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Potential Industrial Synergies in the Steelmaking and Metal-Processing Industry: By-Products Valorization and Associated Technological Processes

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Abstract: Steelmaking and ferrous metal processing companies are suppliers of great importance to a wide array of industries, thus being quintessential for the social and financial growth of regions and countries. Most used processes (i.e., blast furnace, basic oxygen furnace, and electric arc furnace-based) are, however, highly pollutant, generating hazardous wastes that were usually landfilled. Generated wastes are important sources of secondary raw materials such as zinc and iron, presenting interesting market value. Hence, aiming to develop green procedures, industries have been using diverse approaches to treat and detoxify hazardous wastes, extract and reuse added value components, or even use their existing infrastructures to convert the wastes generated by other industries into secondary raw materials for steel manufacturing. This paper reviews the main industrial processes, focusing on the waste-generating steps, and discloses the most recent and relevant industrial synergies toward a circular economy. The final contribution of this study consists of the compilation of industrial synergies and recovery technologies for the steelmaking and metal processes.

Keywords: circular economy; industrial symbiosis; steelmaking by-products; basic oxygen furnace

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1. Introduction

Iron and steel industries are highly demanding regarding materials and energy consumption [1]. Mainly due to the extensive use of coal/coke in blast furnaces (leading to the emission of a significant amount of greenhouse gases, especially CO_2) and the hazardous components and small particle size of electric arc furnace dust, iron and steel production companies significantly contribute to the deterioration of the overall biosphere and global warming [2]. Indeed, steel industries overuse raw materials (e.g., iron ores, scrap, and coal) and are a significant source of persistent contaminants such as heavy metals, hydrofluoric acid, sulfur dioxide, hydrochloric acid, and aromatic hydrocarbons [3].

Iron and steel industries alone are reported to be responsible for 5% of total greenhouse gas emissions (GHG) worldwide [3]. The significant release of CO_2 during blast-furnace-based steel manufacturing arises from the reduction of iron ore using coke, as well as from the decarbonization of dolomite ($MgCO_3$) and limestone [4]. Moreover, the purification of blast furnace gas, cooling of shafts of rollers, and overall dust removal by water spraying lead to an important leaching of cyanides, phenol, sulfur-containing compounds, metals, and ash, among others, in addition to an expressive water loss.

Electric arc furnaces (EAFs), on the other hand, use electromagnetic energy to melt and process charged materials, not requiring the use of coal or limestone. However, fine dust particles rich in heavy metals, such as lead, chromium, and cadmium, are released from EAF (approximately 10–20 kg of electric arc furnace dust is produced for each ton of steel processed) leading to air contamination and significant toxicity to the biosphere [5].

Furthermore, the processing of semi-finished steel products, usually performed by hot rolling, cold rolling, or drawing of steel, also leads to the occurrence of by-products (commonly managed as wastes), intensive energy consumption, and the overuse of disposable oils and emulsions for lubrication and cooling purposes [6].

Therefore, more sustainable technologies have been under development to establish more efficient iron transformation and steelmaking processes. The Organization for Economic Co-operation and Development (OECD) stated, in the iron and steel technology road map, the importance of managing existing assets and near-term investments, in order to create a market for net-zero-emission steel, to develop technologies currently in an early stage, and to accelerate material efficiency [3]. Indeed, recently, steel industries are approaching common production wastes such as blast furnace sludge (BFS) and electric arc furnace dust (EAFD) as sources of secondary raw materials, namely for the extraction of zinc and iron. Moreover, sustainable ways for the removal of toxic elements such as lead and/or arsenic are currently being developed. In addition to slags (by-products resulting from the smelting of iron ores), steel-producing industries have been pushing boundaries to attain sustainability (including zero emissions and zero waste), namely through the establishment of closed-loop processes [7]. With effect, it was reported that the landfilling of steelmaking slags was as low as 14.1% in 2016, with the remainder being used as secondary raw material for construction [8]. It was also reported that, in 2012, Finnish steelmaking companies recycled up to 68% of generated dust, sludges, and scales (and landfilled the remaining 32%), with the increased internal and external recycling of steel-derived residues up to 90%, in 2017 [9].

Nonetheless, developed solutions are still implemented to a small extent, mainly because of the high costs of infrastructure. Moreover, the implementation of new procedures and solutions (mostly based on pyrometallurgical or hydrometallurgical approaches) represents a very significant shift in day-to-day company functions [10,11].

In addition to steel production, metalworking and steel processing industries also seek more sustainable practices. In fact, both hot rolling and cold rolling processes involve the production of significant amounts of wastewater in the form of an oily emulsion [11]. Cold-rolling mill wastewater, particularly, presents a great carbonation potential because of its highly alkaline properties. On the other hand, cold-rolling sludge is a paradigmatic example of a by-product and presents great potential to be considered as a source of secondary raw materials. Depending on the composition of the steel to be processed, a typical discharge of cold-rolling mill effluents usually includes oils, greases, zinc, and iron as major components along with phenol, iron, copper, chromium, nickel, and other trace metals [11,12].

The compilation of industrial synergies is an important strategic tool for companies in the steelmaking and metal processing industry that intends to start and develop circular initiatives. There are various practices of industrial synergies compilations that have been successful in other sectors [13–17].

Regarding the above-mentioned industries, there are various publications that compile some synergies and recovery opportunities that can be developed in the steelmaking and metal processing industry; the vast majority are studies that address a separate opportunity in one of these two industries. Nevertheless, to the best of the author's knowledge, there is no study that compiles the potential industrial synergies for the steelmaking and metal processing industries considering their main processes (blast furnace/basic oxygen, direct reduction, electric arc furnace steelmaking, and metal processing) and the associated recovery technology in each one.

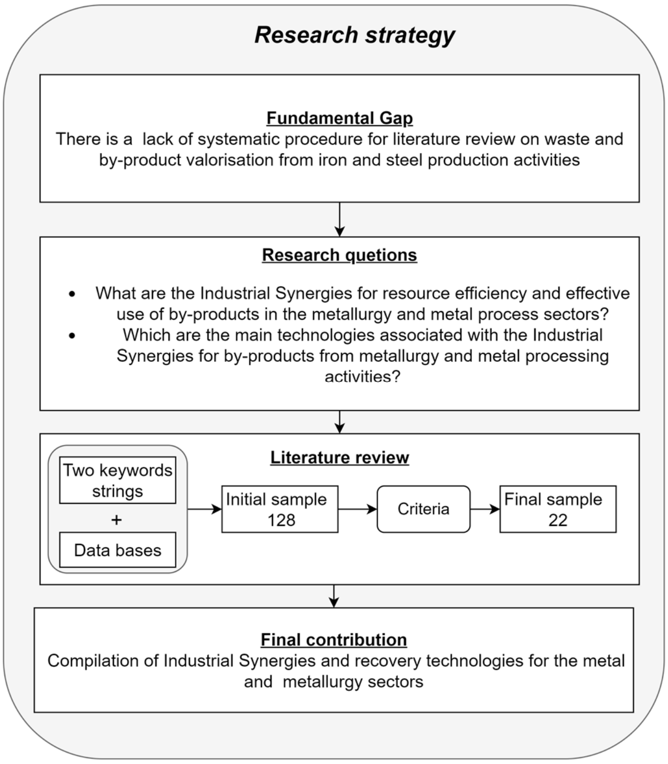
In this sense, this paper aims to advance in the understanding of the pathways to the use of by-products in the steelmaking and metal processing industry by promoting the compilation of industrial synergies and recovery technologies for the steelmaking and metal processing industry.

This paper is structured as follows. Section 1 is an introductory section discussing the context of industrial synergies within the steelmaking and metal processing industry.

Section 2 describes the research strategy followed in this paper. Sections 3–5 typifies blast furnace/basic oxygen, direct reduction and electric arc furnace steelmaking, and metal processing, respectively. Additionally, the route to the industrial synergies and recovery technologies for each one is presented. A critical discussion, conclusions, and future perspectives are presented in Section 6.

2. Research Strategy

In this section, the research strategy followed in this work is presented. The following Figure 1 resumes the research strategy and methodology for this work. In the first stage, this work defines the fundamental gap that is related to the lack of a systematic procedure for a literature review in these research areas (iron and steel production). Afterward, the two research questions that sustain this work are defined. The literature review was performed in the third step of the work. Lastly, the final contribution, the compilation of industrial synergies and recovery technologies, is presented.



There is a lack of systematic procedure for literature review on waste and by-product valorisation from iron and steel production activities

- What are the Industrial Synergies for resource efficiency and effective use of by-products in the metallurgy and metal process sectors?
- Which are the main technologies associated with the Industrial Synergies for by-products from metallurgy and metal processing activities?

Compilation of Industrial Synergies and recovery technologies for the metal and metallurgy sectors

Figure 1. Schematization of the research strategy.

2.1. Gap of Knowledge and Research Questions

Regarding the research gap, the authors identified two main gaps that sustain this research. First, there has been a lack of systematic procedures for a literature review in these research areas. Second, the main aspects addressed by the current literature are related to primary and secondary steel production, while metal processing is largely disregarded. We address these gaps by performing a systematic literature review on the valorization of by-products, including both iron and steel primary and secondary production and the metal processing stages. The following research questions are envisaged:

What are the industrial synergies for resource efficiency and effective use of by-products in the metallurgy and metal processing sectors?
Which are the main technologies associated with the industrial synergies for by-products from metallurgy and metal processing activities?

2.2. Literature Review

The literature review starts by providing a top–down view of the existing literature on waste and by-product valorization from iron and steel metallurgy. In recent years, several reviews have been published on the valorization of wastes and by-products from the iron and steelmaking industries. In this sense, the search was conducted in the search engines Scopus and Google Scholar. The search was developed using two keyword strings: one was related to the iron and steel metallurgic processes, as well as steel processing; the other included terms related to generic terms such as waste and by-product, as well as more specific ones for the types of waste and by-products found in such industries, such as sludges and slags. The following keyword strings were combined (with the operator "AND"):

("steel" OR "bof" OR "blast furnace" OR "rolling" OR "metal process*" OR "pickling")
("waste*" OR "residue*" OR "sludge*" OR "by-product*" OR "slag*").

