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Lead and zinc selective precipitation from leach electric arc furnace dust solutions

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ABSTRACT

Electric-arc furnace (EAF) dust is considered a hazardous industrial waste. In this work, chemical and mineralogical investigations of EAF dust from Siderúrgica Rio-Grandense (RS, Brazil) were performed. The elements aluminum, calcium, lead, cadmium, chromium, magnesium, manganese, nickel, potassium, silicon, sodium, tin, iron, zinc, sulphur, oxygen, and carbon were found in EAF dust. The concentration of zinc and iron showed an average value of approximately 20% (weight basis) and these elements are mainly present as $ZnO.Fe_2O_3$ (zinc ferrite) and ZnO (zincite) mineralogical phases. Also, EAF dusts were submitted to an integrated hydrometallurgical process composed by a hydrolyzed step, followed by a fusion step and a strong alkaline leaching. A subsequent chemical precipitation was carried out in order to promote selective separation of zinc and lead from the leach solution. Sodium sulphide was successfully employed as precipitant agent. When the weight ratio of sodium sulphide to lead was around 2.0, lead could be selectively extracted from leach solution. After lead precipitation without zinc concomitant loss, a weight ratio of sodium sulphide to zinc of around 3.0 was used to precipitate all zinc. Thus, EAF dust has a great potential to be used as a source of metals extraction due to its rich chemical composition and also for the viability of the proposed selective separation process.

Keywords: Electric arc furnace dust, zinc, lead, leaching.

1 INTRODUCTION

Zinc and lead usually occur together in a variety of mineral zinc ores and some solid wastes such as steel mill electric arc furnace (EAF) dust [1]. During the steelmaking process, the EAF can reach temperatures of 1600°C or higher. Under these conditions, virtually all of the zinc, lead and cadmium present in the charge go into the gas phase. Also, the high temperatures and turbulence in the EAF cause small amounts of iron, chromium, nickel and manganese to volatilize. As soon as the metal vapors exit the furnace, the temperature drops and the fumes oxidize and condense. Physically and chemically complex microscopic agglomerates are formed on condensed nuclei such as fugitive dust particles. These materials are then collected as particulate matter in the baghouse system [2].

According to the International Iron and Steel Institute (IISI) [3], world production of crude steel by electric way was about 286 millions of ton in the year 2000. In a typical electric-arc furnace (EAF) operation, approximately 1-2% of the charge is converted into dust [4]. Thus, world production of EAF dust is about 2.9-5.7 millions of ton per year. Its production, only at Siderúrgica Rio-Grandense, Brazil, is about 400 tons per month.

The EAF dust can be stabilized and landfilled, but in this case the metal values are lost. Although various pyrometallurgical, hydrometallurgical and hybrid pyro-hydrometallurgical processes have been developed in order to recover the valuable metals, none of them have been entire satisfactory. Some were commercialized for a period of time and then abandoned. EAF dust contains not only iron, but a numerous of non-ferrous elements that make complex the metals extraction. Thus, it is still more economical to extract metals from their ores and new technologies and processes for metals recovery from EAF dust must be studied.

EAF dusts generated in the electric arc processing of steel differ essentially from one to another by their physical and chemical characteristic to a significant extent. The recovery and disposal of EAF dust is to be approached individually, in a way determined by the physical and chemical characteristics of every sample dust.

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EAF dusts can be treated by acidic leaching processes. Sulphuric acid is often used for EAF dust leaching because of its low cost [5, 6]. However, the zinc content of these dusts is usually low compared with iron and only a small fraction of the zinc can be extracted without leaching iron, lead and elements such as Ca, Fe and Mg. As a result, a large quantity of extra acid will be consumed and a leach solution with complex components will be obtained [7]. According to Youcai and Stanforth [8, 9], alkaline leaching in caustic soda solution is another method widely used in the extraction of zinc and lead from oxidized zinc ores and wastes. In this process, elements such as Fe, Al, Mg, Ca and others will not be dissolved. Hence, the consumption of leaching agent will be reduced to a minimum value and a leach solution containing only Zn and Pb as predominant elements will be obtained. However, the solubility of zinc ferrite mineralogical phase of EAF dusts is quite limited in both acidic and alkaline solutions and thus a hybrid process is preferable in order to recover zinc present in zinc ferrite form. A recent work reported a zinc recovery of only 45% using ammonium carbonate as leaching agent; evidently this is due to the presence of the zinc ferrite species in the flue dust which remained unattacked [10]. After leaching step, Pb can be cemented by the addition of zinc powder in acidic solution, but not in alkaline medium. Thus, an alternative method should be developed for Pb removal from zinc in alkaline solution.

