

Review

Reuse and Recycling of By-Products in the Steel Sector: Recent Achievements Paving the Way to Circular Economy and Industrial Symbiosis in Europe

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Abstract: Over the last few decades, the European steel industry has focused its efforts on the improvement of by-product recovery and quality, based not only on existing technologies, but also on the development of innovative sustainable solutions. These activities have led the steel industry to save natural resources and to reduce its environmental impact, resulting in being closer to its “zero-waste” goal. In addition, the concept of Circular Economy has been recently strongly emphasised at a European level. The opportunity is perceived of improving the environmental sustainability of the steel production by saving primary raw materials and costs related to by-products and waste landfilling. The aim of this review paper was to analyse the most recent results on the reuse and recycling of by-products of the steelmaking cycles as well as on the exploitation of by-products from other activities outside the steel production cycle, such as alternative carbon sources (e.g., biomasses and plastics). The most relevant results are identified and a global vision of the state-of-the-art is extracted, in order to provide a comprehensive overview of the main outcomes achieved by the European steel industry and of the ongoing or potential synergies with other industrial sectors.

Keywords: by-products; circular economy; industrial symbiosis; reuse; recycling; steel industry

1. Introduction

The increasingly stringent European regulation and the ever-higher disposal costs currently affect manufacturing industries, leading them to strengthen their efforts in order to improve the recycling rate of their by-products and waste [1]. Iron- and steelmaking by-products result from the processes producing steel by two main routes: the iron ore-based steelmaking and the scrap-based steelmaking. In total, 70% of the world steel is produced utilising the first one, based on Blast Furnace (BF), where iron ore is reduced to pig iron, which is afterwards converted into steel in the Basic Oxygen Furnace (BOF). Input of this route are mainly iron ore, coal, limestone and steel scrap. Through the second route, mainly based on the Electric Arc Furnace (EAF), 30% of the world steel is produced, using scrap steel as input as well as electricity as energy source. Other raw materials can often be used, such as Direct Reduced Iron (DRI) and pig iron.

During the iron- and steelmaking processes, several by-products are produced, such as slags, dusts, mill-scales and sludges. By providing some figures on the by-product productions, on average,

for one tonne of steel 200 kg (in the scrap-based steelmaking) and 400 kg (in the iron ore-based steelmaking) of by-products are produced [2].

Slags represent the iron- and steel by-products, which are produced in the greatest quantity with a worldwide average recovery rate from over 80% (steelmaking slag) to nearly 100% (ironmaking slag). They mainly contain silica, calcium oxide, magnesium oxide, aluminium and iron oxides. Slags derive from the smelting process, where some fluxes (e.g., limestone, dolomite, silica sand) are introduced to the different furnaces, such as BF, BOF, EAF. Slags tasks include removing impurities, which are present in iron ore, steel scrap and other feeds, as well as protecting the liquid metal from oxygen and maintaining temperature inside the furnace. The slag density is indeed lower than that of liquid metal and this implies the slag itself floats over the metal surface, hindering the contact of the steel with an external atmosphere. Finally, the difference of density between slag and molten metal facilitates the slag removal at the end of the process. During the iron- and steelmaking processes, dusts and sludges are also produced. In particular, sludges derive from dust or fines in different processes, such as steelmaking and rolling, and they contain a high moisture percentage. Dusts and sludges are collected in the abatement plants, equipped with filters. After they are removed from the gases, they contain high amounts of iron oxides and also carbon, which can be used for internal purposes [3]. On the other hand, iron containing residues which are not internally recycled can be externally sold and used by other sectors, in different applications, such as Portland cement or electric motor cores. Mill-scales is mainly produced during the continuous casting and rolling mill processes in oxidising atmospheres. Iron oxides layer is formed at the surface of steel. It can be reused as a raw material in the sintering plants as well as for briquettes and pellets. Finally, iron- and steelmaking gases are mainly coke oven gas, BF gas and BOF gas. Usually they are cleaned and they are internally used (or externally sold), in order to produce steam and electricity, providing between 60% to 100% of the plant power [4].

The emerging concept of Circular Economy (CE) has driven several industrial sectors to cooperate in the reuse and recycling of by-products in order to globally reach the ambitious “zero waste” goal. On this subject, significant efforts and commitments are undertaken within both European and worldwide activities. In particular, the European steel industry, in order to increase its competitiveness, is committed to introducing innovative actions on high performance products and to increasing process efficiency, by also reducing its environmental impacts [5–8] (see Figure 1).

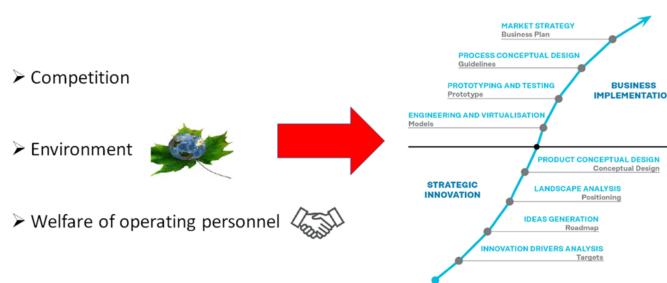


Figure 1. Circular Economy for a cleaner industry.

