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Recycling of electric arc furnace (EAF) dust for use in steel making process

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ABSTRACT

The EAF dust is listed as hazardous waste from specific source, K061, according to ABNT 10004:2004 and constitutes one of the major problems of electrical steel plant. This work suggests recycling of the EAF dust by sintering of a composite, pre-cast agglomerate (PCA) consisting of EAF dust agglomerate to coke particles, mill scale and ceramic fluorite into pellets. The work was divided into three stages, in the first stage the technical viability of using only solid waste industrial to produce a PCA was observed, in the second phase, the main effects between the components of the PCA to obtain the optimal formulation was tested. In the third phase the intensity of the variables, coke and fluorite ceramics, for removing zinc of PCA was checked. Every stage was chemically analyzed by X-ray fluorescence spectrometer and X-ray diffraction. The first two stages of the production PCA were carried out in a pilot plant sintering downstream and the third phase in a pilot plant upstream. As a result of the process two by-products were obtained, the pre-cast agglomerated, PCA, with total iron content exceeding 70%, object of the process of sintering and zinc dust, containing more than 50% zinc resulting from volatilization of this metal during the sintering process and collected by bag filter. In addition, approximately 90% of lead and cadmium contained in the initial EAF dust was extracted.

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1. Introduction

In the production of steel, large amounts of material are consumed, but only a portion is incorporated into the final product. In integrated mills, for each 1 t of crude steel produced are needed 2.40 t of iron ore and other inputs. Electric steelworks for the manufacture of 1 t of steel requires 1.1 t of ferrous scrap, pig iron and other metal [1]. Not only is it a waste of resources, but also an additional cost and potential adverse environmental impact if these residues do not have environmentally appropriate disposal.

The goal of this paper was to propose and evaluate an alternative to recycling EAF dust applicable to an individual facility,

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aiming the possibility of being replicated to other steel plants and complementary:

- recycling the EAF dust for the production of pre-cast agglomerate (PCA) for use in steel plant process;
- extract the EAF dust hazardous constituents to allow reclassification to non-hazardous waste not inert, class II A, according to ABNT NBR 10.004:2004 [2].

1.1. Steel waste

The main recyclable solid wastes in an integrated steel making process are the dust from sintering, electrostatic precipitator dust, powders and slurries from blast furnaces, thin and thick steel mill sludge, mill scale from hot rolled, cold rolled mud and mud from chemical residue treatment [3]. In the semi-integrated process, the main ones are the slag of electric steelmaking, EAF dust and mill scale continuous casting and rolling.

1.2. Electric arc furnace (EAF) dust

The EAF dust is generated during melting of scrap in electric arc furnace and collected by bag filters or electrostatic precipitators. Some researchers have shown that characterize adequately EAF dust is necessary to use various techniques in combination to determine the phases present, and in particular $ZnFe_2O_4$ and ZnO [4]. As Gonçalves et al. [5] the use of various techniques for characterization is important because the presence of two phases of oxides of Zn are essential for the recycling of this waste: to obtain metallic zinc to the zinc industry, or to obtain metallic iron for the steel industry.

Through diffraction of X-rays techniques [6–8] samples to various EAF dust show that the primary constituent is franklinite (zinc ferrite spinel $ZnFe_2O_4$), followed by calcium ferrite (spinel $CaFe_2O_4$) and magnetite (Fe_3O_4), which is, the strong presence of iron oxides and zinc. Several researchers [9] have confirmed the prevalence of franklinite using X-ray diffraction, scanning electron microscopy and mass spectrometry. The particle size distribution is heterogeneous with 60% between 0.90 μm and 4.30 μm and mean diameter of 1.88 μm. [10,11].

The largest recycling companies, to be economically viable, require that the EAF dust containing Zn concentrations greater than 15% [12].

The hydrometallurgical treatment by leaching wants to recover the constituent elements in the waste liquid aiming subsequent electrolytic recovery of zinc in solution. This is the most economical route for obtaining zinc with high purity [13]. Other researchers [14,15] suggest selective leaching of zinc and lead without destroying the iron matrix, aiming its reuse. The leaching is performed in three steps, hydrolysis of dust, destroying the crystal structure of zinc ferrite by fusion and direct leaching with NaOH is able to get 98% zinc recovery [16].

