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Review Article

EAF dust: An overview on the influences of physical, chemical and mineral features in its recycling and waste incorporation routes



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ABSTRACT

Electric-arc furnace dust (EAFD) is one of the several process residues generated in mini mills during steel production. The presence of valuable zinc in EAF dust and the rising costs for waste disposal are the motivating factors for EAFD recycling or its incorporation into other materials. Features such as small particle size, high zinc content and the existence of the decomposition-resistant mineral franklinite have long influenced both positively and negatively EAF dust processing. More recently, the growing presence of deleterious chlorine, lead and chromium is affecting equally the traditional as well as the new recycling routes or waste incorporation processes in a decisive way. In this study, a critical overview on the fundamentals of pyrometallurgical and hydrometallurgical EAF dust recycling or incorporation processes is presented, as a starting point for the understanding of how the EAF dust processing routes are influenced by all cited factors. Especially important is the discussion on the influences of the dust composition – including the effects of the deleterious elements – which can point out some relevant issues that ought to be considered for a successful ending to old and new dust processing proposals.

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1. Introduction

The steel production technology used by most semi-integrated mills or mini-mills includes an electric melting shop, which employs an electric-arc furnace, EAF, as scrap melting equipment. During EAF operation, electric-arc furnace dust, EAFD, is generated as a result of the vaporization of molten iron with nonferrous metals, CO bursting bubbles and the ejection and dragging of particles from the metal bath, slag and other materials in the oven [1]. A basic characteristic of the EAF is precisely the presence of an electric-arc, which exhibits a very high temperature and is placed in an environment exposed to gases – vaporization (and oxidation) of a small metal fraction and the convection of the oven atmosphere can be related to these factors. The EAF dust newly formed, in the form of fine particulates, is carried away from the oven along with gases from the melting and refining of the furnace load, plus air admitted to post-combustion and cooling steps of the exhaust gas. At the end of the pipeline EAFD is usually collected in a dry dedusting fabric filter system commonly known as baghouse.

The exact composition of EAFD depends on the scrap and other process input materials; in principle, EAF dust would consist of iron oxides; however, in view of the presence of different scrap types, containing a range of elements, its composition becomes quite complex. Dust formation mechanisms also interfere in the mineral speciation, in addition to plant specific parameters. Thus, EAFD is actually the end result of a series of physical and chemical phenomena by which the substances giving rise to the EAF dust pass. These phenomena, which initiate inside the oven, and take place through different environments along the gas path, define its physical aspect, and its chemical and mineral composition. As expected, major components of EAFD are solid iron oxides – but also zinc can be present in great amount; Fe is mostly found as magnetite (Fe_3O_4) and in franklinite (ZnFe_2O_4); Zn (from galvanized parts) is contained in zincite (ZnO) and franklinite [2]; several other elements are found in EAFD.

According to Nyirenda [2], the composition of the dust can be widely variable and may change not only from one day to another, but also from heat to heat of the same steel

shop. Pickles [3] cites the presence of calcium (as the third metallic element in larger quantities in EAFD) and numerous other atomic species in lower concentrations, such as chlorine, lead, silicon, aluminum, manganese, chromium, magnesium, nickel, copper and cadmium. Element concentrations may undergo changes mainly due to variations in the scrap quality and amount charged in the electric-arc furnace. Most of these elements appear combined with oxygen. Chlorine forms preferably into chlorides; additionally there are also fluorides, sulphates and sulphides. The presence of heavy metals like lead and cadmium can pose threats to the environment and human health, therefore this waste is considered officially hazardous in many countries [4,5].

In recent years there has been an increase in the chlorine level due to the increase of Cl-containing impurities in scrap metal (namely rubbers, paints, polymers, etc.). Through the thermal destruction of these impurities by the heat from electric-arc, part of chlorine is transferred to the EAFD, forming alkaline metal chlorides – and part goes to the exhaust emissions, mostly in the form of simple gaseous compounds: HCl and Cl_2 . Volatile Organic Compounds, VOCs, are also formed and a small amount of chlorine can generate dioxins and furans [6]. For this reason, chlorine is often the most abundant element in the EAFD after iron, zinc and oxygen. Levels of around 5% by weight of chlorine in EAF dust on average have been reported [7]. Chlorine behavior is especially significant and deserves analysis – as chlorides are impurities that may interfere markedly in recycling (both pyrometallurgical and hydrometallurgical) as well as in waste incorporation processes.

The generated amount of EAFD is about 1–2 wt.% of mill production – which may be a significant amount, depending on mill size; consequently, next to composition, quantity may also play a major role in dust processing.

Once collected, it is necessary to give EAFD a destination. Three main choices are possible: (i) disposal in industrial waste landfills, (ii) recycling/incorporation into other processes/products and, finally, (iii) return to the steel production process.

Considering the first of these alternatives, because of its dangerous nature, EAFD must be buried in special, more secure landfills. However, costs have risen in recent years, both for reasons of greater requirements and control of disposal sites, as well as logistics services. Regarding recycling/incorporation, it can be said that is not a simple task in practical terms, taking into consideration the physical properties, chemical and mineral composition of EAFD. Even the return of this waste to the steel production process, as practiced in some plants, has limitations and operational difficulties [8–11], requiring investments and high process control levels for its implementation.