This strategy needs further investigations in different conditions for new implementations [9], such as the recycling method of red mud, comprised of the carbon-bearing red mud pellets roasting in the rotary hearth furnace and smelting separation in the EAF [10]. Furthermore, the development of new technologies aims not only at reusing by-products in manufacture of conventional products but also at converting them into new products [11], through new destination of secondary materials in a CE perspective, subtracting large quantities of them from the destination to landfills and saving extraction of new raw materials [12]. The previous examples show the role played by the steel sector in the CE context, based on the 4 “R” [13,14]: Reduce, Reuse, Recycle and Restore. Some aspects of this approach are shown in Figure 2. Reduce represents the concept based on avoiding or minimising the environmental impact. Reuse concerns the internal recycling of by-products, such as the sludges reuse (through the thermal technologies, eliminating or reducing its Zn content) as well as the slag reuse

(focused on the lime content reduction, resulting in its direct recycling). The Recycling concept concerns also the creation of Industrial Symbiosis (IS), which aims at developing the synergies among different sectors, identifying new business opportunities for underutilised resources outside the boundary of the production chain [15]. Through the IS concept implementation, by-products from one sector (e.g., the steel industry) can be valuable inputs to other sectors. Restore mainly involves the impact reduction of steel products. For instance, currently, for every tonne of CO₂ produced during the steelmaking process, six tonnes of CO₂ are saved during the application of the steel product. However, the aim of the steel sector is to achieve further improvements in the impact reduction of its products [16]. Indeed, these results do not represent total aspects of novelty in this sector. For instance, the main by-product, slag, is currently internal partially recycled (due to its high content of valuable elements, such as iron) or applied in different fields (e.g., cement production, road building and restoration of marine environments), according to the national legislations. However, there are further potential applications of the steelworks by-products [2], both inside and outside the steel production cycle [17]. Over the last few decades, iron- and steelmaking by-products recovery and use have led to a material efficiency rate of 97.6% worldwide. For instance, in 2013, 81% of production residues in the steel company ArcelorMittal were reused or recycled as by-products, and only 9% went to landfills. On the other hand, in 2013 24% of residues produced in its mining activities were disposed in landfill [18].

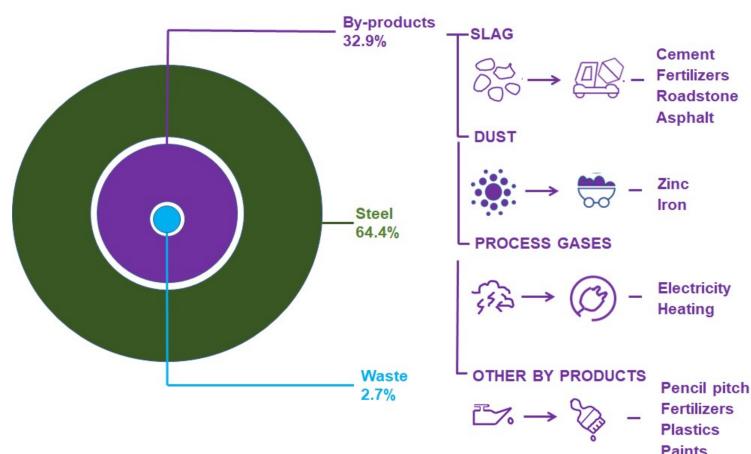


Figure 2. Reuse of steelmaking by-products.

In order to achieve better results, over the last few years, both industries and academic researchers have undertaken several initiatives and activities in order to apply new approaches and techniques aiming at by-product management finalised at increasing their recycling. For instance, the internal recycling of some by-products in the pelletization process has been recently investigated, taking into account achieving a high quality of pellets and reducing environmental impacts and operating costs [19]. In addition, dust recovered from EAF gas treatment has been used for substituting clays in traditional brick manufacturing, by producing energy savings, environmental impact reduction and possible economic benefits [20]. On the other hand, the valorisation of wastes or by-products from different industrial sectors as Thermal Energy Storage (TES) materials has been investigated in depth [21]. Furthermore, simulation models development has allowed identifying the BOF, EAF and Ladle Furnace (LF) slag quality to be internally reused and to provide significant economic and environmental improvements, compared to the current slag use in the steelworks [22,23]. However, there is still significant room for improvement for increasing the recovery rate of by-products, achieving environmental and economic benefits, also according to the principles of IS, as shown in Figure 3.

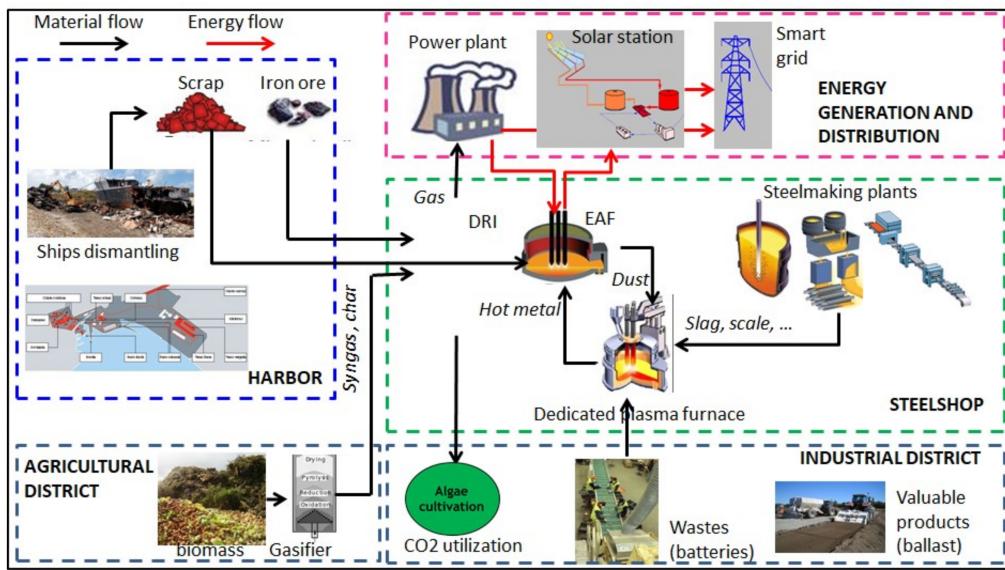


Figure 3. Conceptual design of steel industry-based industrial symbiosis.

