidas mediante separación magnética de cenizas volantes, procedentes de una estación termoeléctrica de Boyacá, Colombia. Se realizó la caracterización morfológica de las partículas mediante microscopía electrónica de barrido. La composición elemental y su estructura cristalina fueron estudiadas mediante espectroscopia de energía dispersiva de rayos X y difracción de rayos X, respectivamente. Los resultados obtenidos muestran la presencia de ferrósferas y cenósferas, que son compuestos irregulares y rugosos con alto contenido en hierro. Las fases mineralógicas presentes en las muestras son principalmente magnetita y hematita, con algunas trazas de mullita. Estas fases pueden aportar propiedades magnéticas y ampliar el rango de aplicaciones de estas partículas a partir de un simple proceso de separación en las cenizas volantes.

Palabras clave: cenizas volantes; cenósferas; ferrósferas; magnetita; hematita; mullita; caracterización morfológica.

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1. Introduction

Fly ash is a product of the coal combustion process in thermal power plants. These ashes are harmful to the environment and human health [1]. It has been estimated that each thermoelectric plant in Colombia produces an average of 200 tons of fly ash each day. The samples used in this research were obtained from Termo-Paipa IV, which is a thermoelectric power plant with a generation capacity of 321 MW [2]– [5].

Recently, research worldwide has proposed possible applications to give an adequate and productive final use to this industrial waste and thus mitigate its negative effect on the environment [6]. In the study conducted by Kang et al. [7], a model was evaluated to predict the appropriate percentage of fly ash added to concrete to improve its mechanical properties and avoid compromising the integrity of the concrete due to the action of corrosion. These researchers found a strong relationship between chemical composition and morphology with electrical resistivity. They also achieved improvements in concrete using ashes obtained in thermoelectric power plants in Indonesia.

The study carried out by Li et al. [8] investigated the use of fly ash in the direct synthesis of carbon nanotubes using fly ash particles obtained in China. They found that these particles serve as catalytic support in the growth of carbon nanotubes through the chemical vapor deposition technique (Flying Ashes). They obtained satisfactory results for high acetylene or hydrogen flows and low sintering temperatures.

Currently, Supelano et al. [9] have developed research on the use of fly ashes for the synthesis of magnetic zeolites for the adsorption of methylene blue. The fly ash products were analyzed and subjected to chemical activation with NaOH at different concentrations. The researchers identified the formation of zeolites with different ferromagnetic properties due to the iron particles present in the ashes and their reactions with the different activations.

The purpose of this work is to obtain and characterize the metallic particles present in fly ashes supplied by the thermoelectric power station in Boyacá, to propose possible applications, which will be studied in future research.

2. Materials and methods

Fly ashes were produced by the combustion of bituminous coal supplied by a thermoelectric power station in Boyacá, located at km 5 of the Paipa to Tunja road, in Colombia. A sample of 550 g of fly ash was sifted by 30, 100, and 200 sieves, to remove unburned particles, and retained 6.2 g, 39.7 g, and 47.9 g, respectively. This process left 456.2 g of the original sample. Then, the new sample was divided into subsamples of 100 g and dispersed on a pasty surface of 400 cm^2 to facilitate the process of magnetic separation of the desired particles. The neodymium magnet reference N52 used for this process has a cubic geometry of 1"(2.54 cm) and an approximate magnetic field of 15.500 gausses. It was wrapped in plastic and approached to each 100 g subsample, to efficiently separate the iron particles, present in the ashes. Finally, 1.5g of particles were easily obtained by removing the plastic from the magnet.

This methodology was based on the analyst's judgment and parameters such as accessibility to the materials used for magnetic separation and their cost.

The morphological characterization was performed by a scanning electron microscopy (SEM) in VEGA3 TESCAN equipment. The semi-quantitative elemental composition was studied through energy-dispersive X-ray spectroscopy (EDS) using a BRUKER XFlash 410-M gun coupled to the SEM. The identification of crystalline structures and mineralogical phases of the fly ash was performed using a PANalytical X-ray diffractometer. The measurements were taken in a range of 2θ=15° and 90°, with a voltage of 40 kV and a current of 40 mA. The patterns obtained were compared with pre-existing patterns in the American Mineralogy Database (AMCDS).

Dynamic and improved access control mechanisms comprise a) authentication scheme based on smart cards and supported by elliptic curve cryptography (ECC) in a secure way for wireless sensor networks using user password [20], b) secret key-based user authentication schemes for heterogeneous sensor networks (HWSN) [21] and adapted to IoT environments, c) user authentication scheme using a bilinear pairing and trusted authority, which authenticates a user and also establishes secure communication between a user and sensor node [22]; d) three-factor key authentication scheme and a suitable agreement for healthcare WSNs, which is based on multiplications of light ECC points [23]; e) two-factor user authentication scheme with decoupling between a user and sensor [24] that improve the sensor registration and user authentication phase, which allows key updating and link capacity optimization, thereby greatly reducing computational costs.