These difficulties have encouraged the development and implementation of innovative solutions to cope with this waste. Among these, there are studies that suggest the separation of dust during the steelmaking process (in process) basically into two fractions: one rich in zinc and another rich in iron [12,13]. As a side effect, these efforts are also meeting the improvement of sustainability indicators for steelmaking processes [14]. Nevertheless, aspects related to the physical properties, chemical composition and mineral content of the

EAFD present challenges to be overcome for the technical and commercial feasibility of new and old destination proposals.

These assumptions justify an analysis on the influence exerted by the physical characteristics, and the chemical and mineral composition of EAFD in recycling processes or incorporation into other materials. Some reviews of EAFD treatment processes have already been conducted [2,15,16], yet, have focused mainly on process description, without fully considering the principles and merits of each technique. Consequently, in this study, based on information derived from various sources, some available in the literature, others coming from operational practice, an analysis of several issues related to the essentials of pyrometallurgical and hydrometallurgical EAF dust treatment processes will be undertaken. Furthermore, whenever possible, some guidance will be provided on aspects that deserve consideration in these processes; issues related to the electrolytic zinc recovery step from sulphate solutions, common in many processes, will be also discussed.

2. EAF dust processing

2.1. Preliminary evaluation of processes

The research and development of processes for treating steel-making dust has existed for a long time and, as a result, a number of processing proposals both hydrometallurgical and pyrometallurgical – or even mixed – have been presented to the steelmaking community. Solutions such as the incorporation of EAFD into other materials, both at room and high temperatures, have been proposed. Nevertheless, only pyrometallurgical processes (high temperature metals recovery, HTMR) have achieved greater commercial exit, most of them variations of the Waelz process [3].

Main attractions – considering the several treating options for the EAF dust recycling – are the levels of iron and zinc, which together reach a value between 50 and 60% [17]. Nevertheless, in most cases, zinc recovery is the main motivation – the value associated with the recovery of this metal contributes significantly to the economic viability of the activity.

In a preliminary evaluation, certain *minimum requirements* must be met for a treating process to succeed – avoiding discontinuities or later reformulation needs, which include:

- (a) an ability to support (within a predetermined range of acceptance) a varying composition and physical presentation of the EAF dust being processed; in addition to zinc content, it is important to observe the presence of elements which are harmful to the recycling or incorporation processes under assessment, especially chlorine levels and metals such as lead, chromium and cadmium (including consideration of human health and environmental issues);
- (b) possession of a clear delimitation in mass and energy streams, in order to enable the assessment of viability in a broad sense, including the economy, logistics and product destination – among other factors;

- (c) consideration of investments required to meet the environmental aspects of the proposal (emission control and generation of waste and effluents);
- (d) economic competitiveness and/or sustainability over other alternatives offered by the market.

Within this context, focusing on recycling, Southwick [18] reports that in the US in the past 22 years most new EAFD recycling processes were unsuccessful, leaving older reliable technologies in operation, such as the Waelz process. Economic reasons and inadequate attention to technical details, beyond deficiencies and lack of previous studies for tuning processes were also cited to explain failure. For this reason, EAFD processing is not considered an easy task; several factors exert significant influence on the viability of proposals, among which are physical characteristics, the chemical and mineral composition – as will be seen in sequence.

2.2. Influence of main EAFD characteristics on processing

Some of the physical, chemical and mineralogical characteristics of importance to be considered in EAFD recycling processes or incorporation into other materials are presented here, as follows:

- (a) *Particle size and bulk density*: The majority of the particles is smaller than 10 μm and the bulk density of EAFD is between 1.1 and 2.5 g/cm^3 [2]. A low particle size requires in many cases agglomeration (as pellets or briquettes) prior to recycling in pyrometallurgical processes, mainly to avoid pneumatic dispersion. In hydrometallurgical processes, it makes the solid–liquid separation difficult, causing the retention of a large amount of process solution in the dust.
- (b) *Zinc content*: The presence of zinc is the main reason for EAF dust recycling; therefore the amount of this metal has an important influence on the economic process viability.
- (c) *Mineral zinc speciation*: Almost all zinc in the dust appears in the mineral species franklinite (Fe_2ZnO_4) and zincite (ZnO). This speciation has significant influence, especially for hydrometallurgical processes. Zincite reacts more easily to the leaching solutions. Franklinite, in turn, is a more stable oxide and requires more drastic thermodynamic conditions for its decomposition.
- (d) *Halide content*: Most halides are present as sodium and potassium chlorides; depending on the content and the process, halides can exert their deleterious influence to a greater or lesser extent.
- (e) *Presence of other metals*: Metals such as Pb, Cd, Cr, Ni and Cu, occur in EAFD in varying levels and often require preliminary steps for their separation, prior to zinc recovery, mostly in hydrometallurgical processes, due to technical reasons; this is not yet a current practice in waste incorporation, until an environmental regulation enforces it. Metals such as copper can contaminate the iron recovered from dust – this holds especially for pyrometallurgical processes, where iron recovery occurs in parallel with that of zinc.

