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PHYSICOCHEMICAL AND ENVIRONMENTAL CHARACTERIZATION OF INDUSTRIAL WASTES IN POWDER

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Abstract. In the present work residual powders of diverse industries are characterized from the environmental and physicochemical point of view, in order to determine the properties of them and establish the feasibility of reutilization or recycling.
Cinders of additives, waste of scrap shredding process, LD converter steel slag and other powders of industrial processes were characterized by using optical and electronic microscopic techniques, semiquantitative chemical analysis, particle size distribution, X-ray diffraction analysis, thermal and thermogravimetric analysis, leaching test, among others.
As a function of the obtained results some possible ways for recycling or reuse of these residual powders were proposed.

Introduction

In the present work several residues, which come from diverse industrial processes are studied: cinders of additives (AC), waste of scrap shredding process (SSP), converter steel slag (CSS), powders of aspiration of electrical arc furnaces (EAF) and blast furnace sludge (BFS).
Cinder is one of the major wastes produced by burning coal. It is of great economical and environmental concern in virtue of increasing landfill costs and its content of several heavy metals that are very mobile and can be leached into the groundwater under acidic conditions. It is meaningful to reuse it properly. Cinder can be used, for example, as support of solid base catalyst for biodiesel production [1]. A mixture of converter slag and coal cinder as adsorbent for the removal of phosphorous and other pollutants in wastewater treatment has been studied [2]. LD converter steel slag is an industrial by-product resulting from the steelmaking process in oxygen converters (Linz–Donawitz process). The slag can be used in several areas, such as fertilizer [3], as aggregates in road construction [4], in cement [5] and as raw material for ceramics [6].
Scrap has become a major raw material of the steel industry. Producing new steel from a scrap based electric furnace operation saves energy, causes less environmental concern and effectively recycles material that might otherwise be wasted. The shredding of that steel scrap before it is charged into electric arc furnaces has proven to be a key factor in an efficient operation. The waste of this shredding process is one of the residues analyzed in this work.
Powders of aspiration of electrical arc furnaces are one of the several solid wastes from steel-making process. Different works have been dedicated to characterize and evaluate possible applications of this type of waste [7, 8].

During the production of pig iron, slurry containing a large amount of iron and coal is obtained as waste. Among other uses, the utilization of blast furnace sludge as adsorbent of heavy metals in aqueous effluents [9, 10] has been investigated.
The aim of this study is to characterize from the physicochemical point of view, the mentioned wastes to determine their environmental aptitude for the reutilization in some way.

Experimental

All the residual materials mentioned are granular, and have been characterized by diverse techniques: electron diffraction analysis X-ray (XRD), optical microscopy (OM), scanning electron microscopy (SEM) with X-ray electron dispersive analysis (EDS), differential and gravimetric thermal analyses (DTA-TGA) and particle size distribution, among others.
The optical observations were made with Zeiss-Axiotech equipment with a Donpisha 3CCD camera and image scanner.
XRD patterns of the residues were obtained with PANalytical X'Pert PRO diffractometer at 40 kV and 40 mA, with CuKα radiation (λ= 1.5406 nm) and monochromator filter. SEM analyses were carried out through a Phillips 515 scanning electronic microscope with an X-ray detector (EDAX-Phoenix). DTA-TGA analyses were performed in a Shimadzu DTA-50, TGA-50 with Thermal Analyzer TA-50 WSI.
Conductivity and pH of the wastes were measured at room temperature after 2 hours with stirring, with SPER-SCIENTIFIC, Model 860032 equipment and ALTRONIX TPX-III equipment, respectively. Soluble solids in these powder materials were also determined (90°C, 2 hours with stirring).
Weight loss on ignition (800°C - 3 hours) was also determined. The wastes have been characterized also through analysis of emissions in relation to the presence of CO_2 during the combustion process.
Leaching test of these samples in powder analyzing heavy metals in the leached liquid, according to the Norm EPA 1310, were made. Chemical analysis of the leachate was carried out by plasma emission spectrometry with a Perkin Elmer ICP Optima 3100 XL.

Results and discussion

The chemical composition determined for the five samples by EDS semiquantitative technique is presented in Table 1, expressed as a percentage of the present elements, regardless of carbon content, which is detailed in the same table. It can be observed a high content of Ca in samples AC and CSS, and Fe in SSP and EAF samples.

Table 1. Chemical analysis (EDS) of the wastes.