This review paper was derived from an analysis performed in the dissemination project entitled “Dissemination of results of the European projects dealing with reuse and recycling of by-products in the steel sector (REUSteel)”, co-founded by the Research Fund for Coal and Steel (RFCS). The aim of the project is to identify, organise, combine and integrate the most relevant and promising outcomes from a large number of previous and running European projects, focused on the reuse and recycling of by-products. Furthermore, some areas with promising results in the same topics will be identified and suggestions for future research will be made.

The paper is organised as follows: Section 2 introduces the context of IS, providing some important examples. In Section 3 the recent achieved developments in slags reuse are depicted. Section 4 describes the main achievements in by-products reuse in cement production, while Section 5 concerns their reuse in road construction. Section 6 discusses the liming and amending properties of by-products, and Section 7 is devoted to the reuse of other by-products not fully analysed in the previous Sections. Finally, Section 8 provides some concluding remarks.

2. Industrial Symbiosis in the Steel Sector

Relevant examples about the recent achieved results in IS implementation, including the steel and other sectors, can be found in the literature. In general, by-products generated in the iron- and steelmaking processes can be used in different sectors. On the other hand, by-products from other industrial sectors can be applied in the steel industry as secondary and recycled materials. For instance, some iron- and steelmaking by-products, such as slag, EAF dust, mill scale and zinc sludge, can be used in a cement plant and a zinc smelter plant as raw materials. In particular, sludge can be used as raw material for zinc ingots, which in turn are used in steelmaking as raw material for producing wire rod in the galvanising process [24] (this process consists of an electroplating process, which coats the wire with zinc, in order to prevent corrosion). Currently, gas from iron- and steel processes are cleaned and internally used, for instance, for producing electricity. Hydrogen, contained in the coke oven gas (about 55%), can provide up to 40% of the power for the steelmaking plant, and ammonium sulphate can be used as fertiliser. In addition, BTX (benzene, toluene and xylene) can be applied in plastic products, and tar and naphthalene for producing electrodes for the aluminium industry, plastics and paints. On the other hand, iron oxides and slags can be used for external applications, such as Portland cement; zinc oxides, produced in the EAF route, can be used as a raw material mainly through the Waelz process with over 85% of the market (source: World Steel Association: <https://www.worldsteel.org/>). On this subject, alternative processes are available, particularly focused on technological solutions for

Zn recovery from EAF dust [25]. These processes are promising and in continuous evolution, based on different approaches. In particular, to recover zinc from EAF dust, present in the form of franklinite (60%), a study based on ultrasound-assisted leaching process has been carried out [26]. In addition, to investigate the selective zinc removal from EAF dust, the microwave heating oven has been used as a heat source [27]. Recovery of zinc from the pre-treatment of coated steel scrap before it is fed to the EAF has also been deeply investigated [28]. Moreover, some examples can be provided about the recovery of valuable metals from by-products [29] as well as the selective leaching processes tested or applied to reclaim pure zinc compounds or metallic zinc from EAF secondary steelmaking [30]. Furthermore, although research towards recycling of the high-zinc fraction of BF sludge is limited, recent studies have been performed in order to incorporate this fraction in self-reducing cold-bonded briquettes and pellets [31] (see some examples in Figure 4).



Figure 4. Exemplar of cold-bonded briquettes, agglomerates and pellets produced at VDEh-Betriebsforschungsinstitut GmbH.

Other significant examples of IS have been recently performed, based on by-products from sources outside the steel sector that can be used in the steel industry as secondary and recycled materials. For instance, carbon bearing materials, deriving from other industrial sectors, such as biomass, residues from food companies, plastic and rubber wastes, represent important materials to be used as partial substitute of fossil materials, such as coal and natural gas. In particular, biomasses or residual plastics, usually landfilled, can be reused as "alternative C sources". Biomass can be used in iron- and steelmaking in order to reduce fossil-based CO₂ emissions [32] (higher than 50%, compared to the current integrated route) and the net increase of direct CO₂ emissions is avoided. Biomass can be used as reducing agent in several iron- and steelmaking processes [33]. For instance, in cokemaking, sintering and in carbon composite agglomerate production, biomass, especially charcoal, can be injected and Pulverized Coal Injection (PCI) can be replaced with high carbon content charcoal. Furthermore, due to its significant economic and ecological potential, the substitution of fossil fuels in metallurgical processes, such as in EAF steelmaking, with biochar-agglomerates has been investigated [34]. In addition, the simultaneous conversion and utilisation of carbon dioxide and plastics into fuels/chemicals in high temperature iron and steel processing can be significantly effective [35]. Moreover, replacing 100% of injection carbon and charge carbon in EAF steelmaking with renewable bio-carbon can produce more than 50% reduction of greenhouse gas emission from the EAF steelmaking [36]. For instance, waste plastics and other materials used in steelmaking processes can reduce ~30% of CO₂ emissions compared to the use of fossil carbon sources [37]. CO₂ reformation with the CH₄ from the waste plastics used in high temperature processes generates fuel gases and reducing gases (i.e., hydrogen and carbon monoxide). These innovative uses represent important aspects pushing toward the creation of new local economies.