This research aimed at the investigation of the chemical and mineralogical phase composition of eight monthly samples of EAF dust produced by Siderúrgica Rio-Grandense (Sapucaia do Sul, RS, Brazil) in order to promote EAF dust characterization. Also, metal chemical precipitation from EAF dust alkaline leach solutions was studied in order to extract lead and zinc as sulphides. These compounds are potentially saleable to a zinc plant, followed by recycling the iron oxide residue to the steel producing furnace.

2 EXPERIMENTAL

2.1 EAF Dust Characterization

In order to investigate the chemical and phase composition of EAF dust, eight monthly samples were taken at the outlet of the dust suppression system from Siderúrgica Rio-Grandense located at Sapucaia do Sul, RS, Brazil. The samples were homogenized and successive quartering provided 1000 g of each sample.

The EAF dust samples were solubilized in acid medium using a Tölg system described in Lenz and Fogaça [11]. Afterwards, the obtained solutions were quantitative analyzed by Atomic Absorption Spectroscopy in a Perkin Elmer 400 Spectrophotometer. The element sulphur was determined by analytic route analysis, according to Allen [12].

Micro-structural examination was performed on the PHILIPS XL 20 scanning electron microscope with an Energy Dispersed Spectroscopy (EDS) analyzer. X-Ray Diffraction (XRD) analyses were carried out on the RMN3Kw-B D/MAX-2100 model RIGAKU X-Ray diffractometer composed by Kα 1.5418 Å radiation and copper tubes. The software from International Centre for Diffraction Data was used in these analyses. This software allows performing a search by matching experimental file and database composed by diffraction patterns. Granular-metric composition of the samples was analyzed using a Micrometrics model (Saturn DigiSiger 5200 model) Particles Analyzer.

2.2 Preparation of Alkaline Solution from EAF Dust Treatment

EAF dust samples were treated using an integrated process that combines three steps: EAF dust hydrolysis, fusion with caustic soda and then leaching, as described by Youcai and Stanforth [8] and Lenz et al. [13]. In the first step, EAF dusts were hydrolyzed for 24 h with orbital stirring using a water/dust weight ratio of 1:1. The leach slurry obtained was filtered and dried in vacuum stove. According to Youcai and Stanforth [8], water changes dust morphology, making easy the further attack of NaOH to zinc ferrite in the next step. Zinc ferrite is a very stable crystallographic structure of spinel type which is present in EAF dust. Only direct leaching by NaOH solution does not affect this compound even if temperature is increased. In the second step, hydrolyzed EAF dust was fused at 350°C for 1 h using a dust/solid NaOH weight ratio of 1:1. Finally, as a third step, hydrolyzed and fused EAF dusts were leached in 5 mol L^{-1} NaOH solution with orbital stirring for 42 hours at room temperature. A solid-liquid ratio (g mL^{-1}) of 1/4 was used.

The leachates (leach solutions) showed concentrations of approximately 50 g L^{-1} of zinc, 2 g L^{-1} of lead, 1 g L^{-1} of Al and 0.05 g L^{-1} of Fe. Thus, 98% of zinc and 80% of lead were selectively leached from the dusts. These solutions with zinc and lead were very stable and could be kept for months without forming precipitates and were used as testing solution for separation of lead from zinc.

2.3 Selective Separation of Lead and Zinc from Alkaline Leach Solution

Sodium phosphate, sodium sulphate, sodium carbonate and sodium sulphide (Merck) were used as precipitant agents. They were separately mixed with leach solutions containing zinc and lead and allowed to stand for 4 hours at 25ºC and 40 ºC under stirring. The lead precipitate was separated from the solution, washed vigorously with hot water for 2 h and dried at 110°C. Further, the lead precipitates were solubilized in sulphuric acid solution. After lead removal, zinc precipitates were separated and treated the same way as lead precipitates. Atomic Absorption Spectrophotometry was used to analyze Pb and Zn concentration. Then, metal extraction efficiencies were calculated.