	Na	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*K*	*Ca*	*Mn*	*Fe*	*Zn*	*C*
SSP	21.48	1.70	3.77	8.84	---	0.77	---	0.74	3.06	---	30.90	28.74	36.60
BFS	18.97	1.34	13.10	30.68	---	8.69	1.16	0.60	1.02	6.66	17.78	---	51.00
CSS	---	6.76	5.41	8.05	---	---	---	---	53.09	3.87	22.82	---	13.20
AC	---	12.10	2.41	5.11	0.80	2.02	---	0.92	70.21	2.14	4.29	---	55.52
EAF	4.95	4.28	0.59	4.10	---	2.61	1.17	4.47	6.06	3.50	53.14	15.13	11.00

Figures 1 and 2 show the OM and SEM micrographs of the studied materials respectively. Some general characteristics can be observed, such as particle morphology, relative sizes and colours.
The powders BFS and EAF are those which present the smallest particulated matter. This turns out to be important during the transportation and deposition of the wastes, due to the possibility of dispersion of the particulate matter with particle sizes less than 10μ (PM_{10}), one of the air pollutants regulated in Argentina and worldwide, whose concentration in air must be below 150 μg/m^3.

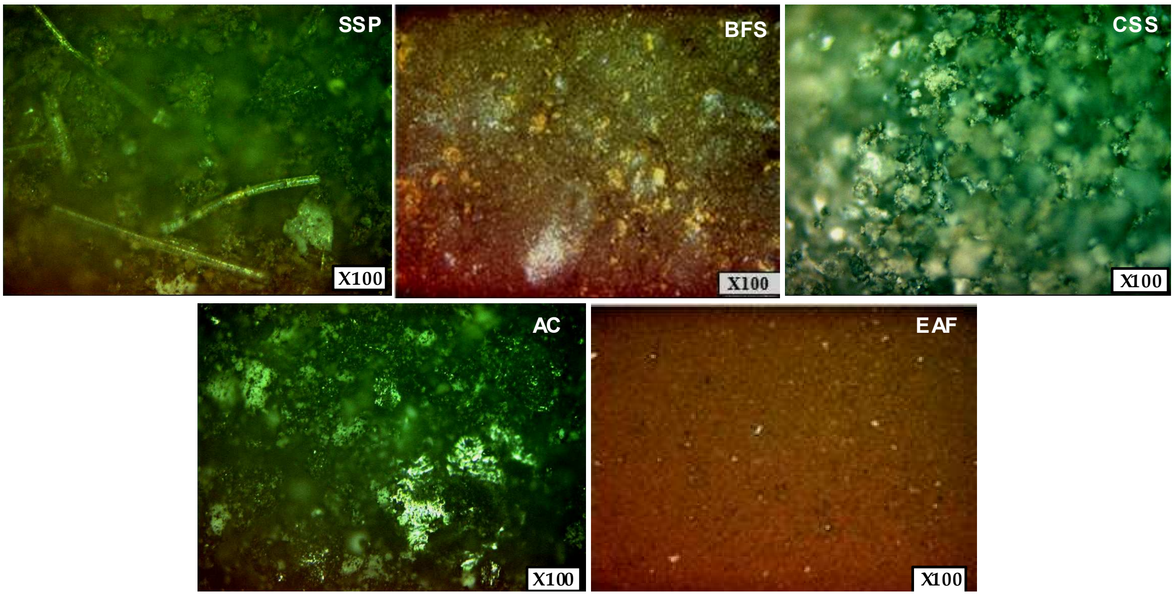

Figure 1. OM characterization of the wastes samples.