3. Recent Developments in Slags Reuse

Among by-products resulting in the iron and steel production, slags represent the main by-products (90% by mass). Worldwide, more than 400 million tonnes of iron and steel slags are produced each year. About 24.6 M tonnes of BF slag and 18.4 M tonnes of steelmaking slags are produced every year in Europe [38]. They are mainly used in the building sector, as aggregates and cement components in hydraulic engineering, and for metallurgical use, and about 9% of steel slags are internally stored, while about 14% are landfilled. A better knowledge of their formation, composition and physical properties is fundamental for increasing slags reuse both internally and in different field of applications. In particular, knowing the phase compositions and, consequently, applying ad hoc stabilisation methods make slags suitable for its reuse and/or inert disposal [39]. Recently, some critical aspects on the steel slags use have been highlighted. Such aspects concern their volume instability (due to the free lime exposure to moisture) and their leaching behaviour (due to the content of metals that can cause water or soil pollution) [40]. On the other hand, steel slags can be used for replacing natural sand as aggregate in cement, often in combination with its CO₂ sequestration properties. However, due to their variability composition that can affect the final product, it can be difficult to internally reuse slags. In order to overcome this issue, a general purpose-monitoring tool was developed and exploited for the simulation and the feasibility assessment of the replacement of lime and dolime with LF slag with or without the partial recovery of EAF slag for the production of two steel families [41]. A small increase of 3–4% of the electric energy has been detected, but compensated through the reduction of about 14–16% of non-metallic raw materials.

The mixture of BF slags and Portland cement with other steelmaking by-products, such as Electrostatic Precipitator dusts (ESP), BF sludge and BOF sludge have shown significant properties, including up to 90% immobilisation of hazardous elements. Moreover, with organic additives (e.g., citric acid) added to the mixture, hazardous constituents can be liberated or immobilised [42].

3.1. Metal Recovery

Steel slags mainly contain iron oxides that can be recycled by reduction methods and metallic iron can settle down to the bottom of the reactor. Recently, a re-melting and reducing treatment, in order to recycle iron and modify the chemical composition of the residue, has been carried out. In particular, SiO₂ can promote reduction and separation of iron and slag. With the 10% of SiO₂, melting time of 30 min, coke of 5%, metallisation rate was 87.30% and metal recovery rate was 96.45%. Furthermore, by reaching a slag with good stability, these results can be improved. The reuse of slag can produce other significant advantages, such as the reduction of its dumping, of occupation of land, and of the environmental pollution. In addition, the use of the energy of molten slag could reduce the process costs [43]. Moreover, bioleaching can be used for recovering metals, depending on the slag composition. Recently, a test on BOF slag for bacterial leaching and recovery of aluminium (Al), chromium (Cr) and vanadium (V) has been performed [44]. Batch test results have shown a significant bioleaching of Al, Cr and V more from steel slag than in control treatments. In addition, the culture supernatant could be used for an upscaled industrial application in order to recover metals. On the other hand, the removal and recovery percentages of metals from the leachate have been relatively modest, due to the high concentration of competing ions (SO₄²⁻, PO₄³⁻) in the culture medium. About this topic, other methods, such as selective precipitation, could improve the performance of the resin. In BOF slag, the mineralogy and element availability, such as chromium (Cr), molybdenum (Mo) and vanadium (V), could provide information about its possible environmental impact. A Sequential Extraction Procedure (SEP), four-fraction-based, combined with X-Ray Diffraction (XRD), of two BOF slags has been applied [45]. In particular, the four fractions are: F1 (water soluble), F2 (acid soluble), F3 (reducible) and F4 (residual). The results have shown that Cr and Mo primarily occurred in F4, rather than immobile elements under natural conditions, strongly bound into/onto Fe minerals. In addition, V has been more mobile with proportional higher findings in the two fractions F2 and F3. By applying the X-ray diffraction, V has resulted bound into Ca minerals (larnite, hatrurite, kirschsteinite

and calcite) and to Fe minerals. Nevertheless, the total amount of recovery cannot be considered an indicator of the availability of analysed elements and, in addition, it did not correspond to the leaching of elements from BOF slag.

3.2. Removal of Harmful Elements

By-products can also be used for removal of harmful elements and compounds that can negatively affect the environment. On this subject, a recent investigation concerned the Induction Furnace (IF) steel slag-based application for removing Cr(VI) ions (hexavalent chromium) from aqueous solution in laboratory conditions at room temperature [46]. Results have shown that the alkali activated steel slag can induce the rate of adsorption of Cr(VI) on the surface of the adsorbent and, consequently, Cr(VI) can be effectively removed from aqueous solution. In addition, a recent study concerned a suitable application of the Water-Spray EAF (WS-EAF) slag. In particular, results have shown that WS-EAF slag can be a promising material for removal, by adsorption, Cd (II) and Mn(II) from aqueous solutions and from industrial wastewater [47]. In addition, other iron- and steelmaking by-products, such as BF slag, dust from the bag filters in the coking installation and dust from the liquid sludge from the scrubber, have shown a relevant ability for removing tricholoroethylene (TCE) from the groundwater. In particular, according to its composition and porosity, BF slag has showed the highest catalytic activity to degrade TCE by using hydrogen peroxide [48]. Recently, some industrial by-products, such as steel slag, iron filings and three recycled steel by-products, have been tested for their abilities for phosphate adsorption, showing a higher ability to do so compared to three natural minerals (limestone, zeolite and calcite) [49]. Due to the strong chemical bonds between phosphate and steel by-products, the adsorbed phosphate can be released to the solution. Consequently, they can be considered as alternative and low-cost effective adsorption media for phosphate removal from subsurface drainage.

