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Review

Towards the Circularity of the EU Steel Industry: Modern Technologies for the Recycling of the Dusts and Recovery of Resources

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Abstract: The EU steel industry accounts for a crude steel production of 140 Mt/y, provided by the integrated (57%) and electric (43%) routes, which respectively require up to 6.0 and 0.6 MWh/$t_{CrudeSteel}$ of energy input, and emits on average 1.85 and 0.4 $t_{CO2}/t_{CrudeSteel}$. The mitigation of such CO_2 emissions is crucial, and would involve the direct avoidance of carbon, improvement of energy efficiency, and carbon capture. However, the environmental burden of the steel industry cannot be limited to this, given the very large amount (approximately 5 Mt) of residues landfilled every year in the EU. This practice cannot be sustained anymore, since it represents a detrimental waste of resources and burden to the environment. These aspects require prompt action to meet the Green Deal goals envisioned for 2030. This review paper aims to provide an overview of the main state-of-the-art technologies commercially (and not) available for the effective treatment of a wide variety of residues. To enrich this overview with further potential candidates towards a more sustainable steel manufacturing process, the combined application of two technologies (a plasma reactor and a RecoDust unit for the recovery of metals and minerals, respectively) at TRL 5-6 is also investigated here.

Keywords: steel; circular economy; sustainability; metal recovery; zinc recovery; landfilling; carbon emissions; synergy; slags; dusts; sludges; efficiency

1. Introduction

Given the unique mechanical properties, durability, workability, and cost, steel is one of the most diffused construction materials worldwide, reaching a global production rate of nearly 2 Gt per year [1]. Considering the EU, over 170 Mt of steel products were manufactured in 2022, with 57% and 43% of the overall production being carried out through the integrated (Blast Furnace-Basic Oxygen Furnace BF-BOF namely Iron&Steel Making, ISM,) and electrical (electric arc furnace EAF) cycles, respectively [2]. The main difference between the ISM and EAF routes, using a BOF and an EAF as crude steelmaking aggregate, respectively, is that the former implies the main use of hot metal (pig iron) as feedstock produced from iron ores by the BF process, whereas scrap iron is predominantly used for the latter. At first sight, it is evident that the EAF would have a lower impact on the environment with respect to the ISM, since no natural resources are subtracted

from the ecosystem [3]. However, both the processes require temperatures of 1600 °C and therefore are largely energy intensive, with the EAF and ISM requiring about 0.6 MWh/t_{CS} and 6.0 MWh/t_{CS}, respectively, and given the very high processing temperatures (approx. 1600 °C) required for the melting of the feed and the primary production of pig iron, which is the precursor of steel for both processes. Apart from the obvious carbon (CO_2) emissions deriving from crude steelmaking (on average 1.85 and 0.4 t_{CO2}, Eq per ton of crude steel produced via ISM and EAF, respectively, and accounting for about the 8% of the global CO_2 emissions) [4], for which several solutions are being investigated, for instance Carbon Capture & Storage (CCS) [5,6], CCS & Utilisation (CCUS) [7], and hydrogen-based metallurgy [8], the limited recycling rate of the resulting residues also represents a major obstacle towards the sustainability of the steel-making process [9]. In fact, over 30 kg of dusts and 230 kg of slag are generated per ton of steel produced in the EU-28, therefore accounting for over 5 Mt and nearly 40 Mt in 2022 only, respectively; coupled with the high contents of elements within (e.g., iron Fe, zinc Zn) such wastes, it is mandatory to find ultimate solutions for their complete recycling. However, the composition of both dusts and slags varies depending on the nature of the feed used in the route considered, the volatility of each single element considered, and the conditions are adopted in each given step. Table 1 below shows the average composition of BF, BOF, EAF, and LF slags (BFS, BOFS, EAFS, and LFS, respectively), and BF, BOF, and EAF dusts (BFD, BOD, and EAFD, respectively); we refer to [10] for an extensive overview about the morphological structure of the phases present in such streams.

Table 1. Average chemical oxide composition of BF, BOF, EAF, and LF slags, and BF, BOF, and EAF dusts. Source [11].
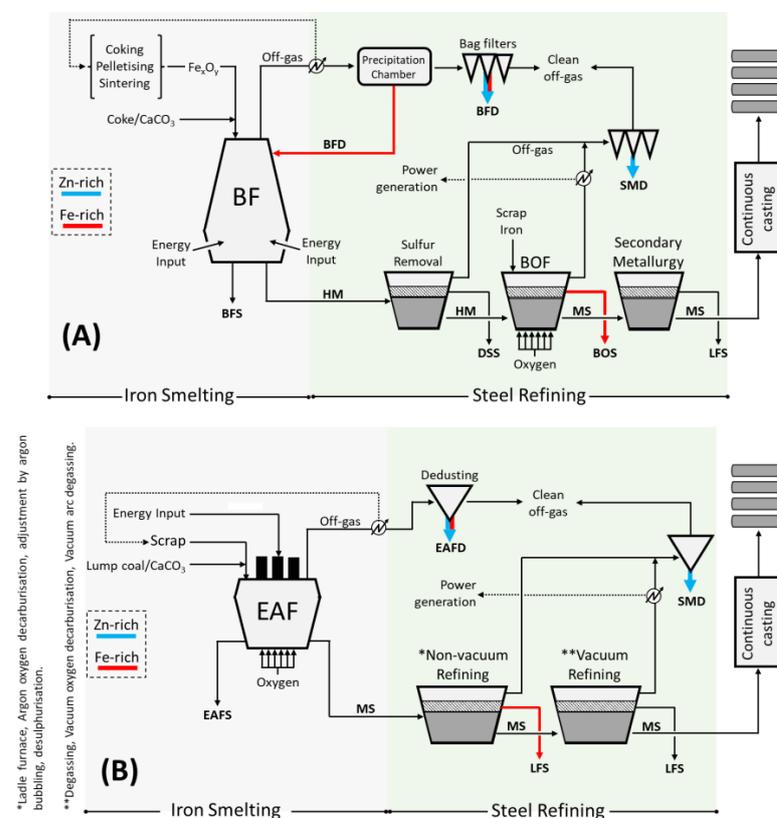
	CaO	Fe	SiO_2	C	Zn	Pb	Mn	Al_2O_3	S	P_2O_5	MgO	Others [4]
BFS [3]	42.0	0.4	35.1	-	-	-	0.7	11.5	1.4	-	9.0	2.7
BOFS	49.6	14.0	15.0	-	-	-	3.4	1.6	-	7.0	3.1	1.5
EAFS [2]	28.0	32.0	19.0	-	-	-	5.0	7.0	-	0.4	7.0	2.1
LFS	27.0	20.0	18.0	-	-	-	<0.5	8.0	<4	<0.2	10.0	<0.1
BFD	10.5	21.0	6.0	31.0	5.5	1.4	0.13	2.7	2.4	0.23	10.2	0.4
BOD [1]	14.9	57.6	-	1.9	3.1	0.3	-	-	0.3	-	-	<0.2
EAFD [2]	10.0	28.0	2.9	1.9	32.0	5.2	3.5	1.6	1.5	0.2	3.2	4.1