Other reduction processes that can perform recycling, already developed or under development as Tecnored, Oxicup, Redsmelt, Primus, Itmk3 [17] have not yet reached the necessary consolidation of its economic viability.

The Rapporti38 [18] considers promising process ILSERV/CSM arc – plasma and thermal processing of intensive type CONTOP (cyclone furnace) but not consolidated and provides for the establishment of new process plants RHF, particularly Primus technology.

One of the most known and used processes is currently the Waelz kiln, there are more than 14 plants in the world using this process [19]. The main objective is to recovery of zinc and lead contained in EAF dust. As Nyirenda [20] using the Waelz kiln for treatment of EAF dust is financially unfeasible for a plant with less than 50 thousand t capacity, considering the EAF dust with an average content of 15% zinc.

2. Materials and methods

The materials used in the development of this work were those with waste iron: EAF dust and mill scale continuous casting/lamination; coke as a reducing and ceramics fluorite as an additive for its excellent fluxes features to reduce the reoxidation of zinc, contributing to lower the zinc content in the PCA.

$$CaF_2 + ZnO = ZnF_2 + CaO \qquad (1)$$

$$CaF_2 + ZnFe_2O_4 = ZnF_2 + Fe_2O_3 + CaO \qquad (2)$$
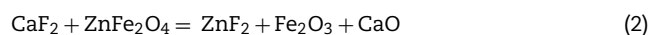
The ceramic fluorite is the residue from filtration of gases from the burning process during the production of commercial ceramic tiles. In this gas treatment system, hydrogen fluoride gas (HF) reacts with the calcium oxide (CaO) in bag filters with sleeve impregnated by hydrated lime. The resulting powder of this process is fluorite ceramics, due to their similar characteristics to the mineral fluorite. The passage of gas through the dedusting system avoids the emission of fluorides into the atmosphere in ceramic processes.

2.1. Methods used

In this paper were used techniques of document analysis, particularly reports of waste characterization according to ABNT NBR 10004:2004 [2]. The methodologies used can be seen in Table 1.

2.2. Production of pre-cast agglomerate (PCA) in experimental range

The output of the PCA in the experimental scale was divided into three phases. The first phase of the experimental scale, made with eight different formulations, aimed to verify through chemical analysis by fluorescence spectrometry X-ray and diffraction X-rays, the technical feasibility of using only waste for the production of PCA. The second phase, also with eight formulations, defined as design of experiments with factorial design tested the main effects and interactions between double and triple the composers of the APF, to obtain the optimal formulation. The third phase tested of the intensity of the variables, coke and ceramics fluorite, the removal of zinc. The first two phases of production tests, in pilot scale, were

Table 1 – Methodologies used in the research.

Parameter	Unit	Method
Homogenization and quartering	–	ABNT NBR 10007:04
Actual density of raw materials	g/cm^3	displacement fluid (Ultrapycnometer)
Particle size distribution of raw materials	μm (Sedigraf) and % (Screens)	Decanting of the material (Sedigraf - IT LABMASS140R4)/Screening (ITAMP204)
Chemical composition of raw materials	%	X-ray fluorescence
Crystalline phases of raw materials	–	X-ray diffractometer
Crystalline phases of the electric arc furnace dust	%	Mossbauer Spectroscopy
Classification of mixtures	Class	ABNT NBR 10004:04
		ABNT NBR 10005:04
		ABNT NBR 10006:04
Classification of PCA's	Class	ABNT NBR 10004:04
		ABNT NBR 10005:04
		ABNT NBR 10006:04
Crystalline phases of mixtures	–	X-ray diffractometer
Crystalline phases of PCA's	–	X-ray diffractometer
Morphology and topographical feature of mixtures	–	MEV-EDS/WDS
Morphology and topographical feature of PCA's	–	MEV-EDS/WDS
Quantification of phases	–	Rietveld crystal structures using database of ICSD – Inorganic Crystal Structures Database (2007)

Author (2012).