The search was restrained to find only review articles published in English, without any restrictions on the timeframe. Afterward, the title and abstract were analyzed, and only then the full paper, if applicable. The paper was selected if the following criteria were fulfilled: relevance for the available wastes (i.e., that studied a circular approach for available wastes) (i); suitable yield (>60%) and selectivity for contaminant removal and/or extraction and purification of valuable elements (ii); technical applicability (robust and straightforward processes) (iii); and industry-oriented processes (iv). It is important to highlight that the article reviewed the iron and steel production process.

A total of 22 review articles were analyzed in view of their research scope and aim and the methodology used (keywords, number of collected papers, time horizon of the research, and fulfilment of the criterion). It was found that only one review article provided a systematic literature review with snowballing procedures. For this search, no time horizon was specified. The remaining articles consisted of literature reviews that did not contain any information regarding the methodology used and how the papers were collected and analyzed and the results derived. A total of 128 articles are considered in the initial sample, and 20 articles are scoped toward primary and secondary steelmaking production, which mention blast furnace, basic oxygen furnace, and electric arc furnace processes. Only two articles refer to the metal processing stage, which mentions the hot- and cold-rolling processes, specifically the pickling process and pickling sludge reutilization and/or valorization.

2.3. Final Contribution

The final contribution of this study consists of the compilation of industrial synergies and recovery technologies for the metal and metallurgy sectors, which is based on the by-product, methods/technology, and the type of valorization.

In the upcoming section, a description of the processes of the blast furnace/basic oxygen route (i), direct reduction and electric arc furnace steelmaking (ii), and metal processing (iii) will be addressed. Subsequently, for each of the processes, a segment will be dedicated to addressing their industrial synergies and recovery technologies. Within these segments, a comprehensive discussion of industrial synergies and associated recovery technology will be presented, outlining viable approaches for each process.

3. Blast Furnace/Basic Oxygen Route

Also named the Linz–Donawitz–Verfaheren steelmaking process, the basic oxygen furnace is the most common steelmaking process. A graphical summary of the blast furnace/basic oxygen route of steelmaking is illustrated in Figure 2.

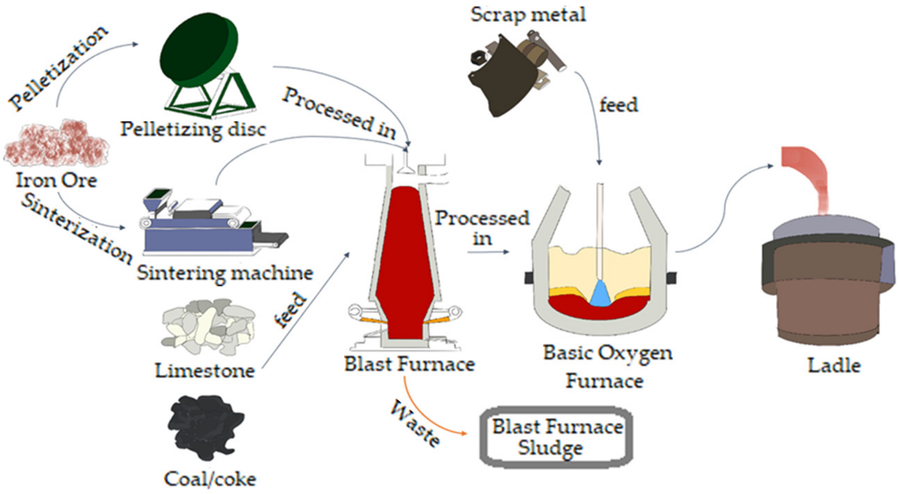


Figure 2. Scheme of blast furnace/basic oxygen route for steelmaking process.

Primary steelmaking usually occurs in three main steps: mining and preparation of raw materials (i), iron production (ii), and steel production (iii). A fourth step, involving casting, rolling, and finishing, may also be performed by some industries. In brief, metal ores are pretreated (if required) and melted in a furnace. A pretreatment step is required if contaminants that can cause physico-chemical quality loss are prevalent in significant quantities in the ore. Examples of relevant contaminants are sulfur, silicon, and phosphorous [18]. Sulfur is usually removed by adding magnesium to the mixture, leading to the formation of magnesium sulfide. Silicon and phosphorous are removed by adding iron oxide and lime as fluxes. Sintering is also a preprocessing method that purifies iron-containing materials of very different purities (e.g., fine ores, downstream by-products such as BFS, BFD, mill scale, and coarse dust, among others) to be finally converted into steel within blast and basic oxygen furnaces [19]. Despite the great diversity of materials that can be sintered, the mixture is prepared using a predesigned blend and requires using additives (e.g., lime). Using sintering as a preprocessing method improves the permeability and reducibility of the iron-rich material.

Afterward, melted metal is poured into a charging isle (hot metal charging step) and further mixed with scrap (if applicable). In addition to the iron-containing material, coke, coal, and a hydrogen source are required within the blast furnace for the reduction of Fe. Then, lime and/or dolomite fluxes are added to the molten metal contained in the charging isle. In the second step, oxygen (99.5% purity) is blown into the mix through water-cooled lances [19]. Molten pig iron and steel scrap are converted into steel by the oxidizing action of blown oxygen. At this moment, the original carbon content (~4%) is reduced to less than 1%, indicating the purification of iron into steel. Vacuum degassing can also be performed, aiming to further improve the quality of the steel. Following this, purified steel is poured into ladles and additives (e.g., Mn, C, Si, and Fe, among others) are supplied to the mixture in accordance with specification requirements. The fourth and final step, slagging, consists of separating the pure iron from the slag. Slag is a glassy material, mainly composed of silicon, magnesium, aluminium, and calcium, and can be removed from the top of molten iron. Slag flocculates and separates from molten iron because of the different densities and melting temperatures. For a comprehensive overview of the blast furnace/basic oxygen furnace route, including its advantages, disadvantages, waste production, and associated quantities, please consult Appendix A and Tables A1 and A2.

3.1. Industrial Synergies and Recovery Technologies-Blast Furnace/Basic Oxygen

In addition to being an intensive energy consumer, the steelmaking industry also generates residues that possess a greatly diverse composition. It has been estimated that only 56% of the material inputs turn into crude steel, with the remaining 44% being converted to residues of different natures [20,21]. Methods based on basic oxygen furnaces generate hazardous gases and semi-solid and solid by-products that are either dispersed into the atmosphere or dispersed/dissolved in water and then landfilled [20,21].

Blast furnace sludges are wastes commonly rich in Fe and Zn but also heavy metals such as Pb, contributing to the high pollutant profile of BFS. Several methods were approached, aiming to convert BFS into sources of secondary raw materials. Rethinking and reusing by-products is being explored for internal utilization and to foster external synergies with various industries. Some examples are summarized in Table 1.

Table 1. Examples of potential industrial synergies from steel-working industries with basic oxygen furnaces.

Material of Interest	Processing Method	Possible Receiving Industries	Uses	Ref.
Iron	Pelletizing	Steelmaking	Secondary iron source (blast furnace feeding)	[22]
Iron	Redox	Steelmaking	Secondary iron source (EAF feeding)	[23]
Iron	Hydroleaching	Methane production	Catalyzation of methane synthesis	[24]
Zinc (acetate)	Hydroleaching	Pharmaceutical	Therapy for Wilson's disease; cicatrisation aiding; other	[25,26]
Zinc	Hydroleaching	Metal processing	Metal galvanizing	[27]
Zinc (stearate)	Hydroleaching	Cosmetics	Anticaking; Cosmetic colorant; Viscosity controlling	[28]

3.1.1. Iron

Iron is the main element to be considered regarding steelmaking and metal processing industries. The OECD has been revising the steel market upward, despite the tensions in the global economic environment (2019), COVID-19 pandemics (2020–2021), and the war in Ukraine (since 2022), indicating the overall stability and increasing necessity of steel to supply a wide array of industries [29]. It is well known that being a commodity, iron is highly dependent on the international political and economic contexts of the moment. Thus, the possibility of using wastes such as BFS as secondary sources of iron might be of extreme importance both for the environment and for business stability and sustainability, also leading to a decrease in dependence on external supply conditions. Blast furnace sludge can be used as a source of iron either by selective extraction (hydrometallurgical route) or by briquetting/pelletizing the sludge to be reintroduced into the blast furnace [22]. A representative scheme of the briquetting/pelletizing process is illustrated in Figure 3.

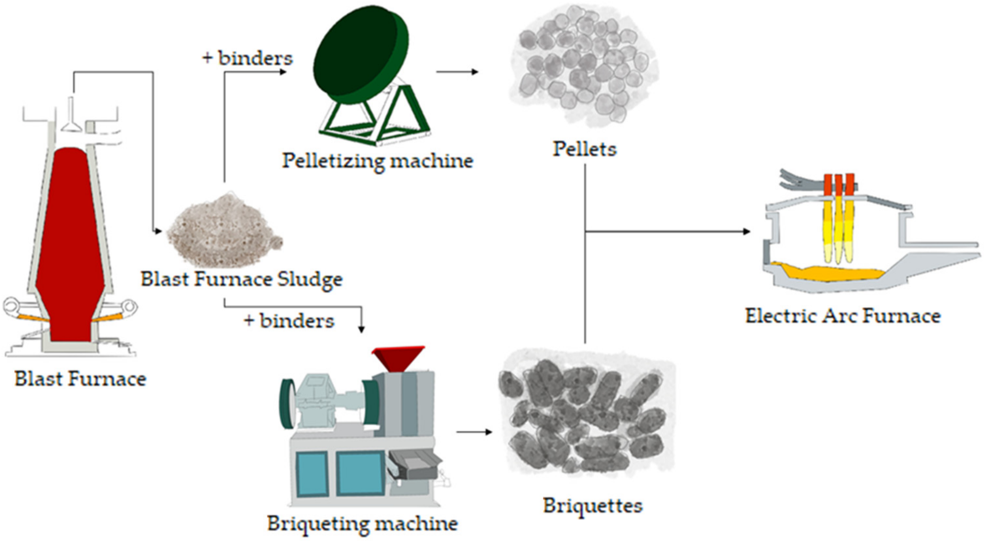


Figure 3. Scheme of the process of extraction and pelletizing/briquetting of BFS to be used as a secondary source of iron, reduceable in an electric arc furnace.