[1] The values expressed here are intended as a sum of the primary, secondary, coarse, and fine dusts. [2] The production of carbon/low alloyed steel was here considered. [3] A slag with a basicity of (CaO/SiO_2) >1 here was considered. [4] Others include: TiO_2, Cr_2O_3, Na_2O, K_2O.
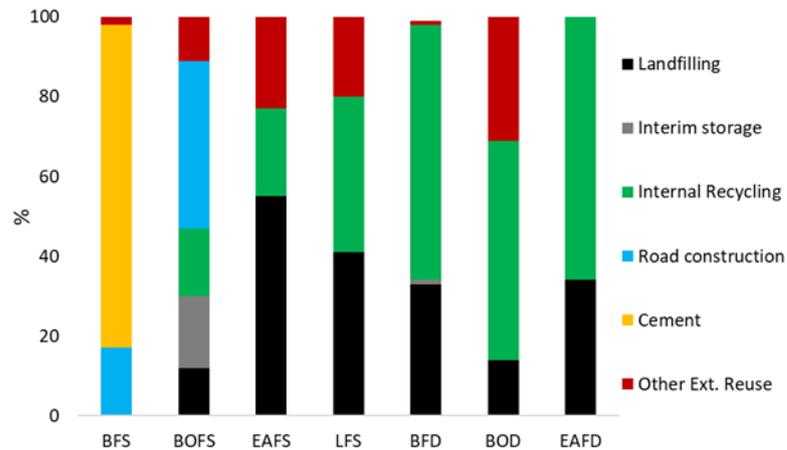
To highlight the source of each waste from both ISM and EAF routes, Figure 1 provides a clear picture of the situation, allowing to group the waste in accordance with the target elements to recover, in this case Fe and Zn.

In the ISM route, about 5–30 kg of BF Dust (BFD)/t_{CS} and up to 18 kg basic oxygen dust (BOD)/t_{CS} are generated [12]; such streams exit the units alongside the respective off gases, whose heat is first recovered through the appropriate exchanger. Following, such streams are conveyed into separated precipitation chambers. The coarse BFD is rich in FeO (up to 50%), and it is separated in the precipitation chamber as gravity dust (GD), which in most cases is recycled into the sinter unit; the remaining Zn-rich dust with finer grain size is then collected using the appropriate bag filters or, more commonly, the so-called Bischoff washers. Such dust cannot be recirculated into the BF since it would lead to technical difficulties related to the so-called zinc cycle [13]; therefore, it needs to be treated to (1) recover the high-value Zn, (2) and to re-use the remaining dust fraction, rich in C and Fe, into the sintering or the BF process. Therefore, the current approach mostly includes the treatment of such sludge through hydro cyclones which separate the coarser and finer fractions; the former is recycled into the sinter plant, whereas the latter, containing mostly of the zinc and lead, is mainly

landfilled. Even the dusts from the BOF unit are separated into coarse and fine dusts, with the former having a higher Fe total (up to 85%) and lower Zn (0.01–0.4%) contents than the latter (54–70% and 1.4–3.2% of FeO and Zn, respectively). It is worth mentioning, that a discrete amount of dust (up to 600 g per t of sinter) is also generated during the sintering step; such dust (SD) has a low zinc content, but a high alkali one, and therefore could be detrimental to the operation units of the plant. Even the dusts arising from other steelworks, i.e., BOF dust (BOD) and EAF dust (EAFD), present technical difficulties for their recycling, given the high Zn content (up to 9.4 wt.% and 27.0 wt.% in BOD and EAFD, respectively [10]); upon Zn removal, coarser dust is agglomerated and reused in the BF and BOF; however, large amounts of high-Fe dusts are still landfilled. On the contrary, no major difficulties limit the use of BF slag (BFS in Figure 1) in Europe; out of the 20.7 Mt of BFS generated in the EU in 2018 (over 35% of the total in Germany), the 80%, 18%, and 2% were used for cement and concrete production, road construction, and others, respectively [14]. Regarding the overall steelmaking slags (16.3 Mt in the EU in 2018), being 52.3%, 34.9%, and 12.6% from BOF, EAF, and others, respectively, only the 72.4% was reused as concrete aggregates (70.6%), fertilizer (13.1%), recycled raw material for metallurgical processes (10.5%), additive in hydraulic engineering (4.5%), and road construction (1.3%) [15]. Therefore, around 5 Mt of slag is currently landfilled every year in the EU, reflecting a large waste of potential resources. The overall picture just discussed, regarding the dusts and slags from the BF, BOF, EAF, and desulphurization units, is schematically presented below in Figure 2. As a clarification, whilst landfilling refers to the permanent disposal of the waste, by interim storage it is intended that such waste is stored onsite as an intermediate step; that is conducted for partial recycling purposes, prior to the permanent landfilling.

Figure 1. Simplified flow schemes of the ISM (**A**) and EAF (**B**) routes with focus on those steps where dust and slags arise; the waste rich in Zn and Fe are blue and red-arrowed, respectively. BFD, HM, DSS, MS, BOS, LFS, and SMS stand for Blast Furnace Dust, Hot Metal, Desulphurization Slag, Molten steel, Basic Oxygen Furnace Slag, Ladle Furnace Slag, and Secondary Metallurgy Slag, respectively.

Figure 2. Overview of the slags and dusts arising from the main units involved in the ISM and EAF processes, with related fate averaged in the EU-28; the scheme does not consider the dusts and slags arising from other secondary treatments apart from BOF and sulfur removal.

The environmental crisis we are facing requires prompt and effective action to maximize the energy and resources recovery from all of the high-impact and key sectors, such as the steel industry. For this reason, the achievement of an optimized circular system must be pursued, and the recovery of Fe and Zn assumes a crucial importance given the high CO_2 emissions and costs linked to the mining, processing, and transport of primary ores. While Fe has always been crucial to the development of the global population, the importance of Zn has been sharply increasing in the last century, and currently being the fourth most used metal worldwide after Fe, Cu, and Al. Steelmaking represents the biggest share in these terms, given that about 5.5 Mt of Zn is currently used in the galvanizing process in stainless steel production, therefore representing the half of the global (11 Mt) Zn production [16–18].