2.3. EAF dust and the pyrometallurgical recycling processes

In general, in pyrometallurgical processes for EAFD recycling, the Zn and Pb compounds react with carbon monoxide (CO) coming from a reducing agent (usually a carbonaceous material such as coal or coke) under appropriate thermodynamic conditions [19].



Alternative processes, tested at least in pilot plant scale, use dissolved carbon in the iron metal bath as a reducing agent as, for instance, the process 2sDR [10] and in highly mixed bath reactors UNO and DUO [20]. The reduction of main metal oxides present in the dust is enabled; iron – among other elements – incorporates into the bath while zinc (as well as Pb) volatilizes and is recovered as oxide. In these cases, according to Colbert and Irons [21], the dominant reaction mechanism is the reduction of zinc oxide by dissolved carbon.



The Waelz process, working under stoichiometric reaction (1), is the most used worldwide, representing more than 80% of installed capacity [22]. The Waelz furnace charge consists mainly of pellets made with EAF Dust plus a reducing agent (coke) and additions like CaO or SiO₂ – depending on operation mode (acid or basic) [23].

Processes based on the Waelz technology aim to selectively reduce most nonferrous metals oxides existing in the EAFD, mainly zinc and lead. Even though Fe is nobler and more plentiful than Zn, in practice, a small portion of iron oxides tends to reduce. To keep iron in the oxidized form, according to Sinclair [19], it is necessary to operate under suitable thermodynamic conditions. This trend (for prior reduction of iron oxides) can be reversed at higher temperatures and/or appropriate iron oxide content (activity) in the slags; the FeO activity in slags can be controlled by their composition.

Temperatures higher than approximately 1300 °C are not suitable for the process, because, in addition to the energy expended, they keep operators watchful of possible excessive shell formations (rings composed of material with low softening point), which ultimately reduce the oven working section, causing unscheduled stops. In this aspect, the basicity index (%CaO + %MgO)/%SiO₂ exerts a substantial influence, as accretions are prone to form at a slag basicity of about 1 [24]. Through careful control of the iron oxide concentration, basicity and the amount of reducing agent, the lower temperature limit can be reduced to a more favorable zone, close to 1200 °C.

During the Waelz process, after the reduction step, gaseous zinc (and lead) passes from the load into oven heating atmosphere. In this process, oxygen-avid zinc cannot be retrieved in the metallic form. In the gas space, due to excess air injected from the kiln end, an oxidizing atmosphere is formed and new thermodynamic equilibria take place, causing zinc re-oxidation. With this technology, due to the joint combustion of carbon (coke, coke fines, anthracite coal) with other fuels, to provide the heating load and the necessary energy to reduction reactions, the zinc content in the gas phase is usually

diluted and there is a high concentration of CO₂, H₂O and N₂ in the gaseous stream flowing through the equipment.

The remaining material, containing iron oxides, residual zinc oxides and other compounds originated from EAFD and process additions is known as ‘slag’ or ‘Waelz clinker’; the fraction of Zn in slags reflects rather an economic (and processing) condition than a thermodynamic impossibility. In other processes, such as Primus and electric smelting reduction furnace (ESRF) technologies [7], besides zinc and lead, iron is also recovered (with characteristics similar to those of pig iron).

In environmental terms, despite its commercial success, the Waelz process generates a significant amount of waste. In Spain, *e.g.*, about 56% of the EAFD processed will leave the Waelz kiln in countercurrent as a residual material which needs proper environmental disposal [25]. Furthermore, dioxin (favored by the presence of chlorine in raw materials) is generated in the process and the dust-free off-gas needs proper treatment. Once again, here the basicity index exerts a notable influence; under basic conditions (basicity between 1.5 and 4), the dioxin formation drops significantly [24].

In general, during the operation of pyrometallurgical processes, an energy surplus exists and therefore there is no significant influence of zinc carrying mineral species (zincite or franklinite) on the process – which is a considerable advantage.

Together with the metals zinc and lead, chlorides (of sodium and potassium) and fluorides vaporize in pyrometallurgical processes; consequently, for instance, when crude zinc oxide is produced it contains most of the zinc, lead and halides from the furnace load, along with minor amounts of other materials pneumatically conveyed from the furnace. According to Nakayama [7], the excess chlorides in EAFD have also given rise to problems in the condensation sector of zinc oxide in some installations. Due to the relatively low melting temperatures of sodium and potassium chlorides (~800 °C), these substances can melt and adhere to the walls of the equipment during the cooling step, upsetting the collection of ZnO. Because of this, processes that operate at higher temperatures, like the electric smelting reduction furnace (ESRF) process, are provided with special cooling systems which can minimize this problem and, as a result, crude oxide with higher zinc content is produced. In processes where liquid zinc is produced (plasma processes), condensed halides can cause troubles when found in an excessive amounts [26].