Fig. 1 – Pilot Plant sintering downstream of Metalflexi installed at ArcelorMittal Piracicaba, with exhaust flow capacity 1200 m³/h that upon ignition produces a thermal front that reaches 1200 °C, to sustain the heat transfer layer top of the mixture, into the pan sintering, to the bottom layer.
Author (2012).

conducted in the pilot plant sintering downstream (Fig. 1) and the third phase in a pilot plant upstream (Fig. 2), both installed at the ArcelorMittal Piracicaba plant.

3.   Results and discussion

The summary results of the first stage of experiments, as shown in Table 2, below, led to the following conclusions, which were tested in the second phase of experiments:

- the lower percentage of the EAF dust in the mixture results in the lower percentage of zinc in the PCA. This result was expected because the source of zinc is in the EAF dust;
- the higher percentage of coke in the mixture results in the lower percentage of zinc in the PCA. This result is in agreement with all the studies related, which indicate that the main factor for removal of zinc is increasing the amount of coke;
- It was expected that increasing the amount of ceramic fluorite elevate the rate of removal of zinc from the PCA.

3.1.   Second phase of experiments

The second phase of experiments showed the following results which can be seen in Table 3. It was not possible to perform the experiment 8, because of high temperatures, due to the use of 7% coke, the grille warped and the hood unbalanced. However, with the seven experiments performed were

Table 2 – Summary of the first stage: zinc and iron parameters of PCA.

Parameter (%)	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8
EAF dust	35	40	45	35	40	45	50	50
Scale	48.5	43.5	46.5	55	49	45	41.5	40
Coke	3	3	3	5	5	5	3	5
Ceramic fluorite	5.5	5.5	5.5	5	6	5	5.5	5
ZnO	7.61	8.67	10.1	6.16	8.94	11.0	11.8	9.74
Fe$_2$O$_3$	72.7	71.9	75.7	70.1	76.8	74.1	74.5	68.8

Author (2012).

Parameter	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8
Al_2O_3	0.61	0.33	0.24	0.30	0.26	0.35	0.32	–
CaO	5.77	5.72	4.00	5.37	6.90	8.28	6.74	–
Cl	0.33	0.04	0.04	0.03	0.10	0.11	0.05	–
SiO_2	5.02	5.05	3.59	4.87	4.32	5.14	3.61	–
F	1.44	0.94	1.44	0.72	3.28	3.11	2.80	–
Fe_2O_3	73.2	69.5	79.4	72.0	71.6	65.1	75.6	–
K_2O	0.21	0.04	0.04	0.03	0.07	0.07	0.06	–
MgO	1.48	1.45	1.08	1.47	1.60	1.31	0.96	–
MnO	1.09	1.32	1.07	1.28	1.01	1.26	1.11	–
Na_2O	2.12	2.16	1.72	2.19	1.92	2.17	1.55	–
P_2O_5	0.35	0.42	0.29	0.42	0.33	0.44	0.26	–
PbO	0.26	0.14	0.06	0.16	0.13	0.19	0.13	–
ZnO	7.26	12.2	6.43	10.5	7.84	11.7	5.87	–

Table 3 – Chemical analysis of PCA's.

Author (2013).

found by chemical analysis, the goal of having an PCA with less than 1% zinc was not achieved by the following factors: limit the use of coke, there was a 7% degradation of the equipment; and compaction of the pellets hindering the diffusion of gases.

Thus, the third stage used a different firing procedure of the previous stages, the airflow was upward, without using grid and sequential deposition of layers of 10 mm pellets. Consequently, with less density of the layers was larger portion of voids and easier to outgassing. Without the use of the grid no

limit to the use of coke, allowing for the increase of the ratio C/Zn.

3.2. Third phase of experiments

In the third phase, as the main objective was to identify the mechanism to optimize the removal of zinc mill scale was not used. To mix formulation was taken as the experiment base 7 of the second phase (35% of the EAF dust, 49% of mill scale, 9% ceramic fluorite and coke 7%), which was obtained PCA

Fig. 2 – Pilot sintering plant upstream (a), with detail of the mixture (b), particulate material volatilized during the process captured by the hood (c) and pre-melting agglomerated – PCA(d).
Author (2013).