Previous research has demonstrated the direct utilization of BFS as an iron source in blast furnaces through the process of briquetting with a suitable binder [22]. However, for successful briquette production, certain properties are essential, including reducible raw materials, high cold strength, consistent chemical composition, homogeneous particle size, low reduction disintegration index, and adequate cold strength [30–32]. In an effort to meet these criteria, researchers conducted a series of steps. Initially, BFS was dehydrated and ground into a fine powder. Subsequently, this powder was blended with laundry starch (30%) and water [22]. The resulting mixture was then briquetted using a pressing load of 2 tons, resulting in briquettes with a diameter of 53 mm, a thickness of 62 mm, and satisfactory mechanical properties, including drop damage resistance and compressive strength [22]. These BFS-based briquettes thus fulfilled all the necessary conditions for producing high-quality pig iron.

Iron is in several minerals in nature, according to its deposition state and associated atoms (e.g., magnetite, hematite, goethite, limonite, and wüstite, among others) [33]. Different iron forms present distinct physical-chemical behavior and might (or might not) present magnetism. Based on this, a different approach for the extraction of Fe from BFS includes the reduction of hematite to magnetite and the subsequent removal of iron content using a magnet [23]. The authors attempted to use CO or H_2 as reducing agents to convert hematite and wüstite into magnetite. Blast furnace sludge was heated to 600 °C for 50 min and a suitable conversion of CO_2 into the reducing agent CO (6%) was attained. Effectively, an atmosphere of 6% CO was enough to convert hematite into magnetite, as verified by the sharp increase in ore magnetization to 80 $A \cdot m^2/kg$.

Microwave-assisted reduction of hematite to metallic iron was successfully attempted and is also performed to increase yield and extraction selectivity. The reduction process started with the reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4), which was further reduced to wüstite (FeO) and, then, to metallic iron (Fe). After being dried (110 °C, 120 min), blast furnace sludge was heated in a microwave oven (900 W, 2.45 GHz) for 15 min [34]. As blast furnace sludge usually contains a high content of C, no further reducing agents are required. The required C/Fe ratio is 1:1. Although the authors do not report a yield of reduction, a scanning electron microscope coupled with an energy dispersive X-ray device was used to demonstrate the successful conversion of hematite into magnetite. Results were corroborated by X-ray diffraction and Fourier-transform infrared analysis (FTIR). The disappearance of the bands at 457 and 495 cm^{-1} (related to hematite) indicates the conversion into magnetite after microwave treatment with C-mediated reduction.

Elements of added value might be extracted from blast furnace sludge with either acidic or alkaline solutions (hydrometallurgical approach). It has been observed that different extracting acids or alkalis lead to a relatively selective extraction of a specific element. Extraction specificity also varies according to the concentration of the solution, temperature, and the sludge's initial composition, among other factors. An example of the hydrometallurgical extraction of Fe from blast furnace sludge is illustrated in Figure 4.

In a hydrometallurgical leaching approach, 1 M sulfuric acid (S/L = 50) at 95 °C and constant stirring of 300 rpm for 30 min was used to extract iron in the form of iron sulfate [35]. It was verified that both temperature and sulfuric acid concentration have a significant impact on iron extraction. Moreover, it was observed that iron leaching peaked at 30 min of reaction, and the concentration of Fe in liqueur started to decrease afterward. As a result, a maximum of 80% of extracted iron was attained.

In a different study, researchers used a hydrometallurgical process for the acid leaching (assisted with redox potential control) of the content of lead and zinc of BFS samples [36]. Experiments took place in a pilot plant. Hydrochloric acid (12 M) was used in a liquid/solid proportion of 1:2, and pH values were set to below 1.5. Redox potential was controlled using a NaOCl solution and maintained above 650 mV. The leaching solution recirculates and passes through an anion exchanger membrane for the entrapment of Zn and Pb. The reaction time of 2 h was sufficient to leach 95% of Zn and 92% of Pb. On the other hand, a significant portion of Fe was also leached (32 to 49%). Nonetheless, Fe does not get trapped in the anion exchanger and recirculates to the solid mass to precipitate, thus leading to a small loss.

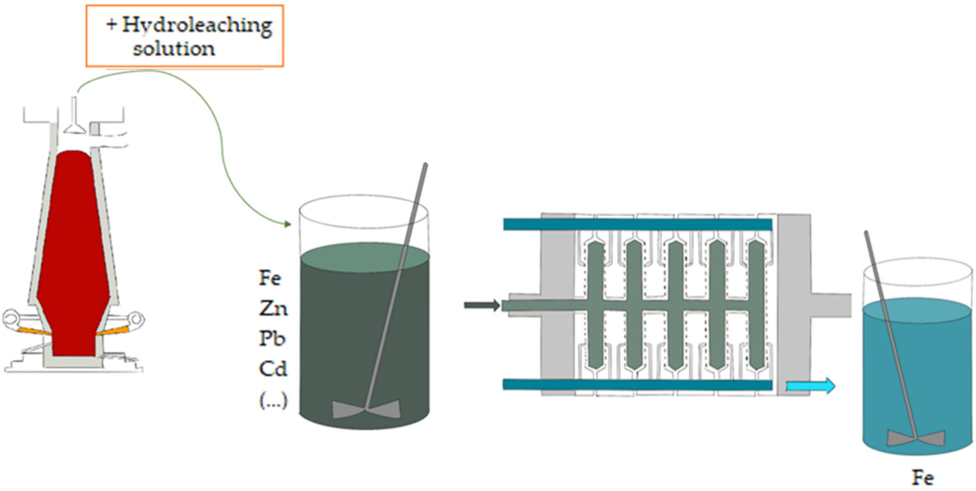


Figure 4. Scheme representing hydrometallurgical extraction of Fe from BFS, followed by filtration and purification (filter press).

Another promising take on hydrometallurgy is through microorganism-assisted leaching processes [37]. The bioleaching capabilities for converter sludge with acidophilic iron and sulfur oxidizing cultures were analyzed in [37]. A high concentration of ferric iron or ferric oxide/hydroxide in the converter sludge may promote the formation of jarosites, which slow down the leaching reactions. It is reported that an adaptation to increasing metal concentrations may promote leaching and prevent metal inhibition processes [38]. Acidithiobacillus are the most used bacterial strains in this kind of process. Bayat et al. [39] investigated the bacterial leaching of zinc and iron from solid wastes at a steel plant using acidithiobacillus ferrooxidans as the bacterial agent. Maximum extraction was achieved at pH values around 1.3 and a solids concentration of 1% w/v, with 35% of the Zn content and 37% of the Fe being dissolved [39].

Knowing that iron is a cheap alternative to nickel as a catalyst for methanation reactions, a new method was studied to produce synthetic natural gas, using BFS as a Fe donor [24]. Allied to the fact that there is a very significant amount of reducing CO in blast furnace gases and coke ovens, Fe-catalyzed methanation can be achieved. Therefore, by using BFS from the Huachipato plant of the Pacific Steel Company as a Fe-based catalyst precursor, the authors performed two successive extractions, using ammonium acetate 1.0 M (pH adjusted to and maintained at 4.5) and hydroxylamine chlorhydrate 0.1 M in 0.01 M HNO_3 (pH adjusted to 2) to remove exchangeable elements as Ca^{2+}, Mg^{2+}, and K^{+}. Furthermore, as iron shall preferably be in the Fe^0 form to work as a catalyst for CO methanation, successive reductions of hematite, magnetite, and wüstite were performed. Selected reduction conditions were 500 °C and 80 mL/min H_2 flux during 2 h. After Fe reduction, 300 mg of catalyst was charged into the reactor, with partial pressures of CO and H_2 of 0.25–3.0 kPa and 10–50 kPa, respectively, with a final H_2/CO ratio of 20:1. Methanization of CO was carried out at 350 °C. The catalyst capacity of BFS was demonstrated to be a good alternative to using extracted Fe to produce synthetic natural gas.

3.1.2. Zinc

Zinc is a prevalent metal in BFS and, usually, the second most representative (10–40 g/kg) after iron [40]. Vaporized Zn reaches the upper section of the blast furnace and condenses, hindering the correct passage of the load from the furnace top. Thus, Zn is removed (as part of the BFS) and usually landfilled or deposited into sedimentation ponds. In addition to being ecologically nefarious, it is estimated that more than 550 kt/y of BFS is generated, and consequently, 280 kt of Zn are lost [40].

In addition to being an interesting element for internal industrial symbiosis (i.e., within the steel production and metal processing industries), zinc has great potential to be integrated within very distinct industries (e.g., automobile, electrical, and construction industries; paints, rubber, cosmetics, food/feed, pharmaceuticals, plastics, soaps, batteries, textiles, lighting, and X-ray screens). Zinc is an element of extensive physiological importance as a regulator of the immune system and nervous signaling, among others [41]. Zinc may also be easily converted into, for instance, zinc stearate, a molecule with technological functions in the cosmetic and paint industries [42]. Even though during the last five years, the prices of zinc as a commodity had positive and negative peaks (a minimum of 1810.50 USD/t in March 2020 and a maximum of 4434.50 USD/t in April 2022), the overall zinc value was relatively constant [43]. In fact, the market quotations for zinc in January 2017 and January 2022 were 2400 and 3070 USD/ton, respectively. However, if zinc is further processed into added-value products, the potential revenues will increase [43].

An approach to extract Zn (along with Pb and Cd) from BFS consists of thermochemically treating BF sludge through the selective chlorination of BFS with steel pickling solution ($FeCl_2$), followed by volatilization [44]. Briefly, 200 g of the previously grounded dried sludge (30 h, 105 °C) was mixed with 200 g of purified water and 77 g of a spent $FeCl_2$ solution from steel pickling, thus granting a molar ratio of 1.1/1 and granting a 10% excess of chlorine to increase the yield of the reaction. The reaction occurred in a horizontal quartz glass tube inserted within an electric furnace. A maximum yield of $ZnCl_2$ and Zn_2Cl_4 extraction (97.4%) was obtained using a temperature of 870 °C, resulting in a co-leaching of 8.7% of Fe ($FeCl_2$). Lower temperatures (600 °C) were required for the removal of 99.9% of lead in the form of $PbCl_2$.

Low-molarity sulfuric acid has also been used for selective zinc leaching [45]. Experiments were performed at 80 °C, using a liquid/solid ratio of 10. Experiments were developed at pH values of 3 (during 6 h) and 1 (during 30 min), and pH was controlled using 5 M H_2SO_4. Leaching residue and liqueur were separated by filtration. Best results were obtained for pH 1 (30 min leaching) as zinc leaching yield was 95% and the recovery of iron in the residue was 91%, demonstrating a good selectivity.