The chlorides and fluorides accumulated in crude zinc oxide must be previously removed before processing for the electrolytic recovery of zinc. This operation is usually effected by alkaline leaching where the soluble salts, mainly composed of sodium and potassium chlorides, and sodium sulphate are removed [27]. These salts can either be recovered in the solid form as may follow (dissolved) with the effluent, for proper treatment.

A pyrometallurgical practice – best understood as a process of treatment rather than a typical recycling process – is the reintroduction of the EAFD into EAF. This procedure aims to reduce the overall amount of dust from the steel shop. Iron originally in the EAF dust – depending on the thermodynamic and kinetic conditions directly linked to the technique used – will distribute itself between the slag and the metal bath,

and part may leave the furnace with the (new) dust from the process. Techniques used for the reintroduction of this material into the EAF may include: (i) *in natura*, injected (with or without reducing agent) through a lance in the slag or molten bath [8,21], or, in containers (bags) together with the load; (ii) as agglomerate (with or without a reducing agent) in the form of pellets or briquettes [28,29]. Zinc, lead and halides tend to accumulate in the 'new' dust being formed, increasing the content of these metals in this stream. This can be seen as a secondary objective for this procedure: improve dust value – in relation to zinc recycling. Nevertheless, some adverse factors associated with this practice include: increased energy consumption; increased chloride content in the newly formed dust, possible deterioration of steel quality, limited zinc enrichment and risk of saturation of the dedusting system by pneumatic conveying of reinjected dust [8,12,29].

In summary, considering the composition of the EAF dust, recycling by pyrometallurgical processes generally shows the following characteristics:

- (a) ability to withstand a wide variation in raw material (EAFD) composition – yet there is a minimum economic content in zinc. On the other hand, the mineral species in which this metal is present – Zincite or Franklinitite – is of no great importance, since in these processes the suitable thermodynamic conditions to reduce such mineral species are easily achieved;
- (b) ability to withstand the presence of chlorides, provided that it is not excessive, although concerning this aspect some processes show more sensitivity than others;
- (c) requirement of greater investment, given that most of them use sophisticated reactors and operate at scale to achieve economic viability;
- (d) pyrometallurgical processes, alone, cannot recover some metals present in EAFD such as copper and nickel economically; thus, they are left with process residues – e.g. in the Waelz process, these metals remain in slags;
- (e) iron present in the EAFD acts as a 'sink' for copper and nickel, turning the use of this metallic product improper for the production of certain steel types (pig iron does not contain these metals because of iron ore purity) – in the case of Fe recovery;
- (f) due to its small particle size, there is a real possibility for EAFD pneumatic dispersion in many of the pyrometallurgical processes. For this reason, a preliminary stage of agglomeration is required (e.g. pelletizing in the Waelz process) – which also serves as an opportunity to adjust the charge composition by the blending of raw materials;
- (g) despite representing the majority of the installed capacity, the Waelz process has some handicaps: it does not recover all zinc carried by EAFD, and may require frequent maintenance downtime – due to the tendency of ring formation by the incipient melting of slags (this material tends to adhere to the inner walls of the characteristic tubular furnace of the process).
- (h) due to the presence of chlorine, carbon and oxygen at high temperatures, pyrometallurgical processes require extra care on exhaust gas cleaning because of the possible formation of PCDD/F during the cooling step.

2.4. EAF dust and the hydrometallurgical recycling processes

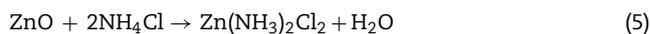
The EAFD hydrometallurgical recycling processes have the dust recycling on or near the point of generation as a major motivating factor [30]. This attribute goes back to various hydrometallurgical techniques that have the potential to operate on a smaller scale, suppressing EAFD agglomeration in most cases, which results in lower transportation costs and investment. These processes are designed to seek selective zinc dissolution from EAFD (leaching); the literature shows a large number of technological proposals which work under the action of a specific chemical compound on EAFD in aqueous medium – usually acidic or basic. Their main objective is to produce an aqueous zinc ion; in the case of acid media:



or, in basic media, because of the amphoteric behavior of zinc, a zincate ion is produced [31]:



In some cases the dissolution of zincite is more complex, like in the Ezinex process, which uses ammonium chloride as leaching agent [32]:



In many hydrometallurgical processes the main objective is to obtain a zinc rich solution with sufficient purity for further processing, for recovering either pure metal (HGI) or compounds – such as an oxide or sulphate. However, zinc is the minor component in an EAFD 'matrix' which is composed mainly of iron oxides subject to dissolve with the zinc in acidic media. In the case of using dilute sulphuric acid solutions as a leaching agent, it is possible to reduce the rate of iron dissolved significantly, by controlling the acid concentration and temperature [33]. In basic media, iron oxides are relatively insoluble and the major part of them remains in leach residue [31]. In both techniques (acid and basic), additional purification steps of 'pregnant solutions' are needed before final processing. In the case of dissolved iron, selective precipitation of jarosite type minerals can be undertaken [34]. For purification purposes, solvent extraction (SOX) can also be used to prepare zinc salts solutions with suitable purity [35].