3. Results and discussion

The morphological results obtained by SEM are presented in Figure 1. The analysis of the image taken with retro dispersed electrons from the metallic particles magnetically extracted from the flying ashes shows a different chemical composition of the particles because different shades of gray are observed, which indicate different atomic weights in the sample. Different types of particles were also identified according to their morphology.

Particle 1 has an irregular morphology and a rough surface. This is mainly because most of the minerals in the coal do not suffer fusion. The temperature of the boiler is relatively low, between 850-900 °C, which is why particle 1 has a considerably larger size than the others. The particle size was measured with the free software ImageJ, thus obtaining a size of 46.6 ± 13.4 µm. These results are comparable to those reported in [10].

Particle 2 shows agglomerations of very small and various sizes, as well as irregular and porous areas. Sometimes it can also present silicon and aluminum glass aggregates with small spherical morphology. The size measured by ImageJ was 38.5 ± 10.8 µm. This result is comparable to the investigations carried out by Xuel et al. [11] and Zyrynov et al. [12], where they found particles of this nature typical of the source material, i.e., fly ashes.

There are particles with high spherical symmetry, some darker than others, such as particles 3 and 4. This behavior is discussed by Santaella et al. [13] and Bajukov et al. [14], who found abundant particles of this type in fly ash. These particles can be of hollow or solid structure, where the first ones can contain in their interior particles of the same nature, but smaller. The particles found had an average size of 134.16 ± 8.6 µm measured by ImageJ (Figure 2a).

Particles 5 and 6 present roughness and protuberances in their morphology. High brightness is also observed by BSE due to the high density of iron. The average size is 182.94 ± 15.8 µm, measured by ImageJ (Figure 2b). Some studies, such as those of Xuel et al. [11], Bajukov et al. [14], Sokov et al. [15], and Golewski [16] agree on the morphology found, which is a well-rounded with pores or roughness on the surface and in many cases contain a portion considered to be a glass aluminosilicate matrix [3].

Figure 3 shows the spectrum of the overall sample analysis by EDS, highlighting the presence of C, O, Al, Si, and Fe. The presence of carbon, silicon, and aluminum in the sample is a typical composition of fly ash. This technique is not conclusive in terms of O detection; therefore, the presence of this element will be verified in the structural characterization of the sample.