Sodium sulphide is not stable and the number of hydrates in the crystal also changes gradually. The chemical formula is $Na_2S\ xH_2O$ ($x = 7 - 9$). Youcai and Stanforth [9] have determined the molecular weight of the sodium sulphide in approximately 222 g mol^{-1} ($x = 8$). Weight ratios of sodium sulphide with respect to lead in the solution from 0.5 to 2 (molar ratio approximately 0.4 to 1.8, respectively) were tested in order to determine the optimum concentration for sodium sulphide addition in leach solution aiming at lead removal. Also, weight ratios of sodium sulphide with respect to zinc in the range of 1 to 3 (molar ratios approximately 0.3 to 0.9, respectively) were tested in the same solutions to promote zinc precipitation.

3 RESULTS AND DISCUSSIONS

3.1 EAF Dust Characterization

The chemical composition of electric-arc furnace dust depends on the quality of steel scrap processed, the type of steel being produced, technological and operating conditions and the degree of return of the dust into the process. Reference data [8-11, 13-16] indicate that the elements in EAF dust vary in concentration: Fe 10-45%, Zn 2-46%, Cr 0.2-11%, Cd 0.01-0.3%, Mn 1-5%, Cu < 3%, Si 1-5%, Ca 1-25%, Mg 1-12%, Al 0.1-1.5%, C 0.11-2.36%, S 1.5 -2.5%, Na 0.5-1.8% and K 0.35-2.3%

Table 1 shows the average elements concentration found in the eight analyzed EAF dust samples from Siderúrgica Rio-Grandense. Instead of being present in EAF dust, carbon, oxygen and chlorine were not possible to detect by Atomic Absorption Spectrophotometry.

X-Ray Diffraction analysis, Figure 1, showed that the two predominant phases are zincite (ZnO) and zinc ferrite ($ZnO.Fe_2O_3$) spinel. Considering only the mineralogical phases observed by this technique, approximately 60% of EAF dust is composed by zinc ferrite ($ZnO.Fe_2O_3$) spinel and about 25% as zinc oxide (ZnO) form. According Donald and Pickles [2] and Pelino *et al.* [17], the element iron was mainly found as magnetite ($FeO.Fe_2O_3$) in the majority of EAF dusts. However the signals attributed to magnetite probably were overlapped by signals assigned to the zinc ferrite mineralogical phase in Figure 1. The same observation was reported by Machado *et al.* [18]. Also, solid solutions of magnetite, zinc ferrite and zincite may be present as well as ferrite (Fe_2O_3) and some metallic iron.

There is also a substantial amount of salt like sylvite (KCl) together with NaCl and some carbon (coke) that could be detected. Other metal phase forms were not possible to identify in average samples due to their low concentration, which lies below the susceptibility limit of this method. As reported by Donald and Pickles [2], lead is present in low concentration and occurs mainly as an oxide but some lead sulphate and lead chloride may also be present. Lead oxide, like zinc oxide, tends to be present in small discrete particles or as smaller regions within a larger particle.

According to particles' diameter distribution analysis, the grain size of the EAF dust samples varies from 0.1 to around 170 μm. The individual particles were generally spherical and very often in aggregate forms. Also, approximately 90% of the particles were smaller than 100 μm, 40% of were smaller than 10 μm and 10% of the particles were smaller than 1.7 μm. Nyirenda [19] found that the EAF dust particles are generally less than 10 μm in size, while the majority of the particles are less than 1 μm. Some of the particles are less than one-tenth of a micron and the fine particles readily agglomerate. Thus, elements physical separation methods exhibit poor recoveries because of the extremely small particle sizes.

Table 1: Quantitative Analysis of EAF dust from Siderúrgica Rio-Grandense.