In the last three decades, large technological advancements have been made in terms of resources recovery and recycling by routes developed, which allowed for a partial residue recycling. These routes for the recovery of resources might be grouped as physical, hydrometallurgical, and pyrometallurgical processes. While the former technologies are generally simple and low cost, they present a partially poor efficiency in metals recovery, and therefore the products cannot be directly recycled; however, a physical pre-treatment is generally carried out prior to any other methods, to ensure a high final efficiency [19]. The hydrometallurgical routes (Ezinex [20], Zincex [21]) would allow for a higher efficiency and selectivity for a given range of metals, i.e., Zn, but the large amount of leaching agent needed reflects high costs and pollution, also leading to a final slag, which cannot be recycled [22]. Finally, the pyrometallurgical routes are energy intensive, since they need to ensure the smelting of the oxides considered. However, they are robust and generally characterized by a high efficiency of Zn and Fe recovery, as outlined in the discussion reported in the following sections [23]. Recent research widely investigated valid recycling options based on the association of hydrometallurgical and pyrometallurgical steps, to overcome the technical issues linked to the challenging leaching of zinc ferrite ($ZnFe_2O_3$) [24].
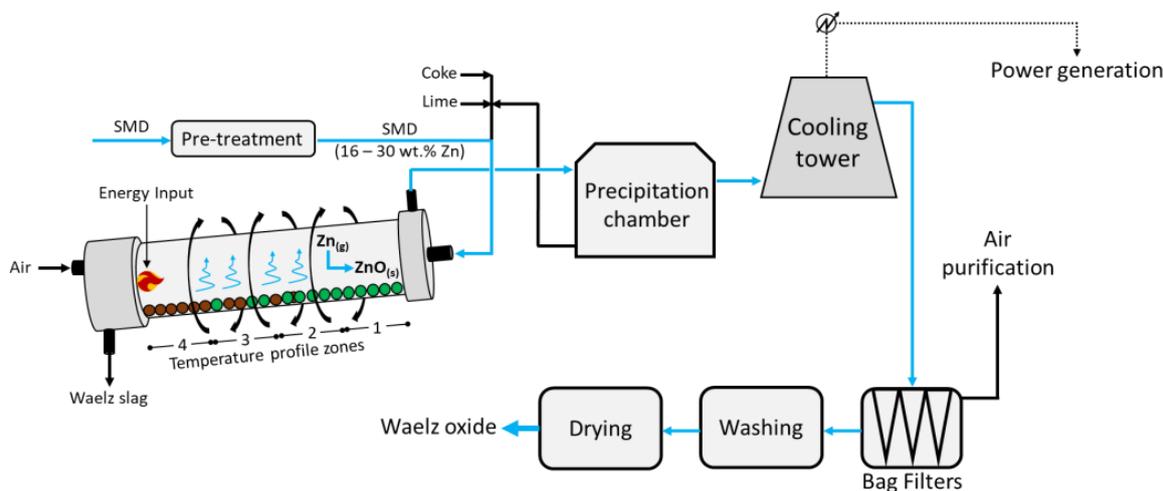
In this review, we focused on pyrometallurgical processes since they are currently the most spread and efficient route for Zn recovery at the industrial scale.

2. Pyrometallurgical Processes: State-of-the-Art

Several technologies have been recently investigated and, in some cases, fully applied to maximize the recovery of metals from the steelmaking slags and dusts, while keeping the energetic expenditure to a minimum; however, a satisfactory objective has not been achieved yet, and further research and investments are needed. The following sections list and describe in detail the most accredited routes for the individual or concomitant recovery of Zn (mainly present as ZnO and $ZnFe_2O_4$) and Fe from both steelmaking slags and dusts.

2.1. Waelz Kiln

The Waelz process is currently the most widely used method for recovering those dusts containing medium levels (16–30 wt.%) of zinc; the vast literature may be found about this technology and eventual improvements will be carried out [9,23–27], and a simplified flow scheme is reported in Figure 3 below.

Figure 3. Simplified flow scheme of the Waelz process, where those streams characterized by a medium-to-high Zn content are highlighted blue.

The feed, composed of pelletized Zn-rich dusts/coke/lime agglomerates, enters at the head of the rotating (~1 rpm) and 2–3% inclined Waelz kiln; despite the different designs, it is usually 50 m long with an inner diameter of about 3.5 m. The kiln has a precise temperature profile which is reported in Figure 3 as zone 1 (600 °C), zone 2 (1100 °C), zone 3 (1300 °C), and zone 4 (1000 °C). The feed occurs in the upper zone 1, whereas counter-current air is injected from the bottom (zone 4); here, the solids achieve a maximum temperature of about 1250 °C. Such operating temperatures fully depend on the chemical composition of the feed; in fact, while too low temperatures would hinder the reduction of zinc, too high values would lead to clumping and products with a lower surface area. In zone 1, the pre-heating and drying of the feed is carried out, while the higher temperature in zone 2 allows for the combustion of the coke, the Boudouard equilibrium (Equation (1)), and the reduction in Fe and Pb in the melt (Equations (2)–(5) below) [28].

$$C + CO_2 \rightarrow 2CO \tag{1}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \tag{2}$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \tag{3}$$

$$FeO + CO \rightarrow Fe + CO_2 \tag{4}$$

$$PbO + CO \rightarrow Pb + CO_2 \tag{5}$$

In zone 3, the reduction in ZnO to metal vapour Zn (Equation (6)) occurs, while zone 4 provides further thermal energy due to the combustion of the residual carbon in the charge, and the partial reoxidation of Fe occurs.
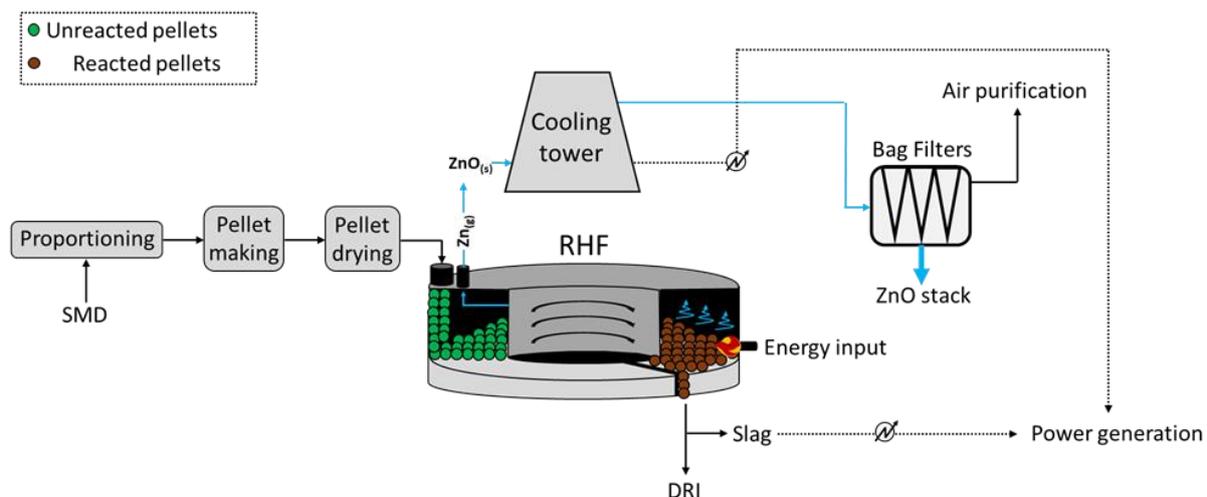
$$ZnO + CO \rightarrow Zn + CO_2 \tag{6}$$