Unlike pyrometallurgical processes, depending on the technology used, there is the possibility of recovering copper and other metals (usually as cements) originally present in EAF dust in hydrometallurgical processes; this is usually performed in a preparatory step, prior to zinc electrowinning.

Despite the various alternatives for the hydrometallurgical route, some difficulties are common to all of them. The most important refers to the relative inability to cope with the diversity of EAFD composition, both mineralogically and chemically [18]. The occurrence of mineral zincite in EAFD is favored by high zinc content [2]. The mineral species zincite is appropriate for hydrometallurgical processing because ZnO is easily dissolved both at acidic and basic solutions, and can also be complexed with other substances such as ammonium salts.

However, zincite is generally found in lower concentrations than Franklinite. In this context, based on theoretical thermodynamic studies, the phase zincite is present in a dust under $p_{O_2} = 0.21$ [atm] with a zinc content ($Zn/(Zn + Fe)$) higher than 37 wt.% [36].

On the other hand, franklinite (Fe_2ZnO_4) is more stable, requiring harsher conditions for the release of zinc. Therefore, in the case of implementation of a hydrometallurgical process, a previous pyrometallurgical preprocessing, to increase the zinc content in the EAFD, may be interesting. This zinc enrichment may, for example, be effected with the recirculation of dust in the electric arc furnace. Yet, there are cases where EAF dust is processed directly, by establishing a preliminary pyrometallurgical stage within the hydrometallurgical process, with the sole purpose of decomposing franklinite. This is the case, in the processing of EAFD in basic medium proposed by Xia and Pickles [31].

Another point of relevance in hydrometallurgical processing is the chloride content in EAFD, which interferes with the electrolytic zinc recovery processes. Thus, processes based on technologies which are not designed to make use of chlorine-containing compounds (HCl, NH_4Cl , etc.) as leaching agents, require a preliminary stage for removal of soluble chlorides. This situation is found in the electrolysis of zinc sulphate solutions – which is the final common step in many processes, both pyrometallurgical and hydrometallurgical. In this process, lead anodes and aluminum cathodes are commonly used. Sinclair [19] reports that when chloride ion is present in concentrations in the range of 400 mg/L or greater, it causes corrosion and chlorine gas generation at the anode, damaging the working environment and impurifying the electrolytic solutions. Thus, low concentrations of chlorides in the zinc sulphate solutions – in the range of 50–100 mg/L – are required [37].

To overcome this problem, processes specifically designed to deal with chlorine chemistry were developed, such as Ezinex, which is in operation and uses ammonium chloride solution to dissolve zincite. In this process, the aqueous solution of cations, after purification to remove lead, copper and cadmium, is electrolyzed. As the conditions are very harsh, with chlorine generation (at the anode), the anode is made of graphite and the cathode of titanium. Another solution to the chlorides problem is the separation of impurities from zinc sulphate solution (chlorides, and metals such as copper and cadmium) using specific organic solvents – as in the Zincex process [37]. A very pure zinc sulphate solution remains for metal electrolysis.

For these reasons, considering the composition and physical properties of steel mill dust, and hydrometallurgical processing possibilities, the following features should be taken into account:

- (a) EAFD zinc leaching faces the fact that this waste has a 'matrix' composed mainly of iron oxides;
- (b) EAFD has a very low particle size; while it favors Zn leaching, it was a tendency to retain large quantities of liquid by capillarity. This fact gives rise to the use of a large amount of water (or aqueous process solution) to assist the process

and promote the washing of waste material, which causes loss of reagents and produces large volumes of wastewater to be treated – in addition to requiring more complex equipment with larger dimensions for the proper EAFD processing;

- (c) EAFD recycling by hydrometallurgical processes produces waste with high moisture content; it is difficult and expensive to dry up to the appropriate levels for various final destinations (return to the steelmaking process, co-processing, disposal in landfills, etc.);
- (d) in hydrometallurgical processes there is a significant influence of mineral species bearing zinc in EAFD, zincite being the most favorable;
- (e) the presence of chlorides in steelmaking dust affects deleteriously the zinc electrowinning process; to solve this problem, there is a need for a preliminary aqueous leaching of EAFD to reduce the chloride content to within tolerance levels. Alternatively, the processes may be based on chlorine compounds chemistry (e.g. NH_4Cl); or, zinc purified solutions, free from contaminants, may be produced with the aid of organic solvents (SOX);
- (f) hydrometallurgical processes have the possibility to recover other metals commonly found in EAFD, for example, copper, nickel, silver, etc.; and, consequently, can generate an iron oxide residue having lower content in metal contaminants;
- (g) hydrometallurgical processes require careful management of water, wastewater and process solutions to their technical and economic feasibility, which is often a side project to the main goal of EAFD recycling [38];
- (h) these processes, depending on their goals and constraints, are likely to be designed for smaller production scales and can be located close to steel plants.