Table 4 – X-ray fluorescence spectrometer (XRF): pre-cast agglomerate (PCA) of the third stage, experiment 1, as the Laboratory of ArcelorMittal.

Parameter	PCA
Al_2O_3	1.12
CaO	2163
NaCl	3.35
SiO_2	1321
F_2	0.84
FeO	54.0
K_2O	0.08
S	0.77
MnO	2.61
TiO_2	0.17
P_2O_5	0.76
PbO_2	0.04
ZnO	0.51

Author (2013).

Table 6 – X-ray fluorescence spectrometer (XRF): zinc concentrate from the third phase of experiment 1.

Parameter	Exp. 1
Al_2O_3	0.19
CaO	0.37
Cl	8.24
SiO_2	0.46
F	0.67
Fe_2O_3	3.41
K_2O	5.0
MnO	0.17
TiO_2	0.02
P_2O_5	0.03
PbO	4.77
ZnO	46.5
PF	28.4

Author (2013).

with 5.87% ZnO. Thus, the initial experiment of the third stage, called experiment 1, was composed of 70% of the EAF dust, 20% coke and 10% ceramic fluorite. Experiment 1 produced a pre-cast agglomerate (PCA) with 0.5% ZnO (removal rate of 96.7%) and 54% FeO, according to Table 4. The PCA was virtually free of lead, an element that confers dangerousness to waste, on the leaching test, the furnace residue was 0.04%

A sample of the mixture and the PCA of experiment 1 was sent to the LCT USP to confirm the results obtained by Arcelor-Mittal laboratory as well as the volatile particulate matter resulting from the experiment, which was collected on bag filter. In the analysis of the LCT the percentage of ZnO in APF was 3.61% (removal rate of 77.1%) in the control sample and the percentage of ZnO was 6.06% (removal rate of 61.6%), according to Table 5. The zinc concentrate showed 46.5% of ZnO and PbO 4.77%, as shown in Table 6.

Table 5 – X-ray fluorescence spectrometer (XRF): mixture and pre-cast agglomerated (PCA) of the third stage, experiment 1, as the Laboratory of University of São Paulo.

Parameter(%)	Mix Exp. 1	PCA Exp. 1	PCA rep. Exp.1
Al_2O_3	0.45	1.19	0.88
CaO	7.91	17.7	8.55
Na_2O	5.94	1.98	1.83
Cl	3.29	0.27	0.05
SiO_2	2.90	10.6	7.49
F	2.15	3.16	nd
Fe_2O_3	22.9	52.5	68.4
K_2O	1.53	0.21	0.10
SO_3	1.31	1.54	0.49
MnO	1.06	2.58	2.09
TiO_2	0.09	0.23	0.16
P_2O_5	0.28	0.81	0.59
PbO	1.97	0.18	0.19
ZnO	15.8	3.61	6.06

Author (2013).

4.   Conclusion

The first phase of the experiments demonstrated the technical feasibility of obtaining a byproduct, PCA, made out only with solid waste generated internally in the steelmaking process plus the ceramic fluoride, waste of the ceramic process and coke. Although in this phase it was found that PCA subjected to leaching test according to ABNT NBR 10005:2004[21] can be reclassified as non-inert non-hazardous waste, Class II, according to ABNT NBR 10004:2004 [2], which represents a huge reduction costs (75.0%) for the steel industry when considering final disposal in landfills. And finally, proved the technical feasibility of treating EAF dust on a compact plant suitable to volume of dust generated by the plant itself.

The second phase of experiments showed like the raw materials that make up the PCA influence to obtain a marketable byproduct for use in small blast furnaces. The tests of the PCA in the blast furnace did not recorded anomalies in the process and chemical composition of pig iron also showed no changes.

In the third phase, without using mill scale, it was indicated that there is a great relation between C/CaF2, located at 20.0% C and 10.0% CaF2 for the extraction of zinc. Out of this condition, even increasing the percentage of C (from 7.0% to 20.0%) there is no increase in the extraction of zinc and even increasing the percentage of CaF2 (from 10.0% to 15.0%) no increase in the extraction of zinc was observed.

Conflicts of interest

The authors declare no conflicts of interest

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