Finally, the vapor metals Zn and Pb are oxidized back to ZnO and PbO, respectively, and exit the kiln from zone 1 at around 700 °C, pre-heating the feed, while the Waelz slag is collected at the bottom of zone 4. Following, the gaseous mixture vented from zone 1 enters a precipitation chamber where coarse dust with medium Zn contents is collected at

the bottom and is recirculated into the kiln alongside the fresh feed. The resulting vapors then undergo cooling to about 200 °C and enter the bag filters, from which a dust rich in Zn is collected at the bottom and air leaves at the top and is further purified. Finally, the solids are washed, dried, and high-purity ZnO is obtained.

Despite the large treatment capacity and the relatively good economic return, the main disadvantages are represented by the medium-to-high Zn content (16–30 wt.%) required in the feed, the additional flux (CaO or MgO) needed in the feed to prevent ring formation in the kiln, which leads to a higher gangue content in the slag, and a large amount of Waelz slag (approximately 80% in mass of the total products) still contaminated with Zn and Pb (and therefore mainly landfilled without recovery of these valuable metals, therefore excluded from material cycles). Given the coke consumption reported in the literature (0.4 t_{Coke}/t_{EAFD} [29]), the emission factor of 3.3 t_{CO2}/t_{Coke} and the heating value of 8.3 MWh/t_{Coke} [DIN EN 19694-2], the Waelz process emits about 1.2 t_{CO2} and consumes up to 3.0 MWh for each ton of EAFD processed. The coke making process is excluded here from this energy and carbon balance, carried out via the CSN EN 19694-2 [30].

2.2. Rotary Hearth Furnace (RHF)

The RHF process is widely used to process dusts for the recovery of Zn and Pb, while generating a secondary stream of direct reduced iron-DRI [31] to be reused in the steelmaking process [32–34]; an overview of the main operational units and material flows is depicted below in Figure 4.

Figure 4. Simplified flow scheme of the rotary hearth furnace (RHF) process, where those streams characterized by a medium-to-high Zn content are highlighted blue.

As a representative of advanced design, the commercially available reheating furnaces from Tenova [35] may process up to 250 t/h of billet/blooms, with a diameter and length ranging between 0.2–0.45 m and 1.4–5.5 m, respectively. The RHF would occupy a large portion of the steelwork, given the average diameter of the furnace at 45 m and more; it generally requires the supply of 5.5 MWh (of which 4.2 MWh is from coal combustion) and this leads to the emission of 1.3 t_{CO2} per ton of DRI obtained [32], calculated through the CSN EN 19694-2 standard.
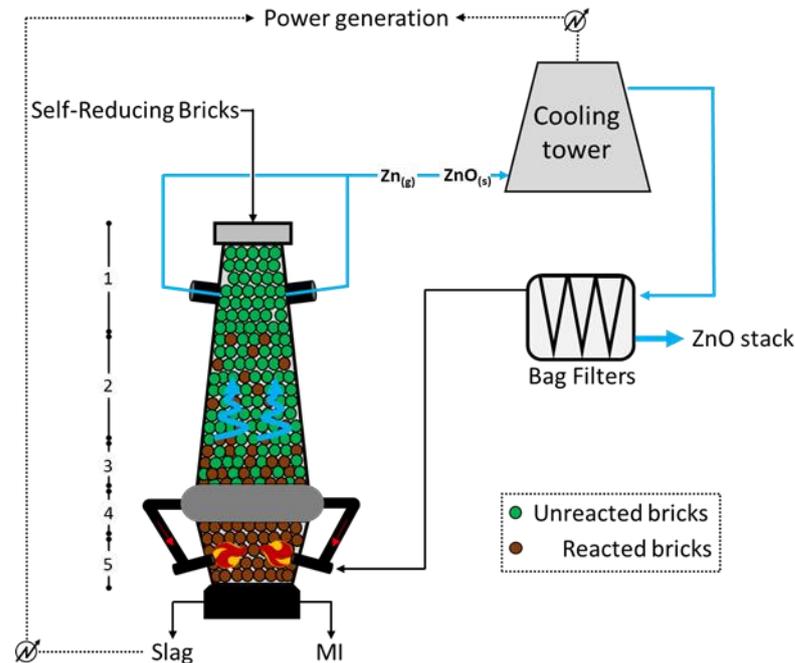
As reported, the process is composed of five main steps, such as the proportioning of the feed, i.e., dusts, reducing agent (coke), and a flux (CaO), pelletization, iron direct reduction, flue gas treatment, and Zn recovery. Prior to RHF, the Zn-rich dusts and sludges require a pre-treatment which mostly depends on the moisture of the materials. The low-to-medium moisture dusts and sludges are easy to treat, whereas those with high moisture imply technical (formation of rigid and free-of-deformations agglomerates) and economic (efficiency of the water removal) issues [33].

To ensure the homogeneous heating of the pellets within the circular furnace, these are inserted evenly on the belt conveyor, where the direct reduction in iron occurs at 1250–1300 °C at a residence time ranging between 10 and 20 min. Such DRI may be returned to the steelwork process upon pre-treatment. At the same time, the zinc oxides in the feed are reduced and Zn vapors are released and conveyed towards a heat exchanger at first, where energy is recovered in the combustion air, and the oxidation of Zn occurs upon contact with cooling air. Following, such stream is conveyed to bag filters, which allow for the collection of Zn-rich (40–70 wt.% ZnO) coarse dust.

Overall, the RHF process is an effective method to recover Zn and Fe from dusts, since it operates at a lower energy intensity, with respect to the Waelz process, and therefore reflects a lower environmental burden. However, despite the relatively simple functioning and low maintenance needs, the large equipment area needed for the operations and the high initial investments represent significant obstacles for its application, therefore requiring further implementation.