2.5. Incorporation of EAFD into other materials

Considering all possible final EAFD destinations, in addition to recycling processes, there is the possibility for incorporation of this waste into other products or materials. The aim of these initiatives is not only to utilize the dust as raw material, but also inhibit the action of harmful elements to the environment by their confinement.

Among the proposals, the incorporation into ceramic products (bricks) [39,40] and cement products [41–43] has received increased attention from researchers for the great demand for products of this nature, having controlled manufacturing and industrial standardization. On the positive side, the low particle size and EAF dust characteristics favor the formation of homogeneous pastes with cement and mixing with clay. However, important aspects related to the dust composition must be considered when this residue is incorporated, both at room (cement and building blocks), and at high temperatures (ceramics, clinker production in cement industry, among others), including:

- (a) The existence of metal oxides as fines favors the merging and the chemical reactions of EAFD with clays; however, the presence of metals such as lead and cadmium acts unfavorably to the incorporation processes in ceramic materials at high temperatures. This is due to the

possibility of reduction and/or volatilization of these metals or their compounds, with the genesis of gaseous emissions during the firing process, with hazardous metal concentration above the limit permitted by law in some countries [44];

- (b) the presence of zinc oxide – zincite – in the dust acts as a retardant in cement setting time when EAFD additions are made to cement pastes [45]; the composition variability of EAFD (ZnO content) hampers product control;
- (c) another favorable effect of EAFD addition to cement is the porosity reduction [41,43]; however, chlorides at high levels can act unfavorably if the EAFD is added to mixes for reinforced concrete, discouraging this practice – the presence of chlorides is one of the major causes of steel reinforcement corrosion [46];
- (d) lead, when present in waste to be coprocessed in clinker kiln, has a tendency to volatilize and accumulate in the residual dust from the process [47] (cement kiln dust, CKD) – a fact that restricts coprocessing to waste with very low Pb content. Zn has not such severe restrictions, however, the real possibility for incorporating the EAFD to the clinker in cement manufacturing (high temperature) faces the fact that EAFD usually contains Pb above tolerance levels [48]; the blending with lower-grade materials can minimize this issue, if available;
- (e) also concerning co-processing, the existing chlorine content in the EAFD is, in most cases, above acceptable limits for alternative raw materials used for the cement industry (0.3–0.5% max [48]). If this option is implemented, it must include a preliminary stage, with appropriate technologies to reduce the chloride content in the EAFD [49–51];
- (f) the wide variability of dust composition, even in the same plant, hinders the effective control of the EAFD incorporation processes in other materials; which implies the need for constant monitoring of EAFD lots, methods employed and manufactured products;
- (g) it is important to evaluate the effective immobilization of contaminant elements (Pb, Cd, Cr) originally present in the dust in finished products. This can be achieved by applying standardized tests provided in technical regulation or standard;
- (h) in view of the nature and the way the products to be manufactured with the addition of EAFD are applied, one should take into account aspects related to their life cycle, as well as their post-lifecycle destinations.

3. Concluding remarks

Based on an analysis of the literature, plus data coming from operational practice methods, it can be concluded that EAFD recycling with a focus on zinc recovery is rather complex and there is a significant influence of the chemical composition and other physical and mineral features.

Pyrometallurgical processes can cope more easily with the broad range of chemical and mineral composition in EAFD, but have a higher implementation cost (because of the needed scale of operation and equipment complexity); they also show limitations in the quality of the recovered iron when this is part of the process goal.

Hydrometallurgical processes, on the other hand, are more versatile when it comes to the recovery of other metals besides zinc, *e.g.* copper; however, they are more affected by the presence of zinc in the mineral species franklinite and by impurities such as chlorides. These processes can generate waste and effluents with high treatment and disposal costs – which frequently prevent their implementation.

With respect to the incorporation of the EAFD in other materials, the presence of elements such as lead, cadmium, zinc compounds and chlorine, may interfere both in processing and in the quality of the products. For this reason, there is a need for constant surveillance both over the process and the products made with the EAFD addition. It may be also interesting to ask: What happens to the product after the end of its life cycle?

Based on the aforementioned statements it can be concluded that recycling or incorporation of EAFD cannot be classified as an easy task, requiring from the project designer a cautious reflection on the many factors that may affect the results, and from operators a careful control over the entire process cycle.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES

- [1] Guézennec A-G, Huber J-C, Patisson F, Sessieq P, Birat J-P, Ablitzer D. Dust formation in electric arc furnace: birth of the particles. *Powder Technol* 2005;157(1–3):2–11.
- [2] Nyirenda RL. The processing of steelmaking flue dust: a review. *Min Eng* 1991;4(7–11):1003–25.
- [3] Pickles CA. Thermodynamic analysis of the selective chlorination of electric arc furnace dust. *J Hazard Mater* 2008;166(2–3):1030–42.
- [4] Brasileira de Normas Técnicas – Resíduos sólidos classificação – NBR 10004. Rio de Janeiro: ABNT-Associação; 2004. p. 71.
- [5] Regulation (EC) no. (1907/2006) – REACH. Available from: <https://osha.europa.eu/en/legislation/directives/regulation-ec-no-1907-2006-of-the-european-parliament-and-of-the-council> [cited 02.07.15].
- [6] Birat J-P, Arion A, Faral M, Baronet F, Marquaire P-M, Rambaud P. Abatement of organic emissions in EAF exhaust flue gas. *La Revue Métall CIT* 2001;98(10):839–54.
- [7] Nakayama M. New EAF dust treatment process – ESRF. Available from: http://www.steelplantech.co.jp/wp-content/uploads/2012/08/201108.EAF_Dust_Treatment_fortlightMetalRecovery.pdf [cited 23.07.13].
- [8] Kashiwaya Y, Tsubone A, Ishii K, Sasamoto H. Thermodynamic analysis on the dust generation from EAF for the recycling of dust. *ISIJ Int* 2004;44(10):1774–9.
- [9] Gudenau HW, Stoesser K, Denecke H, Schemmann V. Environmental aspects and recycling of filter dusts by direct injection or use of agglomerates in shaft furnaces. *ISIJ Int* 2000;40(3):218–23.
- [10] Rosler G, Pichler C, Antrekowitsch J, Wegscheider S. 2sDR: process development of a sustainable way to recycle steel mill dusts in the 21st century. *J Min Met Mater Soc* 2014;66(9):1721–9.