A selective method for the extraction of zinc from BFS was suggested by a research team [27]. In addition to the type of leaching agent and concentration, liquid/solid ratio, and extraction time, microwave power was a tested condition to assess the effect on zinc removal efficiency. Hence, the tested microwave power ranged from 90 to 900 W at a frequency of 2.45 GHz. A temperature range (20–65 °C) was also tested. The selected leaching agent was 0.5 M H_2SO_4, using a liquid/solid rate of 15. Acid-sludge solution was kept at a stirring speed of 350 rpm during the leaching process. It was concluded that it was possible to extract 92% of the zinc contained in the BFS when using a microwave power of 90 W, a temperature of 35 °C, and a liquid/solid rate of 15 (0.5 M H_2SO_4). Under the mentioned conditions, less than 10% of the iron was co-leached, being retained in the sludge for further purification.

Zinc stearate is another zinc-based molecule of interest, namely regarding the production of cosmetics, lubricants, driers in paints/inks, heat stabilizers for PVC, and waterproofing additives, among others [28]. Precipitation and fusion processes are two examples of methods for the synthesis of zinc stearate. The precipitation process uses zinc sulfate as the zinc donor. Zinc sulfate reacts with sodium stearate in a molar proportion of 1:2. In brief, zinc sulfate was dispersed in water and kept stirred at 500 rpm at 30 °C. In another vessel, sodium stearate was dissolved in water at 70 °C while being stirred at 500 rpm. Finally, the zinc sulfate dispersion was added to the sodium stearate solution with a peristaltic pump (13.74 mL/min), and precipitation occurred within moments. Zinc stearate precipitate was washed with deionized water and dried in a vacuum oven (400 mmHg, 100 °C). The precipitation process yielded an 86% rate of conversion of zinc sulfate into zinc stearate.

Zinc stearate might also be produced by the fusion process, which consists of adding zinc oxide to previously molten (70 °C) stearic acid [28]. Stoichiometric conditions dictate that 1 mol of zinc oxide reacts with 2 mol of stearic acid. The reaction occurs at 140 °C under atmospheric pressure and continuously stirring (750 rpm). Even though the fusion process conditions are simpler overall when compared to the precipitation process, the yield of zinc stearate production is lower (80%) and more time demanding (~45 min).

Depending on the oxidation state and association with other molecules, zinc is broadly used in the pharmaceutical industry. For instance, nanoparticulate zinc oxide is used as a UVA and UVB radiation blocker and is widely incorporated as an ingredient for mineral sunscreens. Thus, zinc can be recondensed or leached with relative specificity. Effectively, glacial acetic acid was used as an organic leaching acid for the extraction of zinc [25]. Using glacial acetic acid as a leaching agent, zinc acetate, an ingredient of pharmaceutical interest, is obtained. With a leaching solution of 1 mol/L acetic acid and a solid/liquid ratio of 1:10, at 50 °C during 2 h, 58.1% of the zinc was extracted in the form of zinc acetate. Malonic, acrylic, and citric acids (1 mol/L, solid/liquid 1:10, 50 °C) led to the extraction of a higher amount of zinc from the blast furnace dust slurry: 93.9%, 83.1%, and 82.6%, respectively. Nonetheless, acetic acid led to a higher selectivity, co-leaching less iron (2.7%) than the alternatives. Moreover, zinc acetate is a commercially attractive product that is used as an excipient in the pharmaceutical industry to produce lotions, topical gels, and solutions [26]. Zinc acetate is also administered in oral capsules for the treatment of Wilson's disease. Even though a co-leaching of 2.7% of iron, in the form of iron acetate, compromises the required purity for pharmaceutical grade zinc acetate, a first leaching with a more specific, nontoxic organic acid such as benzoic acid can be performed, followed by a second extraction with acetic acid, to produce zinc acetate [25].

A scheme compiling the wastes and by-products with origins in the blast furnace/basic oxygen route and their valorization possibilities identified in the current chapter is described in Figure 5.

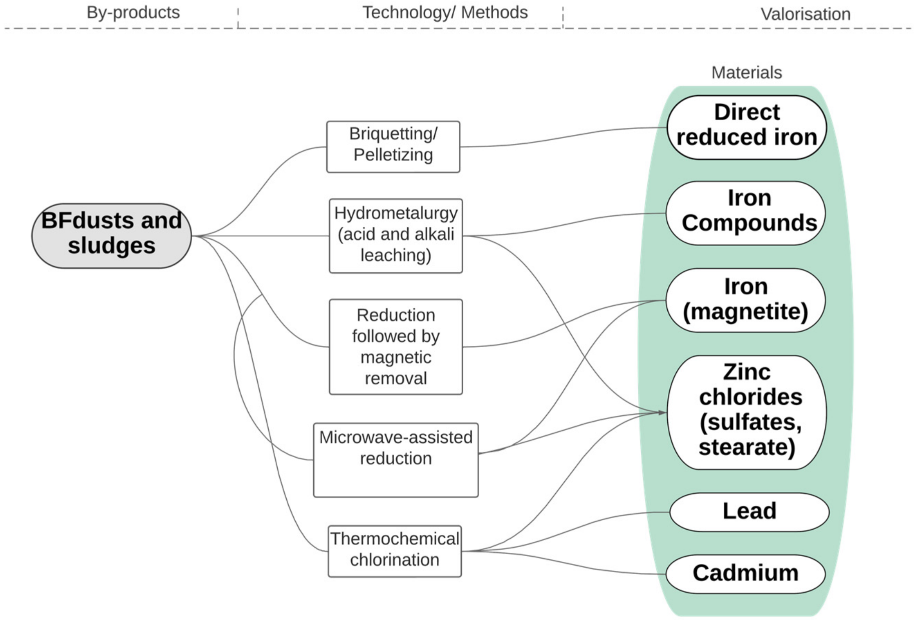


Figure 5. Industrial synergies for BF dust and sludges.

In summary, concerning BF dust and sludges, various materials can be recovered, primarily metals and compounds such as iron, zinc, lead, and cadmium.

Regarding the valorization methods, through briquetting (pelletizing), direct reduced iron can be obtained. Hydrometallurgy, using acid and alkali leaching, allows for the removal of iron compounds or zinc chlorides. The combination of two techniques, reduction followed by magnetic removal, enables the extraction of iron. Techniques such as microwave-assisted reduction facilitate the removal of iron and zinc. Lastly, thermochemical chlorination is effective in withdrawing zinc, lead, and cadmium.

4. Direct Reduction and Electric Arc Furnace Steelmaking

Even though steelmaking processes based on the blast furnace and basic oxygen route are the most common, relative inefficiency and high polluting profile led to the development of alternative methods. A summary of the electric-arc-furnace-based steelmaking process is described in Figure 6.

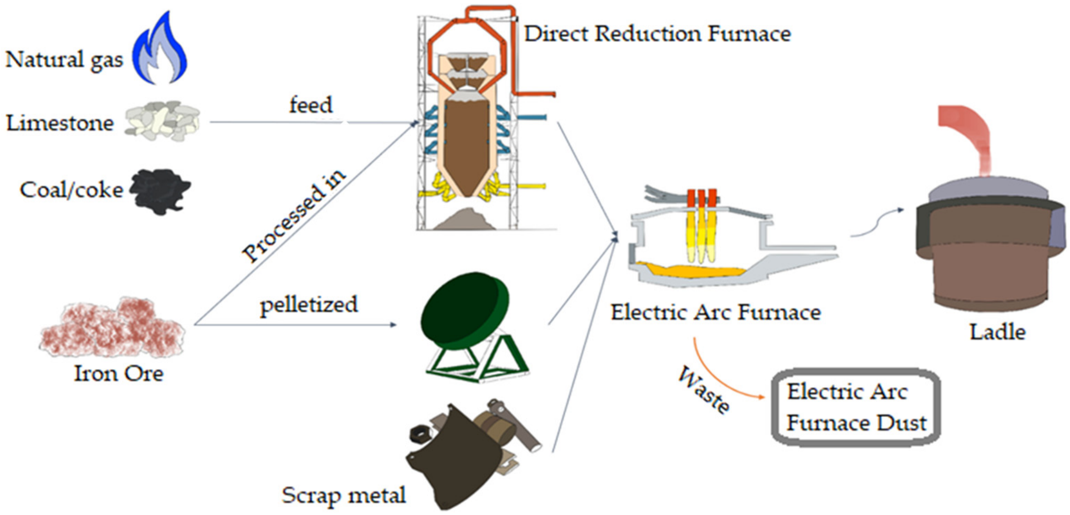


Figure 6. Scheme of electric arc furnace steelmaking route.

Briefly, raw materials are fed into a direct reduction furnace where the iron is deoxygenized by the reducing coal, leading to the formation of carbon monoxide and metallic (reduced) iron, in a reaction that takes 8–10 h. Newformed iron (also named sponge iron) is then cooled, along with the solid wastes (char and dolomite/spent limestone, among others) to prevent the reoxidation of the iron, enhanced at high temperatures. All content is then discharged. Small-sized (<3 mm) material is sieved, and sponge iron is sorted from impurities (e.g., via electromagnetic separation). The off-gases are efficiently cooled to a temperature below 150 °C, then directed through wet scrubbers and a gas-conditioning tower. Following this, they undergo a process in an electrostatic precipitator to effectively capture dust particles. Ultimately, the purified gas fraction is released through a chimney.

Even though the blast furnace method still offers higher yield, methodologies that involve the direct reduction of iron have been gaining importance in the production of steel [46]. While the blast furnace process constantly requires very high temperatures, electric arc furnaces (EAF) work with a more efficient thermal control. Thus, by controlling the temperature in EAF, it is possible to manage the oxygen potential in the system and, hence, obtain cleaner steel by retaining high percentages of alloying elements. Moreover, desulfurization (of paramount importance as sulfur represents one of the main steel contaminants that leads to a steel quality decrease) is more thoroughly obtained when compared with the blast furnace method. The environmental impact of EAF is also significantly lower when compared to blast furnace mechanisms. Electric steelworks allow a reduction in electrical energy, while producing a wider array of products (e.g., mild steel, special and stainless steels, ferroalloys, ceramics, etc.).