2.3. OxyCup Furnace

The pyrometallurgical OxyCup process also allows the recovery of Zn from dusts and other streams from traditional (both ISM and EAF) steelwork industry, while separating and valorizing the iron present in the feed to recirculate it for steel production [36]. It was developed by the company Kuttner GmbH & Co. [37] and realized at industrial scale by Thyssen-Krupp Steel in 2004 in Duisburg, where up to about 500 t/d of agglomerated ferrous dusts and sludges are currently recycled. In China, TISCO erected a double OxyCup plant in 2011 for the treatment of stainless-steel dusts, sludges, and skulls, generating about 850 tHM/d [38]. The crucial unit of the process is an oxygen-enriched cupola furnace, similar but smaller than the traditional BF used in the ISM cycle. It is fed with self-reducing bricks appropriately assembled from sludge, dust, and scale residues, with an iron content of around 45 wt.%. To ensure an effective reducing action of the bricks, a relatively high carbon content (~15 wt%) is introduced in the bricks upon manufacturing with water and cement, therefore including discrete amounts of flux agent (CaO around 10 wt.%); the bricks are fed together with desulphurization skulls, BOF skulls, coke, and gravel. The brick-making process is of crucial importance for the successful operation of the OxyCup; it implies the coordinated action of three main sections, which imply the handling of the materials into the respective silos, the material dosing through the use of a vibrating press, and the curing/hardening of such bricks prior to feed. The overall scheme of the process might be observed in Figure 5 below, which highlights the path of Zn in the input and output materials [36]. The lowest section of the furnace (section 5 in Figure 5) is filled with the reducing agent, generally coke, to allow the achievement of high temperatures (up to 2500 °C) through hot blast injection via water-cooled lances at both sides of the unit. The annular chamber between sections 4 and 3 (at temperatures of 1800 °C and 1400 °C, respectively) collects part of the exhaust gases arising from the combustion at the bottom, retaining most of the unburned/partially burned ash and re-injecting it at the level of the lances; doing so, a smoke-free upper section is ensured. The reduction in Fe, Zn, Pb, and alkalis starts in section 2 (approximately 1000 °C; while the molten metal descends the furnace, the Zn (blue highlighted) and the Pb metal vapors climb the unit and leave it in zone 1 (around 300 °C). Such gas is firstly water scrubbed and then interacts with air to convert metal the Zn to ZnO, which is finally separated though the action of opportune bag filters, from which one part of the combustion air is recirculated, and another part is further processed and released to the atmosphere. With respect to the BF operation, the Oxycup furnace implies a hot blast at a lower temperature (around 650 °C) but with higher oxygen content (generally 30 vol.%), allowing for a higher energy efficiency. Moreover, the molten iron (MI) and the slag at the bottom are continuously tapped and separated through a siphon unit.
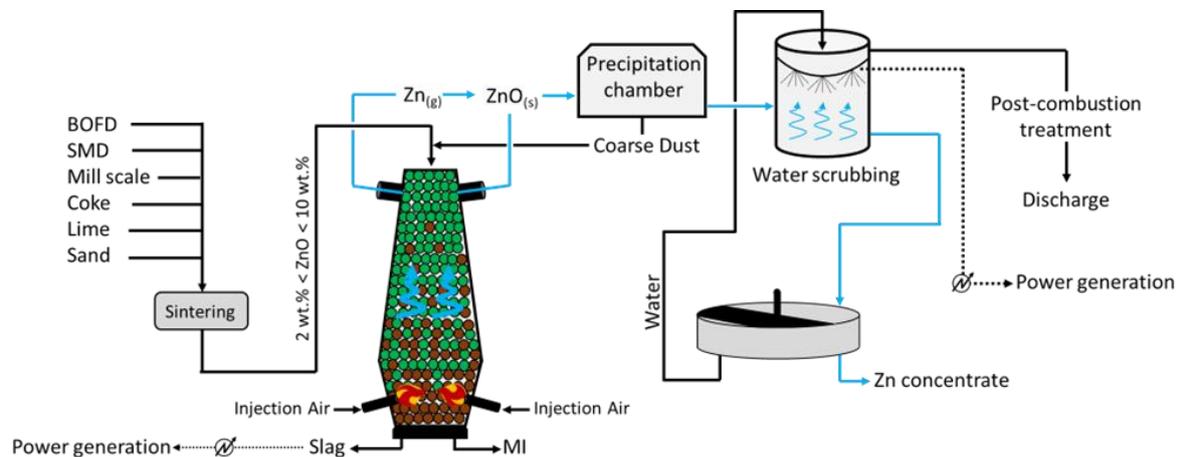
Figure 5. Simplified flow scheme of the Oxycup process, where those streams characterized by a medium-to-high Zn content are highlighted blue. MI stands for Molten Iron.

The OxyCup is very flexible, ideally allowing for a 100% feed of bricks, with an iron content ranging between 40 and 50%; the sludges arising from the treatment of the dusts are relatively rich in Zn (30%), and therefore further treatable. Limiting the balance solely to the coke consumption, the OxyCup process consumes about 0.3 tcoke/tHM, therefore resulting in 1.1 tCO_2 emitted and 2.8 MWh consumed per ton of HM recovered (calculated through the CSN EN 19694-2 standard).

2.4. DK Process (Shaft Furnaces)

The DK process (Figure 6) was first applied by the company DK Recycling and Roheisen in Duisburg (Germany); it implies two smaller-scale BF units of different volumes (580 m^3 and 460 m^3, with an output capacity of 1000 and 500 tHM/d, respectively), alternatively operated and opportunely designed to treat a precise quality of feed. In fact, the residues treated are significantly rich in Fe and Zn (up to 60 wt.%), with the raw material mix being generally composed of BOFD (52.5%), mill scale (12.8%), iron ore (7.6%), BF sludge (5.4%), BOF sludge (5.0%), and others (16.3%, including coke breeze and sand) [39]. Apart from the Zn- and Fe-rich steel streams, i.e., BOD, mill scale, and other raw materials are selected to ensure the generation of resistant (lime and quartz) pellets, which would promptly ignite (coke). To do so, such solids firstly undergo a high-temperature sintering process and then they are fed to the furnace for smelting. The charge is fed at the top of the furnace, while the blast is applied through two tuyeres at the bottom of the unit. The temperature of the gas decreases towards the top of the furnace (approximately 300 °C), while the system achieves values above 1800 °C at the bottom, where strongly reducing conditions are also obtained. The slag and liquid metal (MI) are collected at the bottom of the unit, while the off gas, together with the reduced Zn in a vapor state ascend the furnace and are oxidized (Zn (g) + CO_2 (g) → ZnO (s) + CO (g)) prior to being conveyed in a precipitation chamber where coarse dust, still with small contents of Zn and Fe, is collected and recycled at the top of the furnace. The Zn-rich finer fraction leaving the precipitation chambers undergoes water scrubbing, during which ZnO dissolves and is collected in the liquid stream at the bottom of the unit. Apart from removing Zn from the gas phase, heat is also recovered and used to internally produce power. The remaining of the gas is finally discharged to the atmosphere upon further post-combustion treatment, aimed to