Element	Concentration / weight %
Aluminum	0.0002
Calcium	0.0039
Cadmium	0.05
Chromium	0.0298
Cooper	n.d.
Iron	21.00
Lead	1.00
Magnesium	0.0014
Manganese	1.49
Molybdenum	n.d.
Nickel	1.06
Potassium	0.0017
Siliceous	0.021
Sodium	0.0042
Tin	0.151
Zinc	23.00
Sulphur	0.83

n.d. – non-detected

3.2 Lead and Zinc Chemical Precipitation from EAF Dust Leach Solution

Precipitants like sodium phosphate, sodium sulphate and sodium carbonate in a concentration range of 0.01 to 0.05 mol L^{-1} showed no efficiency in selective precipitation of lead from alkaline leach solution. Nevertheless, using only 0.01 mol L^{-1} of sodium sulphide as precipitant agent almost 70% (weight basis) of lead was precipitated from leach solution even at 25ºC. Thus, sodium sulphide was selected as the precipitant in the following experiments.

According to Youcai and Stanforth [9], precipitates could not form when precipitants like sodium phosphate, sodium sulphate and sodium carbonate were added into the alkaline solution containing Zn and Pb since lead sulphate, lead and zinc phosphates, lead and zinc carbonates, which were insoluble in neutral medium, were soluble in the strong alkaline solution.

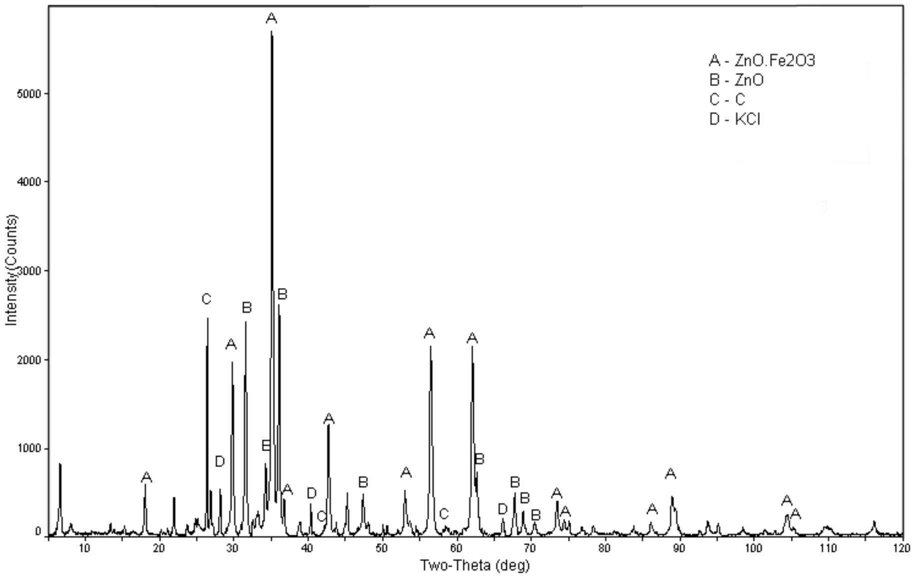

Figure 1: XRD pattern of EAF dust.

3.2.1 Precipitation of Lead from Leach Solution

Figure 2 shows the removal percentage of lead from the leach solution as function of the weight ratio sodium sulphide/lead. Weight ratios of sodium sulphide with respect to lead from 1.7 to 1.9 ensure the selective separation of all lead from the alkaline zinc solution without concomitant loss of zinc.

Lead precipitates may be composed by a mixture of lead sulphide and much less sodium-lead disulphide, according to Youcai and Stanforth [9]. Other possible elements present in the strong alkaline solution include Cu, Al, and Cr(III). The element Cu (100 wt. %) can be easily extracted together with lead. However, Al and Cr(III) could not be removed with sulphide because these two elements are unstable in the solutions. Hence, the separation of Al and Cr(III) from Zn in alkaline solutions should be carried out by other processes after lead has been removed.