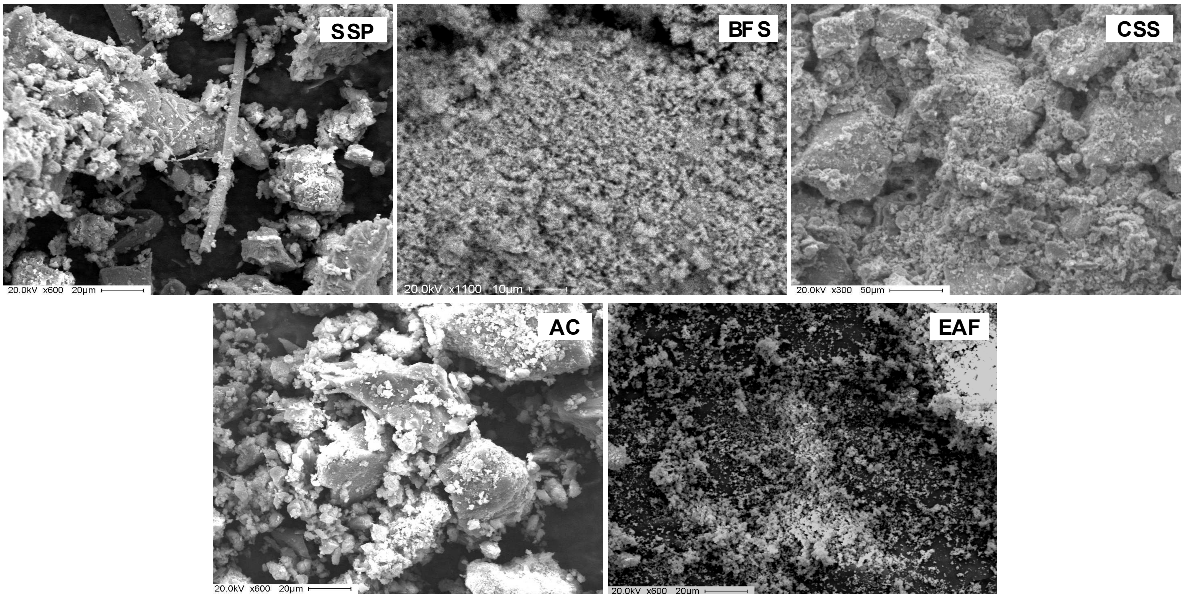

Figure 2. SEM micrographs of the residual powders.

In Fig. 3 XRD patterns of the residues can be seen. BFS sample shows the presence of the iron oxides phases, hematite-Fe_2O_3, magnetite-Fe_3O_4 and wustite-FeO, as well as some peaks corresponding to quartz-SiO_2 and iron-Fe phases. In the case of EAF sample the obtained pattern shows also hematite and magnetite phases, quartz and iron presence and small peaks assigned to zinc oxide-ZnO_2. AC powder shows the presence of calcium carbonate-$CaCO_3$, magnesium and calcium hydroxide, carbon-graphite and dolomite-$CaMg(CO_3)_2$.

Fig. 4 presents the DTA-TGA of these residues. In BFS waste, there is a constant weight loss between 400°C to 700°C which can be attributed to the combustion of carbonaceous materials of the sample.