The final step involves adding the reduced iron (and scrap metal, if applicable) to an electric arc furnace that, by smelting, converts it into liquid steel [47]. Heat is generated between graphite electrodes. Simultaneously, oxygen is fed to the furnace along with lime and other additives that lead to the separation of contaminants (that precipitate and agglomerate into slag). While slag accumulates on the top of the furnace, molten steel is poured out into a different vessel through a tapping spout.

The electric arc furnace steelmaking process generates 15–25 kg of dust per ton of produced steel [48]. As metals are volatilized in the electric arc furnace (EAF), fumes are extracted through an aperture in the roof and an exhaust segregates the dust by particle size in the EAF exhaust system. Particles with higher dimensions are collected, while fine particles are fed into the deduster. In addition to iron, the main components of electric arc furnace dust (EAFD) are hazardous elements such as zinc, cadmium, chromium, and lead that were commonly landfilled, thus presenting an environmental and ecological struggle. Moreover, disposal costs are significant as, yearly, USD 200 million are spent for the disposal of EAFD in the United States of America alone [49].

For a comprehensive overview of the direct reduction and electric arc furnace steelmaking, including its advantages, disadvantages, by-product production, and associated quantities, please consult Appendix A and Tables A1 and A2.

Industrial Synergies and Recovery Technologies–Electric Arc Furnace Dust

Attempting to minimize the inherent drawbacks, EAFD has been used as a structural component of asphalt, ceramics, glass, and mortars, among others [50–55]. More recently, however, EAFD started to be considered as a source of secondary raw materials that can be extracted using different approaches such as processing in direct reduction (direct reintegration of metallurgical wastes), pelletizing/briquetting, and hydrometallurgical methods. The main composition of EAFD is presented in Table 2.

Table 2. Electric arc furnace dust general composition on main elements (average ± S.D.).

Element	Average Relative Amount (wt. %)	Ref.
Zn	25.1 ± 7.6	[56]
Fe	25.6 ± 3.5	
CaO	9.2 ± 6.7	
Pb	2.5 ± 1.8	
SiO_2	3.6 ± 3.2	

Methods for the extraction of EAFD minerals are developed and selected according to the selectivity and yield of extraction of the elements of interest, among which iron and zinc represent important roles because of the wide array of industrial uses of the metals and their quantities in EAFD. The reintegration of metallurgical wastes is a direct-use approach, allowing the immediate supply of the infrastructure with waste material to be used as raw materials. Despite the great advantage of requiring little to no preprocessing of the wastes, the direct-use approach (i.e., by FASTMET®, FASTMELT®, and PRIMUS®, as described below) implies great investment in infrastructure, equipment, materials, and especially qualified labor.

Requiring relatively low energy and being low-pollutant, the rotary hearth furnace (RHF) process has been commonly used to treat metallurgical solid wastes such as EAFD and BFS. The FASTMET® process is an RHF technology that, similar to a rotary kiln, implies agglomerating ore fines with pulverized coal into pellets (using a pan pelletizer) or briquettes (using a dual-roller type of briquetting machine) [57]. Up to two layers of pellets/briquettes are deposited into an RHF with a fast temperature increase to 1350 °C for 6 to 12 min for the direct reduction of iron. Simultaneously, zinc and lead (oxides) are vaporized and extracted in the exhaust gas (with the recovery of heat using a heat exchanger). A very important advantage of the FASTMET® process is the capability of separating zinc from the EAFD with conversion into high-purity zinc oxide (a raw material for zinc refining), along with the production of direct reduced iron at a high reduction ratio. An important drawback of the FASTMET® process, however, is that, depending on the coal quality, a low yield of iron content and/or a possible contamination with sulfur may impede the commercial use of the technique.

Due to the above-mentioned drawbacks inherent to FASTMET®, an updated version named FASTMELT® was developed [57]. Briefly, direct reduced iron is produced according to the FASTMET® process but further transferred to a furnace to be melted (1540 °C) for the removal of sulfur. After sulfur removal, the iron is cooled to a slag, usable to produce molten iron. The final melting step of the FASTMELT® process uses the heating energy recovered in the heat exchanger.

An improved, multiple-hearth process named PRIMUS® was developed by Paul Wurth S.A. in cooperation with ProfilARBED, aiming to use a highly efficient mechanism to produce virgin iron and to recycle by-products such as EAFD [58]. As occurs for the blast furnaces, the charge is added to the top of the furnace and sequentially transported downward by rabble arms driven by a rotating cooled axial column. The charge is mainly composed of coal fines and metal oxides. At the lowest level (1050–1080 °C), direct reduced iron is discharged. In addition to being energy efficient, the number of hearth levels is adaptable depending on the material to be processed (i.e., according to the melting, boiling, or reduction temperatures of the material to be treated). Moreover, formed gas containing CO and coal material escape from the material layer, being burned above by air injection. This combustion is essential for the process to be energetically sustainable, being sufficient to keep temperature above 1000 °C [58]. Volatile metals are evaporated as metallic fumes, flowing upward to a highly oxidative atmosphere. Thus, metallic zinc and lead are readily re-oxidized to ZnO and PbO, respectively, being collected as metal dust particles in a bag filter. Due to a high concentration of ZnO, collected dust presents a commercial value for the zinc industry. On the other hand, less volatile iron is continuously reduced and melted on the bottom of the furnace. Obtained iron is pure enough (50–80% iron content, virgin iron grade) to be used for further processing in electric arc furnaces. Indeed, virgin iron produced via the PRIMUS® process has low content of sulfur (<0.1%) and an ideal concentration of carbon for electric arc furnace usage [58]. PRIMUS® technology allows the treatment of both electric arc furnace dusts (EAFD) and rolling sludges (RS) or blast furnace sludges (BFS). Before being treated, they must be pelletized/micro-pelletized. Masses of EAFD and BFS may be gathered before pelletizing. Starting from an average zinc concentration of 60–65% (mostly in ZnO form) and usually mixed with lead and chlorine, a 1 h treatment leads to a highly significant purification of zinc. Indeed, more than 90% of lead and chlorine is removed and a high purity (~96%) of metallic zinc is obtained [58].

In that sense, zinc oxide and iron represent the main products recovered from EAFD when using the rotary kiln process [59]. The rotary kiln process occurs by direct reduction of wastes in solid form and offers good yields, as for instance, up to 94% of the zinc can be removed. Before reaching the rotary kiln, coal powder, EAFD, and a binder (e.g., K_2CO_3, $CaCO_3$, CMC, Xanthan gum, etc.) are blended and pelleted using, for instance, a pan pelletizer or a balling drum [60]. Then, pellets are added to the kiln and preheated before being transferred to the reduction zone (1100–1200 °C). After reduction, volatized metal oxides are transferred to cooling and/or settling chambers to collect Waelz iron and zinc.

Acknowledging the facts that EAFD consists of up to 50 wt.% of iron and that hematite and magnetite present red and black coloration, respectively, researchers presented the hypothesis that the by-product could be used as raw material for tile pigment manufacturing [61–63]. Pigments for tile glazing require a particle size of approximately 5 µm. Iron particles in EAFD are usually below 20 µm. Therefore, EAFD was sieved (325 mesh) and then homogenized (planetary ball milling, 250 rpm, 60 min) to achieve proper granulometry. Then, the obtained dust was applied to ceramic bodies (concentrations of 2, 4, 6, and 8 wt.%) using a manual serigraphic screen. Finally, the samples were fired in a roller hearth furnace (1130 °C, 23 min). Pigments from EAFD offered the proper average particle size and thermal stability and were appropriate for domestic use (classified as PEI 3, thus being suitable for floor coverings for light to moderate traffic as in kitchens, for instance).

In addition to performing a direct reduction of the dust and other metal-producing and metal-processing processes, elements with potential added value can be extracted from the EAFD, for instance, by hydrometallurgical methods [64]. These involve the use of acid or alkaline leaching solutions and, then, the specific extraction of the leached compounds. The choice of the leaching agent is important since compounds within EAFD will have different leaching affinities based on this. For example, ZnO does not cause any problem when leaching with either acid or alkaline, but zinc ferrite is considered to be resistant to both [65]. Acid leaching is prone to leach iron compounds as well, which increases with the increase in sulfuric acid concentrations [66]. Alkaline may be preferable, although it requires higher leaching concentrations. In the case of zinc leaching, the maximum extraction (around 75%) was achieved by using concentrations higher than 0.5 mol L^{-1} H_2SO_4 [66]. For zinc selectivity, the optimal conditions for zinc removal from used EAF dust at the minimal iron extraction are as follows: temperature 70–90 °C and 0.5 mol L^{-1} H_2SO_4. On the other hand, [67] reported that, in a leaching solution of 3 M H_2SO_4 at 80 °C, zinc extraction reaches almost 100%, and iron extraction exceeds 90%. After the metal leaching, the next step is the purification to remove unwanted species such as iron, lead, manganese, and magnesium, among others. The solvent extraction technique is one of the most used methods for removal, separation, and concentration of metallic species from aqueous media solutions [49]. It has been widely used in the extraction of zinc from sulfate solutions [49].

A scheme compiling the wastes and by-products with origins in the electric arc furnace dust route and their valorization possibilities identified in the current chapter is described in Figure 7. This figure presents the methods and potential valorizations for EAF (electric arc furnace) dust and sludges.

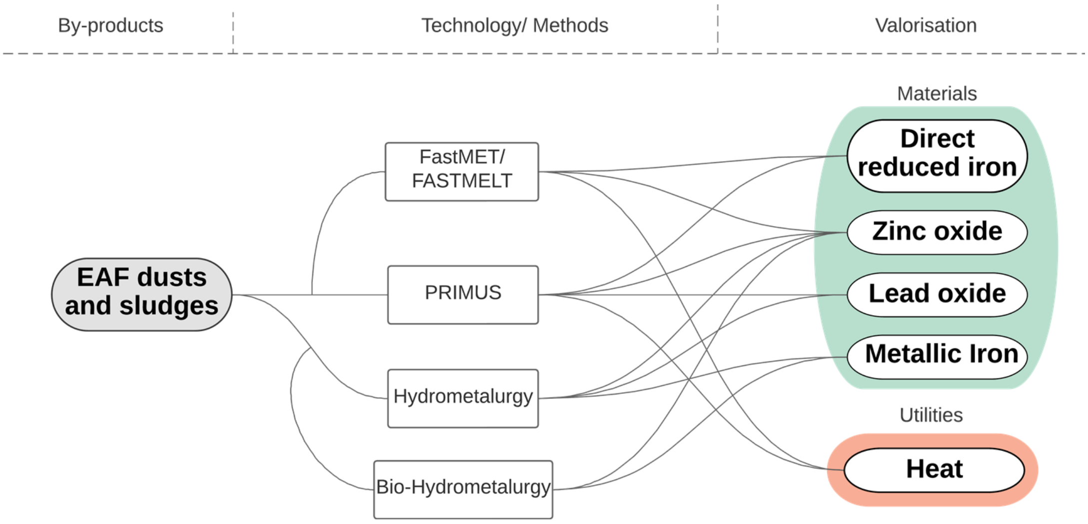


Figure 7. Industrial synergies for electric arc furnace by-products.