- [11] Besta P, Samolejová A, Janovská K, Lenort R, Haverland J. The effect of harmful elements in production of iron in relation to input and output material balance. *Metalurgija* 2012;51(3):325-8.
- [12] Ma N-Y. On in-process separation of zinc from EAF dust. In: *Proceedings of EPD Congress*. 2011. p. 947-52.
- [13] Suetens T, Van Acker K, Blanpain B, Mishra B, Apelian D. Moving towards better recycling options for electric arc furnace dust. *JOM* 2014;66(7):1119-21.
- [14] Silva MJ. Novo paradigma ambiental. *Rev ABM Metal Mater Min* 2015;71:16-9.
- [15] Moraes CAM, Brehm FA. Estado da arte da reciclagem de pó de aciaria elétrica. In: *Proceedings of the XXXVIII steelmaking seminar – international*. 2007. p. 90-100.
- [16] Doronin IE, Svyazhin AG. Commercial methods of recycling dust from steelmaking. *Metallurgist* 2011;54(9-10): 673-81.
- [17] Buzin PJWK, Heck NC, Vilela ACF. EAFD – a thermodynamic analysis and classification of dust types. In: *Proceedings of the 45th steelmaking seminar – international*. 2014.
- [18] Southwick LM. Still no simple solution to processing EAF dust. *Steel Times International*; 2010. p. 43-5. Available from: www.steeltimesint.com/contentimages/features/EAF_dust_Mar10.pdf [cited 15.07.13].
- [19] Sinclair RJ. *The extractive metallurgy of zinc*. Spectrum Series, vol. 13, 1st ed. Carlton, Victoria: The Australasian Institute of Mining and Metallurgy; 2005.
- [20] Heck NC. Untersuchungen über metallurgische reaktionen unter heftiger badbewegung durch induktives rühren in einem neuen reaktor. Aachen: Verlag Shaker; 1994.
- [21] Colbert D, Irons GA. Upgrading of EAF dust by injection into iron and steel melts. In: *Proceedings of fourth international symposium on recycling of metals and engineered materials*. 2000. p. 281-96.
- [22] Rutten J. Application of the Waelz technology on resource recycling of steel mill dust. Bangkok, Thailand: Encol/SEASI; 2006. Available from: <http://www.valo.res.com/pdf/Leoben2006-EN.pdf> [cited 20.03.13].
- [23] Mager K, Meurer U, Garcia-Egocheaga B, Goicoechea N, Rutten J, Saage W, et al. Recovery of zinc oxide from secondary raw materials; new developments of the Waelz process. In: *Proceedings of fourth international symposium on recycling of metals and engineered materials*. 2000. p. 329-44.
- [24] Mager K, Meurer U, Wirling J. Minimizing dioxin and furan emissions during zinc dust recycle by the Waelz process. *JOM* 2003;55(8):21-5.
- [25] Quijorna N, de Pedro M, Romero M, Andrès A. Characterisation of the sintering behaviour of Waelz slag from electric arc furnace (EAF) dust recycling for use in the clay ceramics industry. *J Environ Manag* 2014;132: 278-86.
- [26] Ye G. Characterisation and removal of halogens in the EAF dust and zinc oxide fume obtained from thermal treatment of EAF dust. In: *Proceedings of fourth international symposium on recycling of metals and engineered materials*. 2000. p. 271-80.
- [27] Penchel AS Jr, Takayama Filho T, Dias MJ, Mello LS. Agregação de valor ao sal misto. In: *Proceedings of the XXV Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa & VIII Meeting of the Southern Hemisphere on Mineral Technology*. 2013.
- [28] Buzin PJWK, Heck NC, Schneider IAH, Tubino RMC, Vilela ACF. Study of carbotermic reduction of self-reducing briquettes of EAF dusts and iron scale for use in electric steelmaking. In: *Proceedings of the 66 (Congresso da ABM)*. 2011. p. 1268-79.
- [29] Lopez FA, Lopez-Delgado A. Enhancement of electric arc furnace dust by recycling to electric arc furnace. *J Environ Eng* 2002;128(12):1169-74.
- [30] Nakamura T, Shibata E, Takasu T, Itou H. Basic consideration on EAF dust treatment using hydrometallurgical processes. *Resour Process* 2008;55(3):144-8.
- [31] Xia DK, Pickles CA. Caustic roasting and leaching of electric arc furnace dust. *Can Metall Q* 1999;38(3):175-86.
- [32] Dutrizac JE, Chen TT. The role of hydrometallurgy in the recycling of zinc, copper and lead. *Acta Metall Slovaca* 1998;1:5-28.
- [33] Havlik T, Souza BV, Bernardes AM, Schneider IAH, Miskufova A. Hydrometallurgical processing of carbon steel EAF dust. *J Hazard Mater* 2006;B135:311-8.
- [34] Tsakiridis PE, Oustadakis P, Katsiapi A, Agatzini-Leonardous S. Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: downstream processing and zinc recovery by electrowinning. *J Hazard Mater* 2010;179:8-14.
- [35] Jha MK, Kumar V, Singh RJ. Review of hydrometallurgical recovery of zinc from industrial wastes. *Resour Conserv Recycl* 2001;33:1-22.
- [36] Buzin PJWK, Vilela ACF, Heck NC. Thermodynamic analysis of EAFD generation using the Fe-O-Zn system. In: *Proceedings of the 68 Congresso da ABM*. 2013. p. 423-35.
- [37] Frias C. Secondary zinc. *International Mining*; 2009. October 28-29. Available from: <http://www.infomine.com/library/publications/docs/InternationalMining/Frias2009.pdf> [cited 18.01.14].
- [38] Vega Viveros R, Peña Correa, Lillo D. European patent specification: EP 1 878 806 B1 alkaline electro-hydrometallurgical process for Zn extraction from electric arc furnace dust; 2013. p. 27. January 9: *Bulletin* 2013/02.
- [39] Vieira CMF, Sanchez R, Monteiro SN, Lalla N, Quaranta N. Recycling of electric arc furnace dust into red ceramic. *J Mater Res Technol* 2013;2(2):88-92.
- [40] Silva MC [PhD thesis] *Fabricação de materiais cerâmicos argilosos: controle das emissões atmosféricas de zinco*. Porto Alegre: Ufrgs – PPGEM; 2006.
- [41] Almutlaq FM [PhD Thesis] *Aspects of the use of electric arc furnace dust in concrete*. Birmingham: University of Birmingham; 2011.
- [42] Vargas AS, Masuero AB, Vilela ACF. Investigations on the use of electric-arc furnace dust (EAFD) in pozzolan-modified Portland cement I (MP) pastes. *Gem Concr Res* 2006;36:1833-4.
- [43] Souza CAC, Machado AT, Lima LRPA, Cardoso RJC. Stabilization of electric-arc furnace dust in concrete. *Mater Res* 2010;13(4):1516-39.
- [44] EUA. United States Environmental Protection Agency (USEPA) – EFD AP-42S11.3 – Emission factor documentation for AP-42; Section 11.3: Brick and structural clay product manufacturing; 1997.
- [45] Brehn FA [PhD thesis] *Adição de óxido de zinco (ZnO) em pastas de cimento visando viabilizar a reciclagem de pós de aciaria elétrica (PAE) na construção civil*. Porto Alegre: Ufrgs – PPGEM; 2004.
- [46] Sales A, Sousa CAC, Almeida FCR, Cunha MPT, Lourenço MZ, Helene P. *Corrosão em estruturas de concreto armado: teoria, controle e métodos de análise*. 1st ed. Rio de Janeiro: Daniel Veras Ribeiro/Elsevier; 2014.
- [47] Barros AM, Tenório JAS, Espinosa DCR. Evaluation of the incorporation ratio of ZnO, PbO and CdO into cement clinker. *J Hazard Mater* 2004;B112:71-8.
- [48] ECO-PROCESSA. Specification table for receiving of alternative fuels (AF) and alternative raw materials (ARM) for

- waste materials co-processing in cement industry; 2012.
- [49] Wei-Sheng C, Yun-Hei S, Min-Shing T, Fang-Chih C. Removal of chlorides from electric arc furnace dust. *J Hazard Mater* 2011;190(1–3):639–44.
- [50] Bruckard WJ, Davey KJ, Rodopoulos T, Woodcock JT, Italiano J. Water leaching and magnetic separation for decreasing the chloride level and upgrading the zinc content of EAF steelmaking baghouse dusts. *Int J Min Process* 2005;75(1–2):1–20.
- [51] Gun Yoo G, Kim GS, Min Jo Y. Separation of chlorides from EAF dust. *J Ind Eng Chem* 2004;10(6):894–8.