remove traces of heavy metals and CO_2. Finally, the Zn-rich liquid stream arising from the scrubbing is concentrated in a thickening unit, and a 65–68 wt.% Zn pulp is separated from the water, which is reused for water scrubbing.
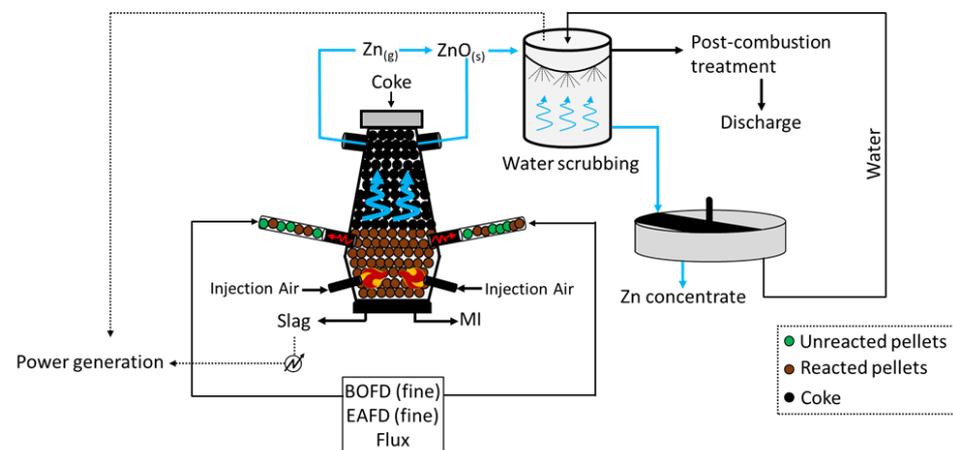

Figure 6. Simplified flow scheme of the DK process, where those streams characterized by a medium-to-high Zn content are highlighted blue.

Given the robust technology and the high feasibility in terms of retrofitting with the pre-existing steel plants, the application of the DK process looks promising, also considering the concentrated Zn, which may be obtained. However, the process has a high carbon footprint (about 2.5 tCO$_2$/tPigIron [40]) together with the frequent maintenance needed in the furnace to prevent blocking and malfunctioning linked to the significant Zn and alkali contents, represent the main drawbacks of such technology.

2.5. Coke-Packed Bed Furnace

The coke-packed bed process is a melting–reduction pyrometallurgical process developed by Kawasaki Steel Corp., which is used to recover Zn and Fe from steelmaking (EAF and BF/BOF) dusts. Originally, such smelting reduction process was applied to the production of ferro-alloys from fine ores [41], but it has been differently evaluated given the possibility of (1) directly using fine raw materials without agglomeration, (2) recovering nearly the whole zinc and lead contents, (3) and avoiding waste at all [42]. The overall flow scheme is reported in Figure 7, where the path of Zn is highlighted blue. As reported, the upper part of the furnace is packed with coke, which is continuously fed from the top. It ensures the effective reducing power necessary for the reduction in the oxides by descending the furnace and combusting. However, the substantial difference, with respect to the other furnace-based processes, is that here the feed is in powder form; therefore, the energy emissions related to the sintering operations can be avoided. Overall, four tuyeres are used in this configuration, all located in the bottom section of the furnace; while the bottom ones allow for the insertion of the blast, sustaining the combustion, the upper ones allow the entrance of the feed. This configuration allows for the achievement of high temperatures (1600 °C) and reducing conditions in the region located between the upper and bottom tuyeres, leading to the partial melting of the oxides even before entering the unit. As for the previous processes, the metals with high boiling points will melt and descend the unit, being collected as liquid iron (MI) or slag [43], whereas those with low boiling points, i.e., Zn, will pass to the vapor phase and will exit the unit at the top together with the off gas. Such gas stream is firstly oxidized, and therefore Zn vapor passes to ultra-fine ZnO dust, and enters a water scrubbing unit which promotes the dissolution of ZnO in water and its removal from the gas phase. Heat is also recovered at this stage, since the off gas leaves the furnace at around 700 °C, and power can be produced for internal use;

prior to discharge, the gases are finally pre-treated, while a Zn concentrate can be obtained from the liquid stream processed in the thickening unit.

Figure 7. Simplified flow scheme of the coke-packed bed process, where those streams characterized by a medium-to-high Zn content are highlighted blue.

This process allows for an effective separation of Zn from Fe and a high recovery rate, without the need to significantly pre-treat the feed; however, the process uses large amounts of coke (1.1 tCoke/tHM), resulting in significant energy consumptions (8.9 MWh/tHM) and carbon emissions (3.5 tCO$_2$/tHM) [42] (calculated through the CSN EN 19694-2 standard). The replacement of coke with biomass could allow for the mitigation of such carbon emissions; however, clumping issues might severely affect the functioning of the unit [44].

2.6. Other Processes

Primus [45] is a direct reduction process for treating EAFD. The primus process is suitable for treating metallurgical solid waste with zinc containing more than 5 wt.% and recovering valuable metals, such as BFD, BFS, BOD, EAFD and sludge, or dust generated by small rolling mills. The main feature of this process is to use multi-hearth technology. Primus's reaction furnace consists of cylindrical chambers with multiple stacked annular compartments to form a multi-stage furnace.