Concerning these by-products, materials, primarily metals such as iron, zinc, and lead, can be obtained. Additionally, heat can also be generated as a utility. The FASTNET/FASTMELT methods allow the obtaining of iron, zinc, and heat. The PRIMUS method allows for the recovery of iron, lead, zinc, and heat as well. Lastly, hydrometallurgy and bio-hydrometallurgy methods facilitate the extraction of zinc and iron.

5. Metal Processing

Ferrous metal processing usually occurs in a sequence of procedures in the following order: pickling, (hot and cold) rolling, annealing, temper rolling (or skin pass rolling), and finishing. Metal processing leads to the formation of a wide array of products, such as tubes, flat sheets, and wires, among others, but also to the application of coatings as occurs in galvanizing and hot-dip-coating procedures. The main methods are the drawing of steel, hot rolling (T°C> metal recrystallization temperature), and cold rolling (T°C< metal recrystallization temperature) [68]. Hot- and cold-rolling process techniques are illustrated in Figure 8.

In brief, rolling is a metal-shaping process aimed to reduce and homogenize the thickness of the metallic input, leading to the desired mechanical and morphological properties [69]. The most common products processed by hot rolling are beam blanks, blooms, slabs, billets, and cast ingots. Metals to be hot rolled must be preheated in dedicated structures (e.g., soaking pits and induction heaters, among others) before being subjected to pressure [70]. Indeed, temperature is a critical parameter and, thus, must be thoroughly controlled during the process. After being hot rolled, metal sheets require either pickling or smooth clean treatments for the removal of mill scale, a metallic oxide that forms with high temperatures and deposits on the surface of the metal sheet [70].

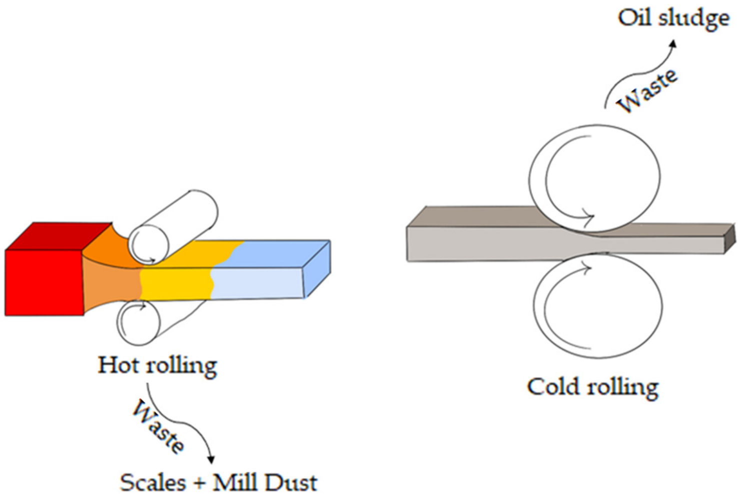


Figure 8. Scheme of the metal processing methods of hot and cold rolling.

The scale is mainly composed of iron, with smaller amounts of manganese and zinc, and is removed from the metal surface in dedicated descaling cabins [71]. Within descaling cabins, cool water is sprayed onto the metal surface at high pressure, thus generating pressure and heat stress. Moreover, the water volume increases while evaporating, leading to significant physical expansion that aids the descaling process. Scale removal is also performed, recurring to the pickling process [72]. Descaling by pickling is performed, recurring to hydrochloric or sulfuric acid or a blend of both, at temperatures usually ranging from 75 °C to 95 °C. Then, the metal strip (or sheet) is rinsed with demineralized water to remove the acidic media and the heavy scale burden from the product. Furthermore, a blend of nitric and hydrofluoric acids (70 °C) is used for the last chemical removal of scale. Finally, the product is dried and ready for cold rolling. A representation of the pickling process is illustrated in Figure 9.

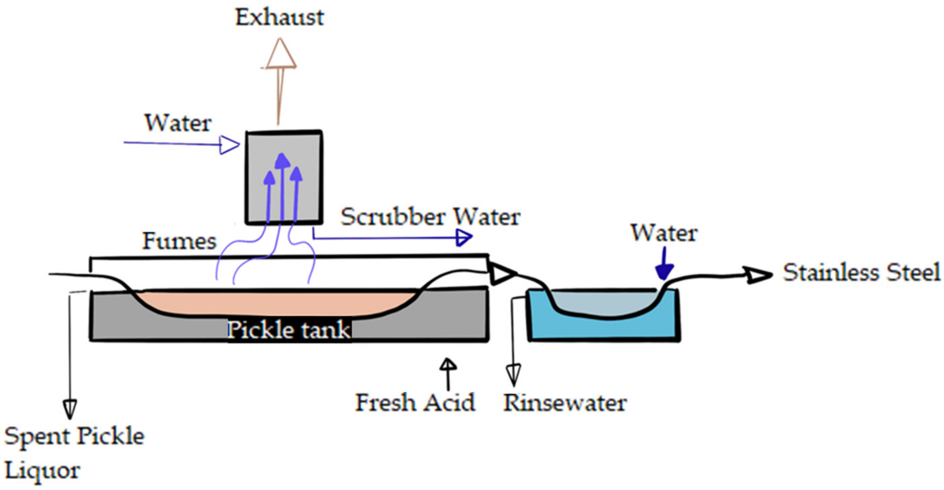


Figure 9. Representation of pickling process.

Hot rolling usually leads to the production of cheaper steel pieces but is also less prone to be manipulated by blacksmiths when compared to steel prepared by the cold-rolling process. Nonetheless, by controlling the non-uniform cooling of metal pieces that lead to heterogeneous stress forces, it becomes possible to create cross-sections, as occurs in I and H beams.

The cold rolling, on the other hand, leads to the formation and morphological structuring of metal with increased strength because of processing below the metal recrystallization temperature [70,73]. Another advantage over hot rolling resides in the fact that cold rolling improves surface finish. Nonetheless, cold-rolled products are usually smaller and thickness reduction of the metal part is less effective when compared with the hot-rolling method, requiring multiple passes to achieve similar results. Different pressure levels may be applied to workpieces (from lower to higher achievable thickness: full-hard, half-hard, quarter-hard, and skin-rolled); a minimum of 0.1% and a maximum of 50% of thickness reduction might be observed.

Metal-processing industries that work with the cold-rolling method generally require using oils (either pure or in emulsions) for lubrification, strip cooling, and removal of Fe particles. In addition, the use of rolling lubricants (usually fats or mineral oils) is of paramount importance to achieve wanted shapes, reduce friction-induced temperature raises, decrease roll wear, and prevent oxidation of the reduced strip [74]. Apart from hydraulic oil and Morgoil oil, cold rolling usually implies using greases and cooling water that will form an emulsion with hydrophobic components. Hydrophobic elements, mostly oils, will accumulate and form a sludge during the rolling, galvanizing, and annealing, constituting a source of waste.

Furthermore, as hot-rolled steel usually presents a layer of scales (containing an array of metal oxides), an acidic surface cleaning–pickling is commonly performed [75].

Industrial Synergies and Recovery Technologies-Metal Processing

Steel mill plants mainly generate three categories of by-products: mill scales, oily sludges, and pickling waste liquid [76]. Between hot rolling and cold rolling, scales must be removed from the surface of the hot-rolled steel part to maximize the life of the work roll and to avoid degrading the surface quality of the product. The spent pickling liquor is, however, usually disposed, representing a significant environmental concern that requires innovative solutions to be avoided [77].

Mill scale occurs when steel is heated to thermal gradients in the presence of high concentrations of oxygen. Around 15 kg of scales are produced per ton (and, thus, 30,000 tons per year) of rolling steel in the Gilan (India) steel-rolling mill. Mill scales are usually sold at low prices, being further used to compose iron ore pellets or recycled into sintering plants to be further converted into steel in melting furnaces. As mentioned above, acid pickling is the common practice for chemical removal of scales from the surface of cold-rolled steel strips. Spent pickling liquor resulting from the pickling process is one of the main components of the sludge and presents a high content of heavy metals [78]. In fact, in addition to the inherent acids (e.g., HNO_3, HF, and HCl), spent pickling liquor contains Fe(III)–35–45 g/L–Cr(III)–5–10 g/L–Ni(II)–3–6 g/L, among others.

Oil sludge is also produced in significant quantities, mostly from cold-rolling mills [76]. Approximately 25,000 tons of oil sludge are reported to be produced by the Gilean steel-rolling mill (yield of about 1.5 L per ton of steel produced). Summarily, after pickling, a liquid emulsion is formed on the surface of the metal strip, aiming to lubricate and cool the material. The succession of rinses and washing leads to the extraction of a plethora of components, with Fe (70.6%), Mn (0.18%), Cr (0.065%), Si (0.058%), Ni (0.049%), and V (0.024%), among others [79]. The emulsion is then removed by rinsing the strip with tap water. Indeed, water is used to rinse the oil out of the scales (scales shall not have more than 0.5% weight of oil in their composition to comply with recirculation criteria), leading to the formation of relatively stable emulsions [80]. Therefore, wastewater is treated with NaOH and polyaluminium chloride to induce the precipitation of Fe into fine flocs [81,82]. It has been estimated that 2 tons of oil sludge are generated from the treatment of 400 t of wastewater. The oily sludge (also known as cold-rolling sludge) is rich in iron, containing 40.5–47.6 wt.% Fe, thus being a potential secondary raw material source [83].