3.3. Waste Heat Recovery

Another recent important use of BF and steel slags consists in the high potential for the energy consumption reduction in the steel sector, through heat recovery from hot slags. On this purpose, some high value-added applications (e.g., cutting edge surface coating technologies) can be performed. In particular, molten slag, with a temperature range of 1723–1923 K and with a slag enthalpy of ~1.6 GJ per tonne of slag, can be used for waste heat recovery by applying different methods [50]. A Slag Carbon Arrestor Process (SCAP), which uses slag for catalysing conversion of tar and Coke Oven Gas (COG) into hydrogen-rich fuel gas, has been recently introduced for recovering waste heat in steelmaking processes [51]. A multi-stage system for effective recovery of the waste heat from BF slag and its environmental and economic impacts has been proposed. In addition, the solidification of molten slag droplets in centrifugal granulation for heat recovery though an enthalpy based mathematical model has been studied. This resulted in low crystal phase content, the desired parameter for high quality heat recovery. Another technique concerns the use of a gravity bed waste heat boiler, by associating heat recovery efficiency with decreasing slag particle diameter. A further application concerns the use of slag as energy storage material in Thermal Energy Storage (TES) systems, which are widely used in Concentrated Solar Power Plants (CSPs) to collect energy [52]. On this subject, EAF slag has shown microstructural and thermal properties that make it usable in TES systems. Another method [53] involves mechanical destruction of liquid slag film by impingement with solid slag particles that have previously been solidified and sieved in the same device with simultaneous heat recovery in a fluidised bed, which produces dry and dust-free granules. Additionally, investigations were carried out where liquid slag was poured into moulds of slag caster and steel spheres were added. The liquid slag heated the steel spheres. When the slag solidified, the hot spheres were recovered and used to produce hot air.

3.4. Ceramic Tile and Biomedical Applications

A further use of the EAF slag has been recently investigated, in particular its recycling as a green source in ceramic tile production. Because of its chemical composition, EAF slag has been considered

also in the biomedical applications, due to the bioactivity and biocompatibility of Fluorapatite-based glass ceramics for some applications (e.g., bone replacement, dental and orthopaedic applications). In addition, the possible optoelectronic applications, due to their chemical and crystallographic structure similar to the apatite structure of the bone, have also been investigated [52]. Further tests have been carried out in China concerning the use hot-poured converter slag in ceramic materials. Fly ash, microsilica and quartz have been mixed and, after heating at 1100–1200 °C, the ceramics have been sintered [54].

4. By-Products Reuse in Cement Production

Over the last few decades, the slags and other by-products reuse in cement production has allowed coping with the increased demand of cement, resulting in reduction of environmental issues, natural resources exploitation and costs. In particular, BF slag presents specific characteristics, achieved after a rapid cooling by water quenching, resulting in a glassy and granular form, that make it an excellent material for producing Portland cement. Among slags, the Ground Granulated Blast furnace Slag (GGBS) presents structural and durable properties. These features make it suitable to cement concrete, resulting in an eco-friendly and economical material when the replacement of cement by GGBS lies between 40% and 45% by weight. In addition, although ultrafine GGBS can improve strength and durability, the addition of new materials to GGBS can increase these properties [55]. Furthermore, the mechanical properties in Self-Compacting Concretes (SCC), replaced by Granulated Blast Furnace Slag (GBFS) in the limestone aggregate from 0% to 60%, have been analysed [56]. Going into detail, it was found that the replacement in mortar the 50% of cement with ground GBFS produced a compressive strength similar to the reference mortar, containing 100% of cement. In addition, the formation of new compounds as well as the formation of stronger bond, due to the paste richer in Si, can improve the mechanical properties of aggregates. On the other hand, due to the reactivity of the slags, replacing sand with the slag can improve compressive strength of the concrete. The resulting reductions in energy and raw material consumptions and in greenhouse gas emissions as well as the preservation of the destruction of natural quarries represent the main advantages of the use of this by-product instead of natural raw materials. However, slag cooled by water quenching can be inefficient for heat recovery and can produce harmful wastes such as H₂S, heavy metals and SO₂. For this reason, new methods have been developed (e.g., dry granulation) for preparing molten slag, providing a material with better properties. Among them, the use of insoluble chemical activators aims at improving the hydraulic activity of slag blended Portland cement, which results in the improvement of the compressive strength, obtained through the application of optimum proportions of chlorine chemical activators and quality improvers. In addition, tests on the temperature effect on the binders of BF slag and metakaolin (MK) have been carried out [52]. Alkaline activated aluminosilicate precursors, also known as geopolymers, have been tested as a cementing material alternative to Portland cement, due to their high mechanical characteristics and durability. BF slag mortar activated with Olive-stone Biomass Ash (OBA) presented a lower zeolite content and average pore diameter compared to commercial industrial reagents and other processes that result in high CO₂ emissions. Recent studies on the improvement of BF slag use in cement production have been carried out in both Europe and China. Due to the increasing amount of industrial by-products, linked to the increasing steel production, an investigation of the production of a novel green cement containing superfine particles with high volume fly ash and BF slag addition has been performed [57]. This novel green cement can present significant properties, such as better mechanical properties with respect to commercial blended cement as well as better hydration properties than Ordinary Portland Cement (OPC).

To sum up, the use of BF slag is mainly devoted to replace cement in concrete, but steel slags are mostly used as a filler material in embankment construction, due to their relatively low hydraulicity and problems with their volumetric expansion. However, recent progresses in the slag quenching process have also allowed the improvement of steel slag properties. In particular, BOF slag, EAF slag and LF slag, currently used in road construction, asphalt concrete, agricultural fertiliser and soil

improvement, can be valuable materials for cement clinker production. This potential use can result in environmental and economic advantages. Recent studies have been focused on the challenge aiming at using steel slags as cement replacement and aggregate in cement concrete. To this purpose, due to the low cementitious ability of steel slags in concrete and the requirement of their activation, suitable aging/weathering and treatments have been carried out for improving the hydrolyses of free-CaO and MgO, aiming to mitigate their instability [58]. In addition, the use of steel slag aggregates with wastewater in concrete has been shown to be possible without any significant deterioration of fresh and hardened concrete properties [59]. On this subject, a comparative study, evaluating the mechanical properties of concrete containing EAF oxidising slag, steel slag and GBFS, has been performed [60]. Replacing cement with EAF oxidising slag has produced the delayed of the hydration reaction at early ages, without significant issues in setting time, shrinkage or strength development. Additionally, research was carried out to adapt the chemistry and mineralogy of BOF slags to improve the hydraulic properties, by the reduction of iron oxides [61] and the addition of raw materials as sand and clay followed by heating and a rapid cooling to gain hydraulic active phases.