Romelt's [46] process for ironmaking is a smelting reduction process to produce hot metal. Romelt's process can treat any iron containing material, e.g., iron ore fines and concentrates, BF and BOF dusts and sludges, mill scale, iron bearing slags, scarfing wastes and turnings, and iron dusts etc. Romelt's process employs single-stage smelting reduction technology for the production of hot metal. The process utilizes non-coking coal for the reduction of oxides.
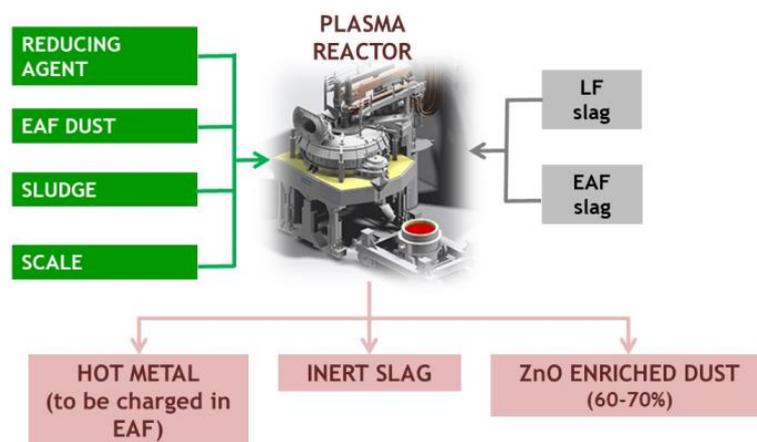
3. Novel Routes for the Recovery of Fe and Zn

As reported in the previous sections, multiple solutions have been recognized to have a high potential to maximize the recovery of elements from the steel industry wastes; however, technical and economic challenges still need to be assessed, and further technological advancement must be pursued. This might be performed by enhancing the efficiency of these affirmed routes, or by developing novel ones, which have not been fully recognized as potential leading technologies. Differently from the previous designs, the following configuration reported does not aim to recover Fe and Zn in one step, but it intends to recover it separately and maximize the removal efficiency and rate.

3.1. Recovery of Fe: Plasma Reactor

A plasma reactor is based on the collisions between gas molecules and electrons, to generate excited and highly unstable ionic species with high energy; the electrical energy is generally supplied through three graphite/tungsten-based electrodes, which generate an

electric arc for EAF. Usually, the full operation of the plasma is preceded by a stabilization of the flame under an Ar flux. It is widely accepted that the application of plasma technology to the steel industry would lead to lower costs and environmental impact, given the higher calorific power, which may be obtained at parity of the reducing agent source. For this reason, the plasma technology might also be applied to the recovery of iron from steelworks wastes, to minimize the expenditure associated with the resource recovery; here, the metal recovery is attempted through an opportunely engineered twin Ladle Furnace design, functioning with a traditional electric arc. This technology would be feasible for the processing of a wide range of feeds, including slag, scale, dust, and sludge from the steel industry, as well as other streams containing heavy metals (V, Mn, and Co), and Si-based ones; moreover, alternative and more sustainable reducing agents might be used, such as biomass, waste polymers, petrochemical residues, and hydrogen. The plasma reactor could be fed with a large variety of raw materials, and the output will be obviously varying in correlation with that; for instance, if BFD and EAFD, with high Fe and Zn contents, are fed to the plasma reactor, the outputs will be molten iron, mineral slag, and a gas/dust stream rich in Zn, therefore requiring further treatment for a full resource recovery. That would be in line with the state-of-the-art technologies investigated above, but the lower energy consumption and environmental impact associated with the use of plasma energy could allow the exploitation of this process solely for the recovery of iron, whereas Zn could be obtained separately in another process, starting from different raw materials and from the dusts arising from this step. Under this light, the ideal candidates would have high Fe contents, i.e., rolling mill scale, sludge from cooling water circuits, EAF/BOF dusts and slags; an overview of a generic plasma reactor-based process is reported in Figure 8 below. The C-source, labelled as Reducing Agent in Figure 8 will be coal and natural gas, or more sustainable fuels with lower to zero environmental impact, such as plastics, tires, and biomass, which need to be opportunely treated to make them feasible to the scope. The plasma reactor would allow for temperatures up to 2000 °C with minimal energy consumption, and the outputs would be MI to be directly reused into the steelmaking process, and molten slag rich in minerals, which must be somehow valorized. In these terms, the cooling rate might play a crucial role for its application into the cement industry. The temperature of the reactor walls is constantly monitored and cooled down by water circuits at the bottom, i.e., where the charge melts, and at the top, i.e., where the flame is formed. Relatively high Fe reduction rates can be achieved (1–6 kg Vol.%Fe^{-1}·min^{-1}), and faster operations could be achieved by increasing the potential and therefore the processing temperature.
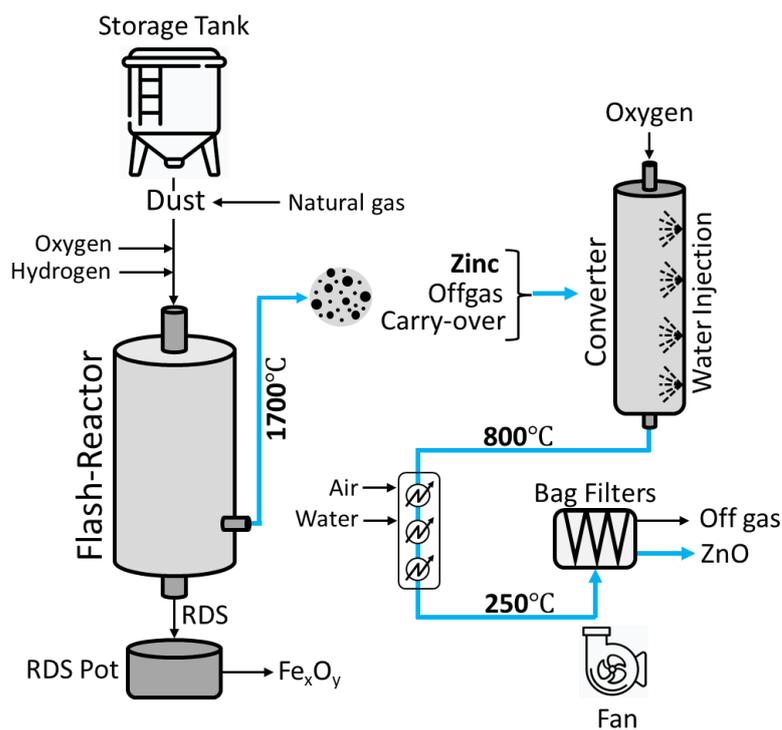

Figure 8. Simplified scheme of the plasma reactor-based pyrometallurgical process, including the input and output streams.

The use of the plasma reactor for the recycling of resources from steelwork residues is currently under implementation during a Horizon EU-funded project (ReMFra, proposal

No. 101058362), aiming to demonstrate the achievement of a TRL8 at Tenaris Dalmine steelwork (Dalmine, Italy). With this regard, the industrial process is designed to work in a semi-batch mode with the continuous supply of FeO into the slag with the fed material, together with reduction agent and, if necessary, with slag forming. The slag is periodically tapped, while the liquid metal is tapped at the end of the complete processes, indicatively every 3 h. The ReMFra plant is based on a modified Ladle Furnace (LF) system. LFs are usually designed to increase the melt temperature up to 5 °C/min and they are equipped with a water-cooled roof of either direct or indirect suction (controlled atmosphere) type, as well with other related facilities, such as wire-feeding machines and powder injection systems. The envisioned capacity of charge residue material based on available electrical power is 15 t/heat, which could fulfil the needs of a steel plant with the same production capacity as Tenaris Dalmine (~1 Mt/y).