Several methods have been developed to purify and extract added-value components from oil sludge and mill scales. For instance, a solution of 6 M sulfuric acid, at 85 °C for 4 h, was used as a leaching agent for the extraction of iron from cold-rolling mill sludge [84]. Then, a series of filtrations were performed aiming to separate the hydrophilic and hydrophobic parts (further used as fuel or chemical feedstock for further processing) of the sludge. The acidic hydrophilic liquor was oxidized by hydrogen peroxide (30 wt.%), and iron was extracted mainly in the form of $Fe_2(SO_4)_3$. Then, under continuous stirring, the liquor was neutralized using ammonia, allowing the iron salt to precipitate. Finally, the salt was stirred with a solution of 8 M sodium hydroxide (60 °C, S/L of 1:12) and poured into a reaction kettle at 200 °C for 2 h. The obtained micaceous iron oxide, a red pigment commonly used to produce paints, was separated from the suspension by centrifugation and further washed with water and dried at 80 °C.

In a different study, researchers attempted to use green solvents for the extraction–flocculation of oils from cold-rolling sludges [85]. Oil-containing sludge was mixed with 1-Butanol (solvent/oil ratio of 5, *w*/*w*) mixed with 2 g/L KOH and further centrifuged (4000 rpm, 20 min). The supernatant was collected and recovered on a rotary evaporator under vacuum (13 mbar). The oil-collecting vessel was washed with n-hexane followed by 28 mL of isopropanol. The mixture was centrifuged, and purified oils were dried in an oven (80 °C, 1 h). The developed and optimized extraction process yielded an 8.5% removal of oil from sludge.

Aiming to extract the oily content, gas–fuel, and purified iron from cold-rolling mill sludge, a vacuum distillation followed by iron reduction mediated by hydrogen was performed [6]. The initial distillation occurred in a rotary furnace, with the pressure set to 0.1 Pa and then heated to 600 °C (rate of 10 °C/min) for 3 h, continuously stirring (50 rpm). Purified distillation oils were condensed, and tail gas was trapped in the gas collector. The remaining sludge was further reduced by feeding hydrogen (flow rate of 0.4 L/min) into the rotary furnace (1000 °C, 2 h). With effect, distilled oil and gases that represented ~18% of the original sludge (suitable as fuels) were successfully obtained. Moreover, hydrogen reduction led to the conversion of iron content into magnetite, allowing the recovery of the metal via magnetism.

Industrial pickling waste liquid, containing hydrochloric acid and iron chloride (mainly in the form of $FeCl_3{\cdot}6H_2O$), represents another potential and, yet, relatively unexplored source of iron. Attempting iron extraction, tributyl phosphate was added to the pickling aqueous solution in a proportion of 2:1 [86]. The mixture was stirred (200 rpm) for 5 min. Once homogeneous, stirring was stopped and settled until the aqueous and organic phases were completely separated. The organic phase was collected and subsequently mixed with fresh water and kept stirred (200 rpm) for 8 min. Aqueous solutions were then separated and added to the spray pyrolysis machine, and the total inlet pressure from the air compressor was set to 0.5 MPa, and the power of the spray generator was controlled at ~21 W. After pyrolysis, Fe_2O_3 could be collected in the form of fine particles. Gasified hydrochloric acid could also recovered after being trapped in the porous gas washing recipients and dissolved in the containing deionized water. This process yielded an extraction efficiency of 63%.

Acid pickling solution is also an interesting source of red oxide pigment (Fe_2O_3). Nonetheless, the pickling solution is usually contaminated with zinc that must be selectively removed. Moreover, a high demand for zinc is occurring to produce batteries and for galvanization procedures, and pickling waste may represent an important source. Therefore, an innovative method, based on the precipitation and selective extraction of zinc from pickling solution, was developed by [87]. Briefly, oxalic acid was added to a beaker containing 250 mL of acid pickling solution (Zn ion: oxalic acid molar proportion of 1.4:1). Extraction was optimal at 25 °C and a stirring speed of 100 rpm during 20 min. As zinc oxalate starts to be produced, a precipitate starts to form, which can be removed using a filtration mechanism (e.g., by vacuum filtration). As a result, almost 95% of zinc was extracted from waste pickling solution. Nonetheless, a high co-leaching of iron was also observed, and further processing would have to be performed in order to obtain purified zinc and red oxide pigment in the required grades.

Pickling liquor may also be used by paper companies for the treatment of paper mill wastewater. Indeed, it was suggested that the acidic iron contained in the pickling solution could work as an ingredient for the preparation of inorganic coagulants to be added to paper wastewater treatment systems in a "treating waste with waste" methodology [88]. While mechanical and aerobic/anaerobic treatments represent the primary and secondary steps, the coagulation process represents an important part of the tertiary treatment of wastewater. Thus, the authors attempted to use pickling liquor waste as raw material for the preparation of a polymeric ferric aluminium sulfate chloride (PFASC) compound. Iron sulfate, aluminium sulfate, and sulfuric acid (for pH adjustment) were dissolved in the waste pickling liquor. Iron sulfate and aluminium sulfate react in a molar proportion of 4:1. Then, under intense stirring, sodium chlorate was added to the previous solution. The temperature was set to 50–60 °C, and reaction occurred for 30 min. Iron chloride (from the pickling solution) and iron sulfate shall represent, respectively, ~82% and ~18% of the final PFASC content. A dosage of 1.0 mL/L led to a maximum COD removal of 65.3% and a maximum chroma removal of 71.2% of wastewater.

Iron-rich pickling sludge (obtained from the alkalinization of the liquor with lime) and liquor were also used to obtain P-doped polyferric chloride (PPFC), a widely used coagulant for water treatment [89]. The sludge obtained from acid pickling waste was dried (105 °C). Dried sludge was then mixed with the waste pickling liquor (200 rpm, 1 h, at room temperature), and the suspension was further filtered. An HCl solution was added to the filtered sludge for the thorough extraction of iron content. The resulting solution was then filtered. Liquors obtained after the first and second filtration were homogenized, and a 30% (*w*/*w*) H_2O_2 solution was further added (liquor/H_2O_2 proportion of 1:1.15), aiming to oxidize the Fe^{2+} contained in the liquors to Fe^{3+}. Finally, Na_2HPO_4 was also added to the solution, respecting a P/Fe = 0.05 proportion. Reaction occurred at 200 rpm for 2 min, followed by 60 rpm for 1 min. The solution rested for 6 days to let the PPFC precipitate. Obtained PPFC was tested regarding chemical oxygen demand (COD) and chroma removal, reaching an effectiveness of 96.25% and 65.91%, respectively, with a relatively small concentration of 1.0 mL/L.

A scheme compiling the wastes and by-products with origins in the metal-processing route and their valorization possibilities identified in the current chapter is described in Figure 10.

For the three by-products described in this section (mill sludges, oily sludges, and pickling waste liquid), metal and compounds and fuels and other liquids can be recovered. For mill sludges, the recovery methods are green solvent for extraction, leaching (with agent), and vacuum distillation; those techniques allow the obtaining of oil, iron oxide, and gas. As for oily sludges, the identified method for recovery is chemical synthesis, which enables the retrieval of PPFC.

Lastly, pickling waste liquid: in this by-product can be applied three types of methods, chemical reaction (i), precipitation and selective extraction (ii), and solvent extraction and pyrolysis (iii). These three methods allow the recovery of iron (chloride and sulfate), zinc, and hydrochloric acid.

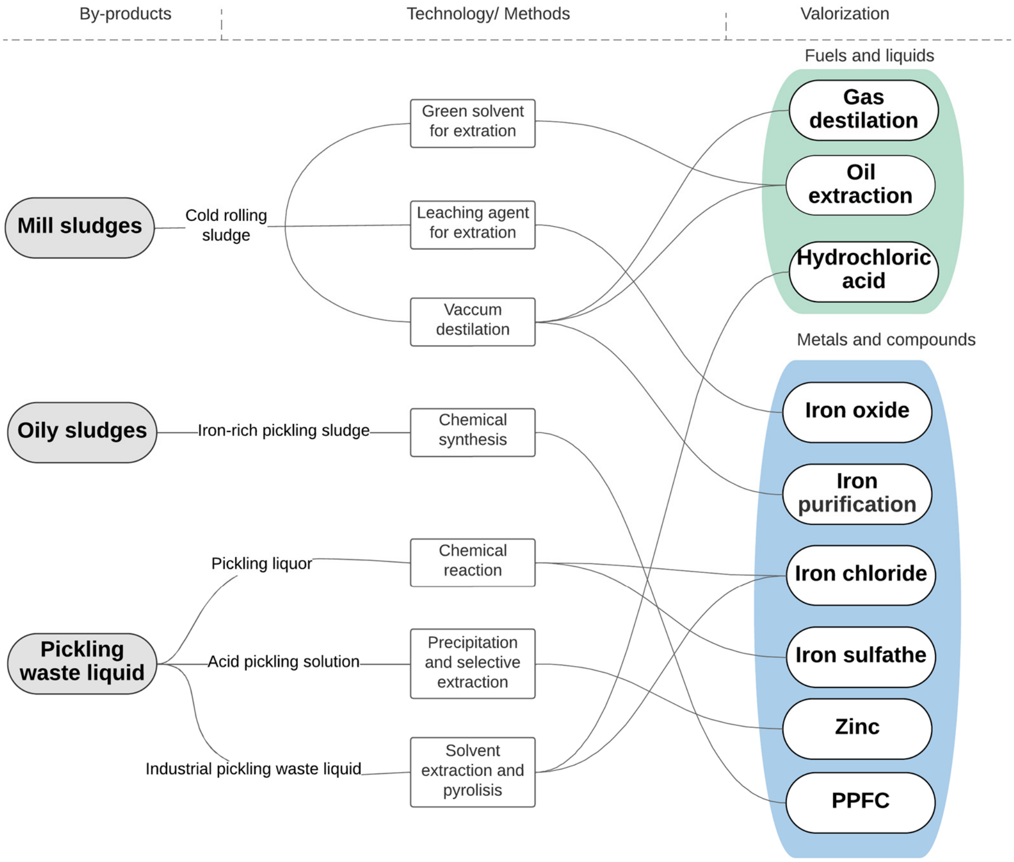


Figure 10. Industrial synergies for mill sludges, oily sludges, and pickling waste liquid.