Another important by-product generated in the iron- and steelmaking processes, the BF flue dust, mainly contains significant quantities of iron oxides and coke fines. Recently, its potential use in replacing the traditional fuel and raw materials in cement production in India has been studied [62]. The application of magnetic separation to reduce the iron content in the flue dust has been evaluated. Although the results have shown that it does not effectively segregate the iron in the flue dust and the energy content does not increase, the cost analysis has shown that flue dust can be effectively used by the cement industry. This can produce advantages for both steel and cement industries.

In the last few years, other by-products coming from different sectors (e.g., steel fibre, asphalt, slag, asbestos, lead, dry sludge, wet sludge, fly ash, bagasse ash, red mud, plastic, glass etc.) have been tested for concrete preparation [63]. These tests have included compressive strength, flexural strength and slump value, which aim at finding out the most suitable by-product to replace natural materials.

5. By-Products Reuse in Road Construction

Industrial by-products can also be used in road construction with good results without compromising the quality and the performance of the road and with the advantage of reduction of their disposal to the landfills. In this regard, the recycling of some industrial by-products to replace conventional natural aggregates can be used for producing hydraulically bound mixtures for road foundations [64,65]. Recent achievements have been shown by combining Foundry Sands (FS), EAF steel slags and bottom ash from Municipal Solid Waste Incineration (MSWI) in five different proportions to be applied in road foundations [66]. Additionally, in Asian countries, such as Vietnam, under local legislation, steel slags have been considered as a solid waste to be processed and landfilled. However, over the last few years, this concept has been revised and now steel slags are considered as a normal or non-deleterious solid waste. This new consideration has paved the way to important studies aiming at steel slag reuse in the construction sector, as a replacement for mineral aggregate, in Hot Mix Asphalt (HMA) [67]. In particular, two HMA mixtures using steel slag have passed the Marshall stability and flow test requirements. In addition, its skid resistance for the surface course has satisfied the national specification for asphalt. Finally, the pavement sections with the surface course of steel slag HMA has showed a significant higher modulus than the conventional one. Only the roughness of the paved surface course has not met the requirement of the specification.

Recent studies on the recycling by-products in road construction have taken also into account other materials, associated with steel by-products. On this subject, aramid fibre, a synthetic fibre chemically produced through the reaction between amine group and carboxylic acid group, is currently applied as a reinforced material to improve the asphalt mixtures performance [68]. The replacement of natural coarse aggregate with EAF steel slag in the asphalt mixture reinforced by aramid fibre has been assessed. The results have shown that asphalt layer thickness and transportation costs have been reduced. In addition, the immersion of steel slag aggregate in water for 6 months can reduce

(by 68%) the content of free lime and free magnesia, in order to avoid the expansion volume due to their characteristics. A further combination, including steel slag and bottom ash, has been studied as aggregate in asphalt pavement. After the characterisation of physical, chemical and morphological features, a comparison of the bottom ash and the steel slag with the conventional granite aggregate was performed. The results have highlighted that ash has presented weaker characteristics in terms of strength than the steel slag; on the other hand, steel slag, due to its content of iron oxide, has shown to be much stronger than granite. In addition, lower silica content in steel slag and bottom ash has shown to be potentially more resistant to moisture damage than granite [69]. BF slag has also been taken into account in recent studies as an alternative substitute of natural crushed aggregate. To this purpose, three asphalt concrete types, with different maximum aggregate particle size and one stone mastic asphalt mixture for low noise surface layers, have been selected [70]. It has been found that using BF slag aggregates in asphalt mixtures does not influence the quality or durability of the mixture. However, in some cases, it could even improve its properties. Due to its physical properties and mineralogical and chemical composition, BF slag can be used as granular aggregate in the production of HMA. The effect on the resistance of HMA, after the replacement of the coarse fraction of a natural aggregate with BF slag, has been evaluated by performing specific tests. Although significant enhancement in the properties of the HMA mixture has been detected, when limestone is totally replaced, the adhesive properties of the asphalt-aggregate system will be worse [71].

The improvement of the reuse efficiency of steel slag through the composition adjustment and activation of steel slag has been studied in China. This has resulted in an optimal slag-based composite with improved cementation efficiency, in the suppression of the swelling potential and in strength improvement. Furthermore, the Chinese standard for first-class road/highway has been satisfied [72]. A recent work concerns the use of BOF slag as coarse aggregate as well as the Blast Furnace Dust (BFD) as a fine aggregate for manufacturing asphalt hot mixes for pavements [73]. The physical characteristics and the susceptibility to water and plastic deformation of each type of mixture have been assessed. The use of BOF slag and the feasibility of BFD use as fine aggregate resulted useful for partially replacing conventional aggregates in road paving. Finally, waste foundry sand and BF steel slag have been tested in an Indian study for gradation, specific gravity, morphology, chemical composition and compaction as well as engineering properties, shear strength and permeability [74]. In addition, compaction behaviour of these analysed by-products has resulted to be similar to granular soils and they have been tested for fill applications. Tests on leachate behaviour has allowed assessing the environmental impact of their use.