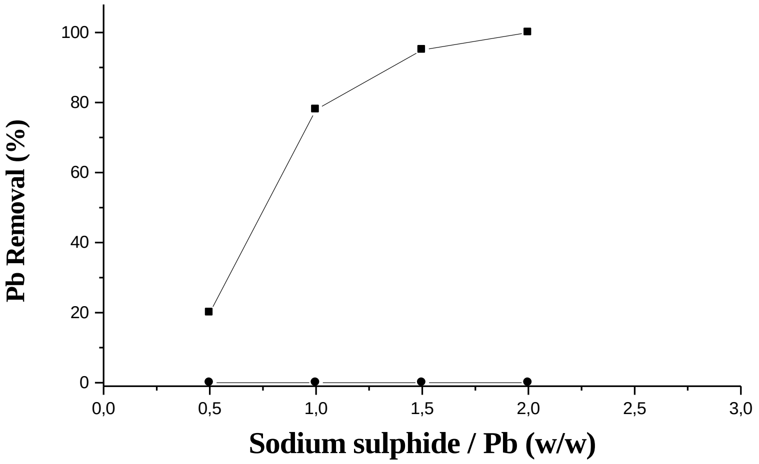

Figure 2: Removal of lead from leaching solution of EAF dust by addition of sodium sulphide. Leaching solution composition: 50 g L^{-1} of zinc, 2 g L^{-1} of lead, 1 g L^{-1} of Al and 0.05 g L^{-1} of Fe.

3.2.2 Precipitation of Zinc from Lead-Free Leach Solution

After lead precipitation from the leach solution, 100% (weight basis) of zinc can be precipitated using weight ratios of sodium sulphide with respect to zinc higher than 2.6–2.7 (molar ratios approximately 0.7–0.8), as shown in Figure 3.

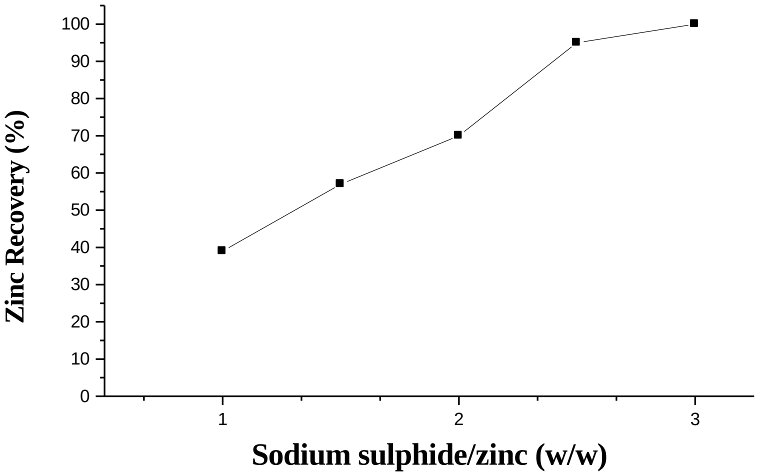

Figure 3: Recovery and precipitation of zinc from Pb-depleted alkaline leach solution by addition of sodium sulphide.

According to Youcai and Stanforth [9], after washing thoroughly the precipitates of lead and zinc, their composition are the simplest forms: PbS and ZnS, respectively.

4 CONCLUSION

The chemical and mineralogical characterization of the EAF dust showed that the dust is composed essentially of Zn and Fe. Approximately 60% of EAF dust is composed by zinc in a zinc ferrite ($ZnO.Fe_2O_3$) spinel. The Zn remainder, about 25% of the dust, occurs as zinc oxide (ZnO) form. Lead, another heavy metal, is also present in the dust. Many other elements are present in very low concentrations, making the EAF dust a waste of complex composition. Thus, EAF dust is properly considered as hazardous waste.

Almost 100% of zinc and 80% of lead could be extracted from EAF dust employing an integrated hydrometallurgical process composed by leaching the hydrolyzed and fused EAF dust in a strong alkaline solution. Sodium sulphide was then successfully used as precipitant agent. Lead could be removed selectively from alkaline leach solutions when the weight ratios of added sodium sulphide to lead were kept at around 2.0, while the zinc remained in the solution. Lead can be further used in foundry industries. Zinc could be successfully precipitated from lead-free alkaline leach solutions using a weight ratio of sodium sulphide to zinc of around 3.0. Thus, an effective process of zinc and lead removal from alkaline leach EAF dust solutions was developed.

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