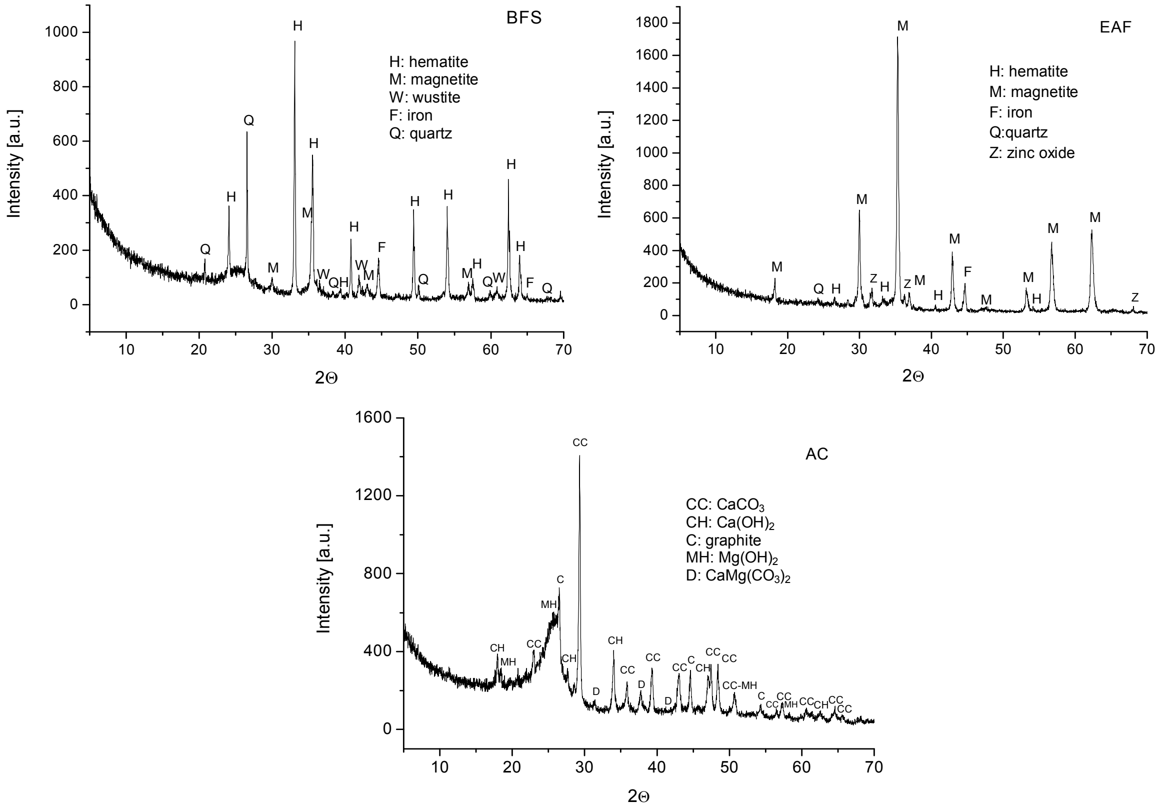

Figure 3. XRD patterns of the BFS, EAF and AC residues.

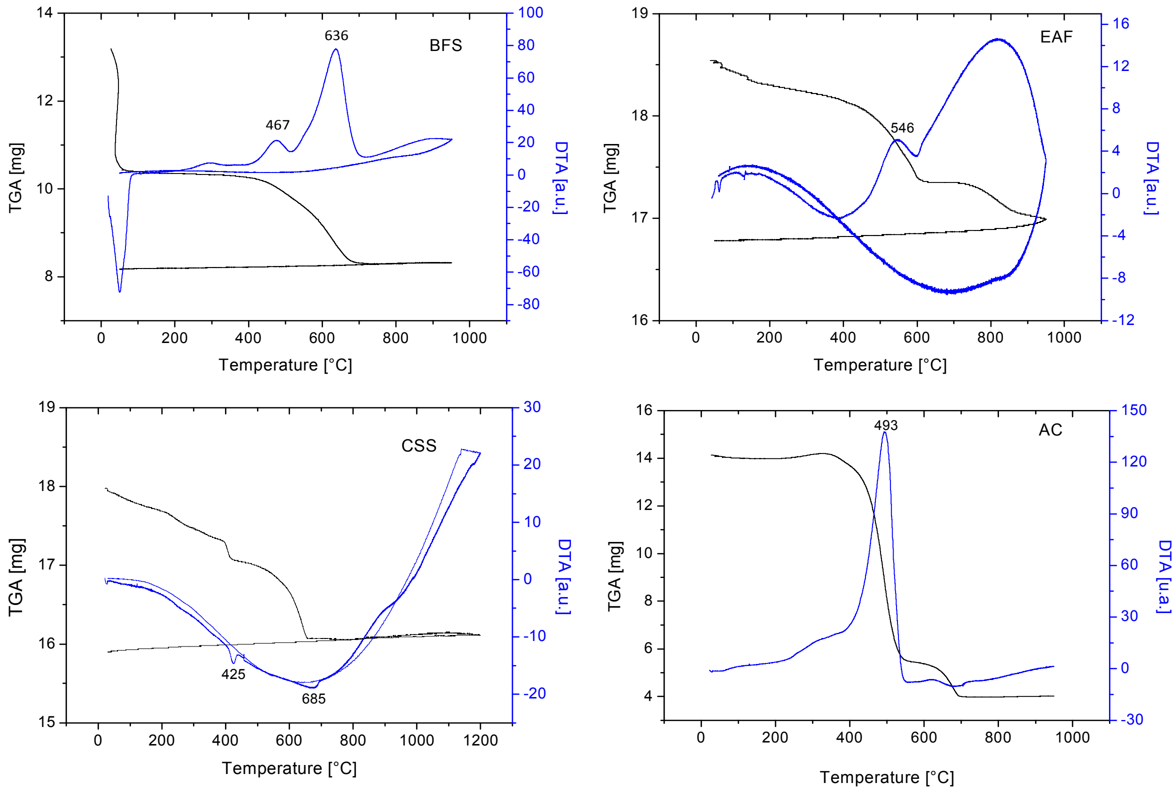

Figure 4. DTA-TGA of the BFS, EAF, CSS and AC residues.

DTA analysis shows two exothermic peaks at 467 and 636. They are interpreted as exothermic oxidation reaction from Fe_3O_4 and FeO (determined by XRD) to Fe_2O_3, which is the only oxide detected by XRD in the calcined sample [11].