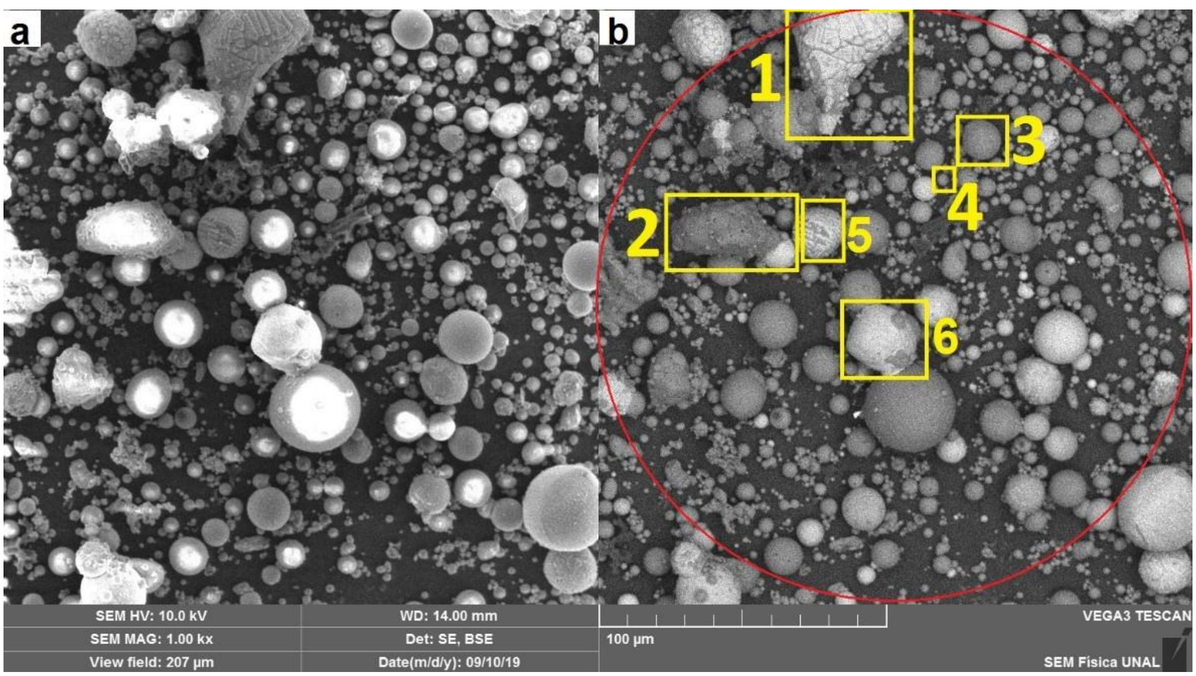
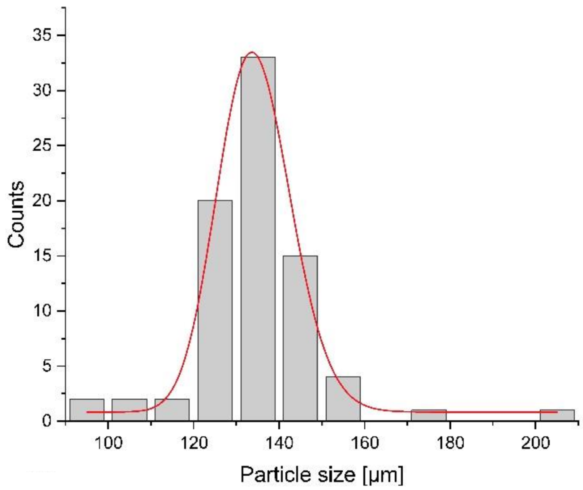
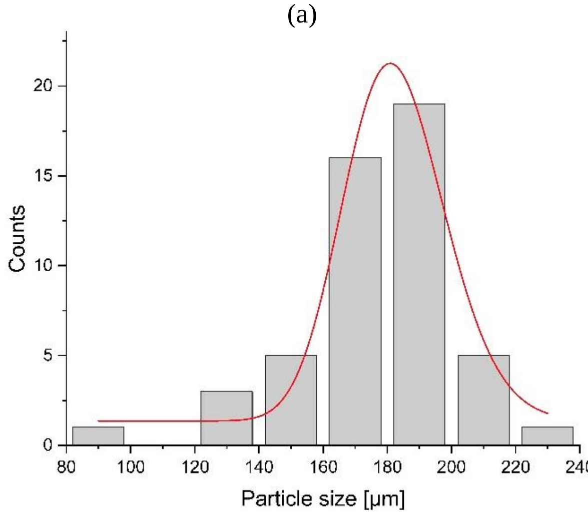


Figure 1. SEM image. Identification of the different types of particles present in the sample by their morphology: (a) secondary electrons (SE) and (b) Backscattering electrons (BSE). Source: authors.

These detected elements are consistent with the results reported by Wang et al. [17]. Due to the nature of the coal and specifically to the sample extracted from the fly ash.



(a)



(b)

Figure 2. Particle size of the (a) 3 & 4 and (b) 5 & 6 particles obtained magnetically from fly ash. Source: authors.

Table 1 presents the results of the semi-quantitative analysis of elemental composition in particle 1, from the most to the least concentrated elements. It is observed that the predominant element is Fe, followed by O and there are elements in smaller proportion, such as C or Si. This result is comparable to the ferrosphere composition reported in [18].

Particle 2 has an elemental composition of mainly Fe and O, then, less C, Si, and Al, as shown in Table 2. These elements may correspond to aluminosilicate compounds. These results coincide with research reported by Chen et al. [19].

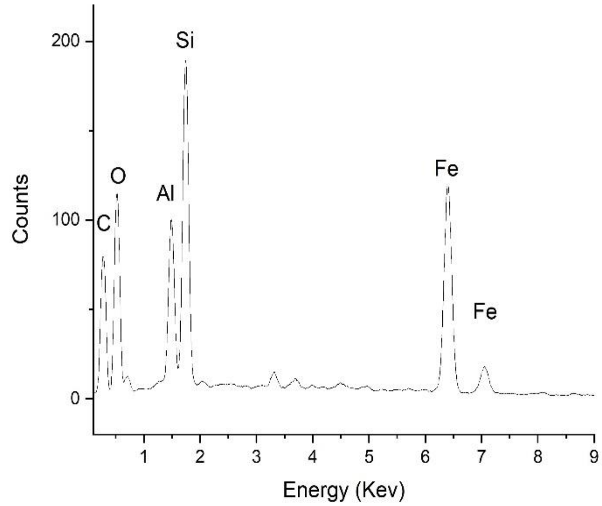


Figure 3. General EDS spectrum of the particles obtained magnetically from fly ash. Source: authors.