3.2. Recovery of Zn: RecoDust Process

The RecoDust process is a recent pyro-metallurgical treatment for different kinds of steel mill dusts, especially BOFD, aiming for the recovery of highly pure ZnO, called Crude Zinc Oxide (CZO), and the generation of the iron rich RecoDust slag (RDS), which may be recycled into the ironmaking process (sintering plant, BF, or possibly direct reduction). The process, whose flow scheme is reported in Figure 9 below, allows for high processing temperatures (1700–1900 °C) within the central part called Flash-Reactor, fueled by a natural gas oxygen burner. Also, the use of a natural gas–hydrogen admixture as fuel gas is possible.

Figure 9. Simplified scheme of the RecoDust (RD) process based on [47], including the input and output streams, such as the RecoDust Slag (RDS).

The feedstock in the pilot plant is blown pneumatically with natural gas as conveying media directly into the burner flame; therefore, resulting in extremely high heating up and reduction kinetics allowing for a selective and efficient separation of Fe and Zn. Natural gas is used as both the fuel and reducing agent (there is no need for an additional solid reducing agent), therefore reflecting a lower carbon burden when compared to coke-based pyrometallurgical processes. The reducing conditions are ensured by an air excess ratio below 1, which leads to the reduction of ZnO or zincferrit to metallic zinc; at such

temperatures, zinc volatilizes alongside other species within the dust, i.e., lead and halogens, and it is therefore separated from the non-volatile ones, i.e., Fe, Mg, Ca, Si. The slag phase (RDS) is tapped from the bottom of the Flash-Reactor into a slag pot, whereas Zn conveys towards the upper section of the reactor with the off gas (including halogens) and the carry over, i.e., non-volatiles containing slag particles. The next process step resembles a converter (post-combustion), in which a pure oxygen stream is used to convert all of the reduced species and the unburned species into stable oxide phases. The injection of water simultaneously cools down the process gas to ~800 °C. Afterwards, a further quenching (three units of water/air cooling) is carried out to achieve a final temperature of about 250 °C. Finally, the cooled gases can be safely passed through bag filters for the separation of the Zn-rich dust (CZO), while the cleaned off gas is discharged to the atmosphere.

Overall, the RecoDust process presents obvious advantages with respect to the Waelz route, or the other coal based treatment solutions like DK or OxyCup, such as the use of natural gas rather than coke and therefore leading to lower carbon emissions, the possibility of switching to hydrogen-based designs, the absence of any pre-treatments for the dust, the generation of no waste, and the possibility to treat dusts with Zn content below 20 wt.%. Furthermore, the compact plant size allows for easier integration at the steel plant.

4. Conclusions and Recommendations

The achievement of a fully circular steel industry is mandatory to meet the environmental goals set in 2015 and more recently confirmed during COP26 and COP27 for the European community. In fact, the full recovery of Fe and Zn from steelwork residues would significantly lower the environmental burden of the manufacturing process due to the reuse of the metals as secondary raw materials. In detail, the carbon emissions linked to the mining, transportation, and preparation of the raw materials would be avoided, whilst minimizing the surface destined to the landfilling of such resources. Scientific and technological advancements have been pursued in the last three decades in these terms, with the Waelz process in the frontline to contrast the deleterious landfilling trend. However, the process is expensive, and the efficiency associated does not allow for a full recovery of resources, therefore discouraging its application given the limited advantages from an economic point of view. To stimulate the steel manufacturers to adopt a recovery route to avoid landfilling and further mining, a more economical and efficient process should be considered. Under this light, a series of alternatives have been arising recently, outlining the potential of such approach and the wish to achieve a circular economy steel industry. However, despite the clear advancements that could be observed, a maximized recovery of resources and full technical feasibility are not a reality yet; in fact, Table 2 below reports high values of CO_2 emissions and energetic consumption of the most diffused pyrometallurgical processes for the recovery of Fe and Zn.

Table 2. Summary of the average CO_2 emissions and energy consumption for the Waelz kiln, rotary hearth furnace, OxyCup furnace, DK process (Shaft furnace), and coke-packed bed furnace, normalized per ton of product, respectively being tEAFD processed, DRI obtained, hot metal recovered, Pig Iron, and hot metal obtained.

	CO_2 Equivalent	MWh
Waelz kiln	1.2	3.0
Rotary Hearth Furnace	1.3	5.5
OxyCup Furnace	1.1	2.8
DK process	2.5	N/A [*]
Coke-Packed Bed Furnace	3.5	8.9

(*) Not Available.

Therefore, the need for a continuous effort towards novel routes and potential solutions is clear, to set a wider range of possibilities to adopt and adapt to the pre-existing operations.

A pyrometallurgical approach based on the use of a plasma reactor and Recodust technology for the recovery of Fe and Zn, respectively, could be the key to achieve the goal of being part of the ReMFra research project funded within the Horizon Europe framework program (Clean Steel Partnership). In fact, the technologies have been demonstrated to be more efficient, more sustainable, and more effective than the state-of-the-art Waelz process. In fact, plasma technology avoids significant CO_2 emissions while ensuring a competitive source of energy using natural gas rather than coke. The operating conditions would allow for the switch to more sustainable options, i.e., waste plastic, biomass, than coke as a reducing agent. Considering that the electricity needed to generate the plasma could fully be retrieved from renewables, i.e., concentrated solar power, wind, or hydrogen, the overall carbon burden of the plasma reactor could be abated. Moreover, the pig iron obtained could be directly fed to the EAF or BF, to avoid the energetic expenditure necessary for the heating and melting of the feed. As for the recovery of iron, the removal of Zn through the RecoDust process would have obvious advantages when compared to the Waelz process, whose slag must be landfilled representing over 80% of the total solid products. The zinc removal efficiency of RecoDust was attested to be nearly total (~98%). Compared to the Waelz process, the RecoDust technology uses natural gas instead of coke as a reducing agent. Therefore, CO_2 emissions can also be reduced significantly. Furthermore, the use of hydrogen as a reducing agent within RecoDust is possible, which would lead to a CO_2-free recycling process.

Despite the investment costs associated with the building of the plasma and RecoDust process, units would likely be high, the steel plant could be easily retrofitted to accommodate these extra steps, abating the overall installation costs. The advantages in terms of resource recovery and CO_2 emissions avoidance (with a current carbon tax of 85 €/tCO_2) could overcome the risks associated with the investment, putting these alternative routes in the frontline towards the achievement of the circularity in the steel industry.

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