A weight loss and the presence of an exothermic peak in the range 400°C-600°C are detected in the EAF sample. This is explained as the combustion of carbonaceous materials present in the sample. CSS sample presents two ranges with weight losses 400°C-430°C and 600°C-700°C ranges, and the corresponding endothermic reactions in the DTA at maximum temperatures of 425°C and 685°C. They are interpreted as calcium hydroxide and carbonate decompositions respectively.
AC powder shows an exothermic reaction with weight loss also in the 400°C-600°C range, with a maximum value in 493°C indicating the combustion of carbon. Other weight loss at 600°C-700°C range indicates probably the calcium carbonate decomposition.
These results are related with the essays of loss on ignition (LOI). The determined values are shown in Table 2 together with the results of the soluble solids (SSs) essays.

Table 2. Weight loss on ignition and soluble solids of the samples.

	SSP	*BFS*	*CSS*	*AC*	*EAF*
LOI [%]	2.82	6.99	0.46	3.05	5.30
SSs [mg]	53	34	77	85	970

During the LOI essays, the combustion processes of organic and/or carbonaceous materials can be followed by means of air quality equipment which measures CO_2 emissions. Figure 5 shows the analysis performed on the five samples during the calcination process. These results are consistent with the LOI values, except in the case of BFS sample which presents a greater weight loss and low CO_2 emissions. For this residue significant emissions of CO were determined (by electrochemical sensor technology), indicating partial combustion of the combustible material contained in this powder.

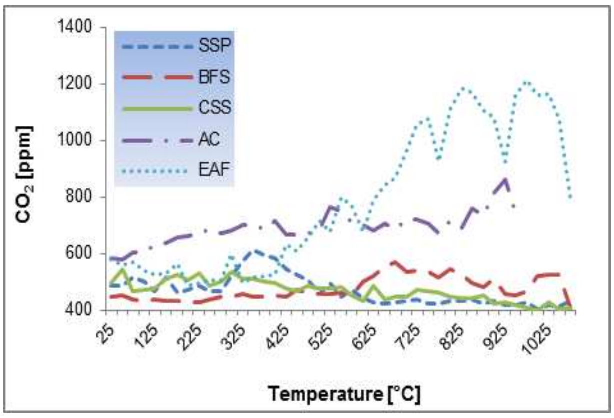

Figure 5. CO_2 emission during calcination process.

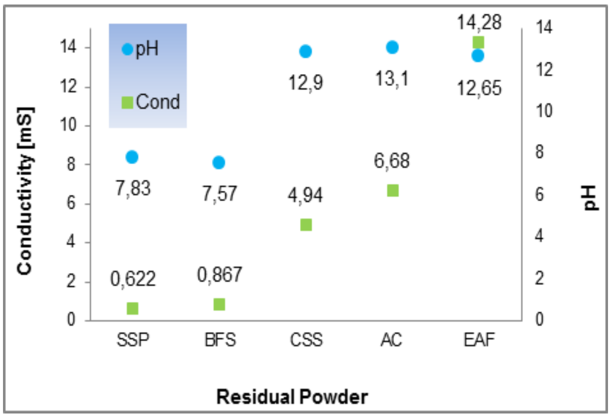

Figure 6. Conductivity and pH in wastes suspensions.

Conductivity and pH were determined on the studied wastes suspensions at room temperature after 2 hours with stirring. Figure 6 shows the obtained values. These results are in direct relation with the soluble solids determined for all samples (see Table 2). These parameters are important especially when the wastes can be used as filling, road improver or land elevator, because they allow inferring the possible influence of these residues on the soils base when they are disposed. Since it can be observed, the corresponding values for CSS, AC and EAF samples appear as those of major influence taking into account the standard values of these parameters in diverse soils [12].
The results of the leaching test of these residual powders are analyzed bearing in mind the definitions and limits established in the Regulatory Decree of the Argentine Law 24051 on dangerous wastes (Decree 831/93), in order to determine the risk or danger of this process of leaching. From the obtained results it is possible to establish that EAF and BFS samples exceed the established limits, in relation to Zn concentration in the leached liquid.

Conclusions

In the present work diverse residues from processes of the steel industries are studied in order to determine their physicochemical characteristics and environmental aptitude for reuse. The analyzed wastes are: cinders of additives (AC), waste of scrap shredding process (SSP), converter steel slag (CSS), powders of aspiration of electrical arc furnaces (EAF) and blast furnace sludge (BFS).
EAF and BFS can't be used as filling, road improver or land elevator due to the observed leaching essays results. They can be used as aggregates in ceramic materials only if the results of leaching tests on sintered samples do not exceed the established limits.
The CSS and AC samples can be used in the mentioned applications but they will possibly change the soils conditions (pH and conductivity).

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