Table 1. EDS results in %wt. of particle 1

Chemical element	Particle 1 %wt.
Fe	57.99
O	35.57
C	3.20
Si	1.76
Al	1.49

Source: authors.

Table 2. EDS results in %wt. of particle 2

Chemical element	Particle 2%wt
O	55.23
Si	26.33
C	9.46
Al	7.59
Fe	1.39

Source: authors.

Table 3 shows the results of the analysis by EDS for particles 3 and 4. It is evident that their main component is oxygen, followed by silicon, which is associated with aluminum. These particles are composed primarily of Fe, C, O, Si and Al, which are characteristic of the cenospheres. as reported by Kutchko et al. [20]. This means that this type of particle has a considerable amount of Si and Al, in accordance with the morphology and as reported in [11], [12], [19].

Table 3. EDS results in %wt. of particles 3 and 4

Chemical element	Particle 3 and 4 %wt.
O	53.48
Si	25.28
Al	11.50
C	5.59
Fe	3.83
K	0.32

Source: authors.

The elemental composition of particles 5 and 6 obtained by EDS is reported in Table 4, where a major presence of Fe is observed, followed by O, which indicates that these particles in the sample are ferrospheres. Also, C, Si, and Al have been detected in smaller proportions. This facilitates the recognition of the particles known as ferrospheres. These results are comparable to those reported in the literature [21].

Table 4. EDS results in %wt. of particles 5 and 6

Chemical element	Particle 5 and 6 %wt.
Fe	63.21
O	27.83
C	6.14
Si	1.62
Al	1.20

Source: authors.

The structural and mineralogical analysis performed by XRD is shown in Figure 4. In this sample, the presence of 3 crystalline phases is observed. The presence of hematite and magnetite was detected, which coincides with the diffraction patterns identified with the reference AMCDS No. 0000143 and AMCDS No. 000945, respectively. These crystalline structures represent the iron oxides (Fe_2O_3) and (Fe_3O_4) present in the sample, identified as ferrospheres. These results are comparable to those reported in [16], [18], [21], [22].

The mullite was also identified as matching the AMCDS diffraction pattern AMCDS No.0001351, which represents the aluminum oxide (Al_2O_3) and silicon oxide (SiO_2) present in the sample. These oxides correspond to the mullite crystal structure [19], [23].

The result obtained by performing a Rietveld refinement showed that the percentages of the phases present are the following: 75.4% of magnetite, 13.5% of hematite, and 11.1% of mullite, with a chi-square of 1.2.

This result confirms the presence of the elements found by the EDS technique and the quantitative result of the percentage of the mineralogical phases present in the sample by Rietveld refinement, where ferrospheres were predominant in the sample.

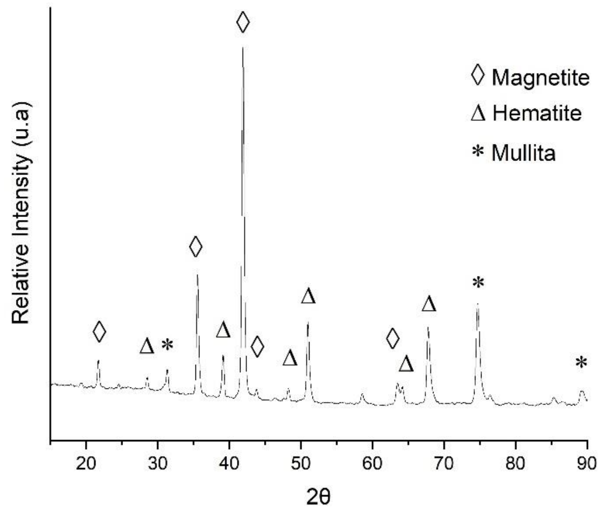


Figure 4. X-ray diffraction pattern of particles present in the sample. Source: authors.

4. Conclusions

The analysis through SEM allowed identifying different types of particles and morphologies. Some of them presented irregular morphology and rough surface, as well as agglomerations of particles of varied sizes. Other particles showed high spherical symmetry, commonly known as ferrospheres, which present roughness and protuberances. Also, elemental composition analysis identified that the material extracted from the fly ashes is mainly composed of Al, Si, and Fe.

An XRD and Rietveld's analysis revealed that the material extracted from the fly ashes presents oxides of Si, Al, and Fe in three mineralogical phases. The predominant mineral was magnetite with 75.4%, followed by hematite with 13.5%, and finally mullite with 11.1% with a chi-square of 1.2.

The elemental composition, structure, and morphology of the analyzed particles confirm the presence of mainly cenospheres and ferrospheres. Future research will focus on magnetic properties and their possible applications.

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