6. By-Products Use as Liming and Amending Materials

The use of by-products from the steel sector for soil amendment is a consolidate practice in some countries, not only in Europe but also in other worldwide countries. In particular, over the last few decades, the use of steel slags as a liming material to raise the pH in acidic soils and to improve the physical properties of soft soils have been deepened and consolidated [75]. Recently, a study based on the application of BOF slag to alkaline soils, affected by excess sodium, has been carried out through lysimeter trials, by producing significant results in decreasing the exchangeable sodium content of saline sodic soil irrigated with saline water. The observed effects of BOF slag application have been mainly related to the improvement of the yields, thanks to the reduction of the negative effect of sodium [76]. An example of these achieved results is shown in Figure 5. Furthermore, the assessment of the technical and economic viability of a slag treatment plant has been carried out in order to obtain an amendment material to be sold in the fertiliser market [77]. The high porosity and large surface area of steel slags make them successful materials to also be used in marine environment for coral reef repairing [78] and for building artificial reefs. In addition, they can be used for H_2S and metalloids adsorption in marine environments [79].



Figure 5. Improvement of the tomato yields, due to the reduction of the negative effect of sodium after BOF slag application.

However, due to the content of trace amounts of heavy metals, the application of the BOF slag as liming material need to be carefully analysed. Among different metals that can be present in the slags, chromium (Cr), under environmental conditions, exists in two stable oxidation states, +III and +VI. CrIII is an essential nutrient, while CrVI is highly toxic. In soils, soluble CrIII is oxidised to CrVI by manganese (hydr)oxides (MnO_2). Due to its liming properties, BOF slag can reduce the CrVI, while adding synthetic $Mn^{IV}O_2$ promotes oxidation of CrIII. Generally, the oxidation risk of CrIII present in BOF slag to CrVI, promoted by MnO_2 present in the soil, is very low, due the low solubility of CrIII in soil [80]. Recent studies have shown that the Linz-Donawitz (LD) converter slag applied as amending material at a rate of 2.0×10^3 kg/ha in submerged rice cropping systems has significantly ($p < 0.05$) allowed the increase of grain yield by 10.3–15.2% [81].

In addition, CH_4 emissions have been mitigated by 17.8–24.0%, and inorganic as concentrations in grain have decreased by 18.3–19.6%. Furthermore, higher yield (due to the increase of photosynthetic rates) has been achieved, with the increase of nutrients availability to the rice plant. Finally, the observed decrease of CH_4 emissions could be due to the higher Fe availability in the slag amended soil. In this context, it works as an alternate electron acceptor by suppressing CH_4 emissions. The LD slag is also an amendment material in decreasing the arsenic uptake by rice. This effect could be due to the more Fe-plaque formation adsorbing more arsenic and the competitive inhibition of arsenic uptake with higher availability of Si [81]. On the other hand, the effect of iron materials from the casting industry on the arsenic mobility in two soils by a long-term (about 100 days) flooded soil incubation experiment has been evaluated [82]. In particular, immobilising arsenic in soils can be achieved using iron materials, resulting in the reduction of arsenic concentration in rice grains.

7. Reuse of Other By-Products

Other by-products, although produced in lower quantities during the iron- and steelmaking routes, are currently studied in order to be reused in a sustainable way. Among them, mill scale is a by-product formed during the hot rolling process. It can be a potential material used as Bipolar plates (BPP), a component of Proton Exchange Membrane Fuel Cells (PEMFC). As mill scale presents high iron content, it can be a source for current collector in BPP. This can allow providing a contribute in decreasing the overall cost of PEMFC-based fuel cell systems. For this application, the mill scale powder is sieved, mechanically alloyed with the carbon source and pressed under inert gas atmosphere. Through the analysis by XRD, optical microscopy, scanning electron microscopy and micro-hardness measurement, the study of the of powder particles structural changes has been performed [83]. The achieved results have displayed the potential application of the mill scale to BPP. Nevertheless, these results should be confirmed by further investigations and evaluations in the next future.

Concerning solid and gaseous steel by-products, their potential use as raw materials and reducing gases has been studied in order to be used for synthesising rich iron bearing products like iron powder.

For producing this value-added product, a chemical reduction technique is suitable through the use of steel by-products. The optimisation of the process parameters of the applied techniques aims to produce pure iron powders [84]. Furthermore, by applying the Sequential Chemical Extraction (SE), analysis information on the composition of solid steel processing by-products can be provided, resulting in the possibility to their classification process to improve the environmental protection. In particular, SE can provide more refined classification through information for potential reusing and then reducing hazardous materials. On this subject, the distribution of potentially toxic elements such as zinc, lead and copper between sensitive and immobile phases has been obtained [85].

Further by-products that can be efficiently reused include fly ash, coming from burning pulverised coal in electric power generating plants, and GGBS, obtained by quenching molten BF slag to produce a glassy, granular product, then dried and ground into a fine powder. Over the last few years, the use of fly ash bricks has increased, due to their long-term performance and their good mechanical and durability properties. Replacing the 50% with fly ash can improve the strength of concrete blocks, and can allow to achieve the maximum compressive strength and split tensile strength. Furthermore, the addition of 30% of glass powder can increase the compressive and flexural strength [86].

The mix of Steel Furnace Slag (SFS), Coal Wash (CW) and Rubber Crumbs (RC) have been recently tested for achieving an energy-absorbing capping layer with the same or higher properties compared to conventional subballast [87]. The analysis of seven parameters (i.e., gradation, permeability, peak friction angle, breakage index, swell pressure, strain energy density and axial strain under cyclic loading) have been carried out. Results have shown that a mixture with SFS:CW = 7:3 and 10% RC (63% SFS, 27% CW, and 10% RC) represents the best mixture for subballast.