6. Discussion, Conclusions, and Future Perspectives

6.1. Discussion

The increase in awareness of steel production and metal-processing industries became a driver for the sustainable transition toward a low-carbon footprint and overall greener practices [90,91]. Transition steps may include optimization of production processes, investment in innovative technological developments, implementation of energy usage and saving strategies, or using greener state-of-the-art materials [92].

According to our analysis, there are a set of aspects that must be reinforced in order to achieve the transition to a greener industry.

6.1.1. Technological Challenges

Our research indicates one of the most pivotal areas for investment and development is the technological domain. While many of the processes outlined in this paper are relatively simple and technically executable, it is critical for the iron and steelmaking sector to conduct additional experiments and optimize processes to ensure that both raw materials and output meet stringent criteria, particularly regarding quality and safety.

Furthermore, it is important to highlight the need to bolster financial support for technological adaptation, given that some of the technologies are readily available but require a large investment for integration into existent plants and processes for the reception of by-products. On the other hand, it is imperative to increase funding and research opportunities for newer technologies, strengthening the transition from small to pilot/industrial scale.

6.1.2. Policies Implications

Reusing by-products represents significant advantages such as higher independence on suppliers of virgin raw materials, minimizing the effects of political (e.g., tax politics [93], foreign relations [94], upcoming conflicts, etc.), geographical (e.g., distance from raw material sources [95]), and social phenomena (e.g., stakeholders and community engagement [96]).

Nevertheless, the establishment of external industrial symbiosis requires that by-products are processed and comply with specific norms. In this sense, for appropriate recovery of materials in the iron and steel sectors, it will be imperative to have policies that support the transition of this industry.

For instance, aspects such as innovation and development should be bolstered by co-financing programs [97], which provide essential funding for acquiring the necessary infrastructure, utilities, and human resources to support companies as they embark on the journey toward circularity. Additionally, policies that encourage industrial synergies are essential. Some of these policies have already been successfully implemented in European Union countries, including carbon taxes [98] and landfills [93,99].

6.1.3. Rethinking Process and By-Products

From a complementary perspective, rethinking by-products as added-value ingredients that may potentially serve as secondary raw materials tackles fundamental issues by reducing the pollutant profile and treatment/landfilling needs. This innovative approach not only potentially results in substantial cost saving but also gives rise to new sources of revenue streams. Moreover, it opens the door to industry diversification and the creation of synergies beyond the traditional steel- and metal-processing sectors. There are, however, some challenges intrinsic to symbiotic relationships and tight criteria and mandatory quality assessment, for example, with the pharmaceutical, nutraceutical, cosmetics, or even food industries [100].

6.2. Conclusions and Future Perspectives

This paper has systematically reviewed the most used processes (i.e., blast-furnace-, basic oxygen-furnace-, and electric-arc-furnace-based ones) in steel-production and metal-processing industries, in order to disclose the most recent and relevant industrial synergies toward a circular economy, sustainability, and industrial symbiosis. The methodology developed allowed us to extensively identify the compilation of the industrial synergies and recovery technologies of those three processes.

Steelmaking and metal-processing industries are, more than ever, challenged to adopt sustainable practices. There is an opportunity to not only reduce the environmental footprint but also to enhance process efficiencies and establish symbiotic relationships with diverse sectors and, thus, generate new business opportunities. The valorization of generated wastes with a high-polluting profile represents a double advantage: improving the green profile of the companies and creating new (and, in some cases, innovative) sources of income.

Blast furnace sludge, electric arc dust, and rolling-mill oils are representative wastes from which components of interest (e.g., iron, zinc, cadmium, chromium, and oils, among others) may be extracted and transformed to produce not only new sources of metal to refeed steelmaking/metal-processing industries but also of different products for very distinct industries such as cosmetics (e.g., zinc stearate) and food/feed supplementation (hematite iron).

Our findings suggest that for a successful industrial symbiosis, along with a sustainable approach to circularity, to occur, thorough efforts must be undertaken to strength several aspects. These include addressing technological challenges, considering policy implication, and rethinking process and by-products.

As a main recommendation for future studies, the authors consider that the next step for this area of investigation is to sort out the principles of sustainability (economic, environmental, and social) in the technology compilation identified in this study. The main objective is to guarantee maximum quality safety, sustainability, and profit for potential industrial users in the steel-production and metal-processing industries.

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Abbreviations

Glossary Terms	
EAF	Electric arc furnace
BFS	Blast furnace sludge
BFD	Blast furnace dust
BOF	Basic oxygen furnace
COD	Chemical oxygen demand
rpm	Rotations per minute
MIFA	Municipal incinerator fly ash
RHF	Rotary hearth furnace
IS	Industrial symbiosis
OECD	Organisation for Economic Co-operation and Development
EAFD	Electric arc furnace dust
PVC	Polyvinyl chloride
PPFC	P-doped polyferric chloride

Appendix A

Table A1. Advantages and disadvantages of steelmaking processes.

Process	Advantages	Disadvantages
Basic Oxygen Furnace	Possibility to reduce the total cycle time to less than a 10th of the cycle time of open hearth furnaces, enabling significant energy savings for a given metal mix. Substantial cost savings, even though material costs can be higher. [101]	Basic oxygen steelmaking and casting key environmental issues for the sector are fume collection and treatment, BOF gas recovery and treatment, and zinc in collected dusts. [1]
Electric Arc Furnace	Important way to recycle scrap resources. Energy saving and emission reduction when compared to the BF-BOF. [102]	Electric arc furnace steelmaking: key environmental issues for the sector are dust, organochlorine compounds, energy efficiency, and recycling solid wastes. Production of steel from scrap consumes considerably less energy compared to production of steel from iron ores. The problems with the quality of scrap-based steel introduces restraints and the use of direct reduced iron (DRI) as feedstock enlarges the possibilities of the EAF steelmaking route. Fine dust particles rich in heavy metals such as lead, chromium, and cadmium are released from EAF. [1]

Table A1. *Cont.*

Process	Advantages	Disadvantages
Blast furnace	The BF the route allows the recycling of various solid wastes/by-products which would not be available in many DRI processes. The desulfurizing capability of the blast furnace allows higher-sulfur-containing fuels and reductants to be used in an environmentally friendly manner. It can reduce the demand for primary aggregates because of its possible valorization solutions. [1]	Blast furnaces: the key environmental issues for the sector are BF gas containment, treatment, and utilization, fumes from casting, and dealing with slags. Blast furnaces require coke, and coke plants are expensive and have many environmental problems associated with their operation. The minimum blast furnace coke rate is approximately 200 kg/t pig iron. Emission of a significant amount of greenhouse gases, especially CO_2. Leaching of cyanides, phenol, sulfur-containing compounds, metals, and ash, among others, in addition to an expressive water loss. [1]
Direct reduction	When compared to a blast furnace, the direct reduction unit uses natural gas or coal as a fuel; therefore, a coke oven plant is no longer needed, significantly reducing the emissions. Reduced impact on the environment with little dust emission, which is easy to collect. Low consumption of water and can be recycled to a large extent. Methane-based direct reduction unit produces much less CO_2 than a coal-based unit. [1]	DR processes make use of iron pellets, which cause environmental impact because of the releases from the pelletization process. Environmental releases related to the additional processing of the DRI product that typically contains 2–4% gangue. [1]
Metal processing (hot rolling)	Specific properties and applications of the output materials.	High quantity of energy needed to reheat the slabs, billets, and blooms and the related emissions that arise because of combustion processes in order to supply the required thermal energy. High water consumption in hot-rolling mills for cooling (direct and indirect), descaling, and transporting purposes. Oil loads of the water and the oil content of the precipitated scale. [103]
Metal processing (cold rolling)	Specific properties and applications of the output materials.	Emissions into the atmosphere from annealing furnaces. Discharges into the water by the rolling and pickling sections. [103]

Table A2. Principal waste, quantity of waste, and average composition of steelmaking processes.

	Blast Furnace	Basic Oxygen Furnace	Electric Arc Furnace	Metal Processing (Casting and Rolling)	Direct Reduction
Principal By-product	Sludge	Sludge	Dust	Sludge	Dust
Quantity of by-product	2–22 (kg/ton Hot metal) [104]	15–16 (kg/ton liquid steel) [105]	10–20 kg/ton liquid steel [5]	12 kg/ton steel [104]	250 kg/ton DRI [106]

Table A2. *Cont.*

	Blast Furnace	Basic Oxygen Furnace	Electric Arc Furnace	Metal Processing (Casting and Rolling)	Direct Reduction
Composition	Fe (41.44%), C (18.54%), SiO_2 (7.02%), CaO (4.28%), MgO (1.87%), Al_2O_3 (1.74%), Zn (1.98%), Pb (0.06%) [27]	Fe (47–70%), Ca (6.8%), CaO (3–11%), Mg (0.55%), Zn (0.9–3.2%), Pb (0.1–1%), Cl (7.09%), SiO_2 (0.71–1.97%), C (0.7%) [5]	Zn (8–33%), Fe (26.5–45.24%), Ca (0.9–3.85%), Pb (0.2–5.59%), Cr (0–0.46%), Mn (1.68–4.11%), Si (0.34–2.5%), Cd (<0.01–0.11%), Ni (0.02–0.1%), Cu (0.14–0.35%) [35]	Fe (70.6%), Ni (0.049%), Mn (0.18%), Cr (0.065%), Si (0.058%), V (0.024%), Oil (17.4%), H_2O (0.8%) [6]	Fe (43.1%), Zn(7.8%), Al (10.9%), C (6.2%), Ca (1.4%), CO (2.2%), Cu (2.1%), k (1.9%), Mg (1.2%), Mn (2.8%), Na (1.4%), Ni (1.1%), Pb (1.2%), Si (5.4%), Ti (3.8%) [107]

Notes: In the context of iron- and steelmaking, diverse waste materials are generated. However, this table exclusively focuses on the primary residues associated with each process. The quantities provided represent average production levels, accompanied by respective compositional details. In the case of the blast furnace and basic oxygen furnace route, the chosen waste is sludge enriched with iron, possessing a zinc concentration that is difficult for direct reutilization in the blast furnace. As for casting and rolling, the sludge exhibits a notable iron content along with a minor fraction of approximately 17% oil. For processes involving an electric arc furnace and direct reduced iron, the predominant waste identified is dust. Both types of dust are characterized by elevated levels of iron and zinc content.

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