Refractory materials play a primary role in the steel sector, as they are present in the main furnace of the iron- and steelmaking routes, from the BF to the Casting Machine, including furnaces, converters, vessels, nozzles etc. The current internal recycling of spent refractories includes their use as slag formers or conditioners or the partial substitution of raw materials in the mixtures for new refractories. An example of the use of spent refractories as slag conditioner and, in particular, in order to decrease the slag power to corrode the ladle refractories is provided in Figure 6.

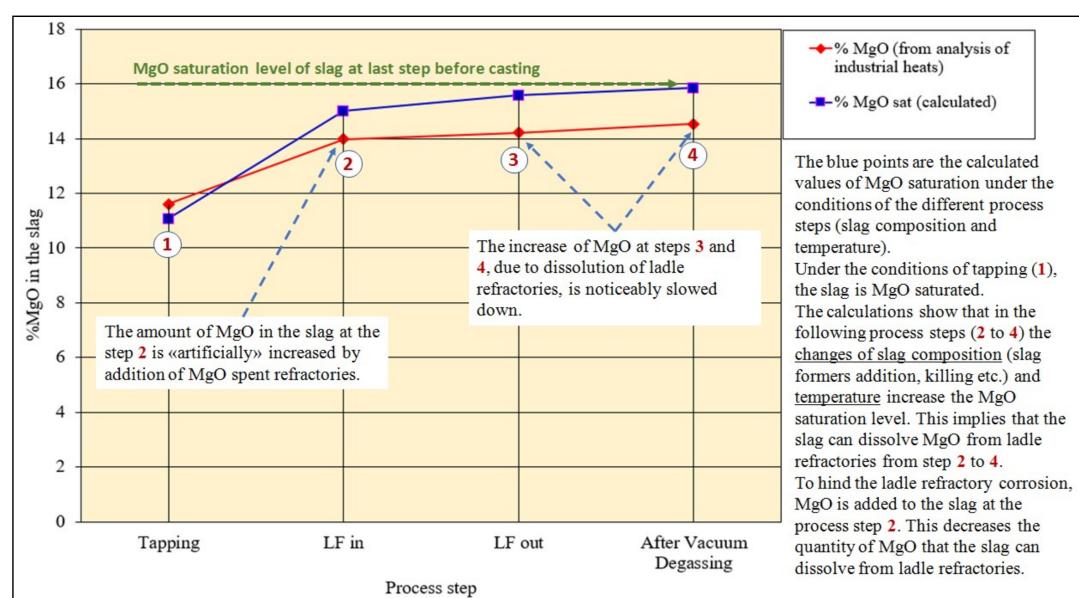


Figure 6. Use of spent refractories for slag conditioning with the aim to decrease the slag power to dissolve ladle refractories (comparison between calculated and experimental values. The experimental values have been obtained from an Italian steel plant).

As far as this last aspect is concerned, the Nippon Steel & Sumitomo Metals Corporation has developed a virtuous model about a method resulting in a recycled material to be used for on-site additions to monolithic refractories or for concretes [88]. Furthermore, the strategic alliances between steel producers, refractory recyclers and refractory manufacturers paved the way to a circular economy approach, also favouring the IS implementation [89]. This also provides the possibility to the external recycling of refractories, such as in the glass and cement sectors [90]. On this subject, the steel sector has been recently committed to the mutual exchange of materials among a steelmaking plant, vendors and other business partners in a network of industrial companies.

8. Conclusions

The performed study concerns the analysis of potential and future applications of iron- and steelmaking by-products, by highlighting both positive and critical aspects as well as the cooperation actions with other sectors, according to the principles of the IS. On this purpose, some significant examples have been provided.

The results discussed in the paper showed that, in order to improve the reuse and recovery rates, it is fundamental to increase the quality of the by-products recovered. New technological solutions need to be developed and implemented, aiming at achieving higher by-product qualities, in order to increase their reuse in an environmental and economic sustainable way. This results in approaching the “zero-waste” goal in the steel sector as well as a viable way for saving natural resources and reducing the environmental impact of the production processes. In addition, replacing natural resources with by-products can also allow saving energy and achieving higher energy efficiency in the production processes. For this reason, the future of the steel industry is closely linked not only with its innovation and the implementation of new technological solutions, but also with the reduction of its negative impacts, making its processes cleaner. On this subject, the steel sector should continue its path to the circular economy, by increasing its by-products reuse in a sustainable way. This includes the reduction of natural resources exploitation, such as CO₂ and pollution reductions, use of alternative raw material with less environmental impact as well as the control of existing impacts.

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Abbreviations

BF	Blast Furnace
BFD	Blast Furnace Dust
BOF	Basic Oxygen Furnace
BPP	Bipolar plates
BTX	benzene, toluene and xylene
CCU	Carbon Capture, Storage and Usage
CDA	Carbon Direct Avoidance
CE	Circular Economy
COG	Coke Oven Gas
CSP	Concentrated Solar Power Plants
CW	Coal Wash
DRI	Direct Reduced Iron
EAF	Electric Arc Furnace
FS	Foundry Sands
GGBS	Ground Granulated Blast furnace Slag
HMA	Hot Mix Asphalt
IF	Induction Furnace
IS	Industrial Symbiosis
LD	Linz-Donawitz
LF	Ladle Furnace
MK	metakaolin
MSWI	Municipal Solid Waste Incineration
OBA	Olive-stone Biomass Ash
OPC	Ordinary Portland Cement
PCI	Pulverized Coal Injection
PEMFC	proton exchange membrane fuel cells
PI	Process Integration
RC	Rubber Crumbs
SCAP	Slag Carbon Arrestor Process
SCC	Self-Compacting Concretes
SE	Sequential Chemical Extraction
SEP	Sequential Extraction Procedure
SFS	Steel Furnace Slag
TCE	Trichloroethylene
TES	Thermal Energy Storage
WS	Water-Spray
XRD	X-Ray Diffraction

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