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**Project Acronym: REUSteel** 

Project title: Dissemination of results of the European projects dealing with reuse and recycling of by-products in the Steel sector



**Deliverable 1.1** 

State of the art -

Comprehensive overview of the project

# Summary

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# 1. Project Summary and purpose of the present document

The project intends to develop dissemination and valorisation of the most important results achieved in the 45 mentioned research projects (ECSC, RFCS, FP3, FP4, FP5, FP6 and Horizon 2020) on the reuse and recycling of by-products deriving from the steel production cycle as well as the exploitation of by-products coming from other industrial sectors within the steelmaking cycle, such as alternative Carbon sources (e.g. biomasses and plastics). According to the RFCS programme, the proposal aims at performing an integrated critical analysis in order to improve the effectiveness of the achieved results in the previous projects, to establish a road map for future research in the topic as well as to promote the synergies with other industrial sectors.

Over the past few decades great efforts have been made in European research to improve byproducts recovery as well as their quality, through the improvement of existing technologies and the development of new sustainable solutions. These have led the steel industry to save natural resources and to reduce the environmental impact, resulting in being closer to its "zero-waste" goal. Most of the related projects carried out in ECSC and RFCS, dealt with these topics.

Moreover, in recent years the concept of "Circular Economy" has been strongly emphasized at European level, both by the public institutions as a target for all the industrial sectors and society, and by the industries, as an opportunity to improve the environmental sustainability of the production as well as to achieve considerable savings in both consumptions of primary raw materials and costs related to landfilling and disposal of by-products and wastes. This concept is also highlighted in the Strategic Research Agenda of the European Steel Technology Platform, which participates to the project as subcontractor of the coordinator.

The aim of the project is to review, analyse and organise the most important achieved results on the reuse and recycling of by-products coming from the steelworks inside and outside the steelmaking cycle as well as the exploitation of by-products deriving from other activities outside the steel production cycle, for instance as alternative Carbon sources (e.g. biomasses and plastics). Through an intensive work of dissemination and valorisation of the most relevant results, a global vision of the state-of-the-art will be provided, in order to promote both the exploitation of the outcomes and the synergies with other industrial sectors. This will allow organizing project results in a more organic form in order to present the research results to a wider audience.

A joint critical analysis, carried out by all the partners, belonging to different institutions, will provide new insights and guidelines for future research topics in this field, in order to promote the dissemination and, consequently, the implementation of the achieved results.

Further aims of the project are focused on the re-organisation of the results, in order to present selected groups of topics at planned workshops and seminars. This will provide a clearer vision of the outcomes to stakeholders and new audiences, in order to get new and deeper indications for a new roadmap, future synergies with other sectors and industrial trends.

The present document introduces the framework and the objectives of the dissemination action. Moreover, it proposes a detailed analysis of the state-of-the-art.

The analysis of related previous and ongoing EU-funded project (including the ECSC/RFCS projects as well as other EU funded projects) is not included in the present document, as it is the main topic of **Deliverable 2.1**: "List of projects of interest for valorisation and dissemination".

# 2. Framework of the project

Over the last few years an increasing interest of RFCS programme, concerning actions devoted to the dissemination and the promotion of the projects results, has been observed. These actions represent the key factors for the whole profitability of the RFCS. In effect, due to a wide variety of subjects in different projects, the dissemination of achieved knowledge and results presents the following issues:

- the impact of the results obtained in the European projects on the industrial practices is not enough compared to the potential achievements;
- sometimes various researches have followed different processes, for similar objectives without a clear connection;
- there is often a lack of indication about future developments and, accordingly, future research activities needed;
- once a project is finished the results stay within the beneficiaries without promotion of the results;
- overtime results and achievements get forgotten without a clear summary for new generations of steelmakers and potentially interested parties.

To sum up, the potential impact, general validity and transferability of the results obtained by many RFCS projects is underestimated compared to the potential achievements. This fact is often translated into a lack of indications about future research developments as well as a limited possibility of interaction and synergy with similar research activities pursued in other industrial sectors.

The above stated problem is even more relevant when it refers to research efforts and results, which are related to the improvement of resource efficiency and environmental sustainability of the steel production cycle.

Potential for further application of the by-products can be achieved through deepening some research aspects but also from cooperation actions with other sectors. Knowledge and information are the basis for establishing such cooperation as well as for promoting some revisions in the national regulations which are not yet homogenous at EU level and sometimes hamper the exploitation of the most recent achievements. The present dissemination action aims at overcoming such obstacles by analyzing and disseminating the most valuable research results toward reuse and recycle of by-products in the steel sector, to the aim of their full exploitation and the identification of the most promising directions of the future research activity in this context.

The project follows the RFCS Programme objectives, in order to promote the use of results and knowledge achieved within projects of the Steel Research Programme. By collecting and analysing feedbacks for the stakeholders as well as by promoting synergies with other industrial sectors, the project will contribute also to better understanding of the weaknesses of the European researches to spread out the results of the projects beyond the beneficiaries and to better address future researches. On this subject, the project is in line with the principles of the circular economy, which is based on circular business models, where products are repaired, reused, returned and recycled. The project will contribute in defining future development demands to improve material efficiency for the European steel industry.

This project will also act in a synergetic and non-overlapping way with respect to another Accompanying measure entitled "Exploitation of projects for low-carbon future steel industry" (LowCarbonFuture - GA No 800643), which started in 2018. This project summarizes, evaluates and promotes research projects and knowledge dealing with CO<sub>2</sub> mitigation in iron and steelmaking, by focusing on the main three pathways of the current European research: Carbon Direct Avoidance (CDA), Process Integration (PI) and Carbon Capture, Storage and Usage (CCU). "LowCarbonFuture" is expected to consider by-products only as an eventual alternative energy source contributing to a new CO<sub>2</sub>-lean steel production. REUSteel will focus on the valorisation of internal and external by-products and wastes both inside and outside the steel production cycle including those by-products, which can represent alternative C-sources, so as to reduce the need for fossil C-carriers. REUSteel does not focus on lowering CO<sub>2</sub> emissions, but rather on resources efficiency, lowering of natural resource depletion and of disposal of residues through the implementation of virtuous examples of circular economy. PI proved its efficiency to this aim, but other technologies and applications will be analysed and assessed. The combination of these two accompanying measures will allow the EU steel sector to get a comprehensive overview of all the possibility, research outcomes, possible synergies and directions for future investigations, which can drastically improve the environmental sustainability of the steel production cycle.

#### 3. Aims and scope of the project

#### **3.1** Topics of the project

By-products generated by the steelmaking processes represent 10-15% of the produced steel<sup>1</sup>. Slags, dusts, mill scales and sludges are the main (but not the only) by-products from iron and crude steel production. The project aims at identifying, organising, combining and integrating the most relevant and promising results achieved in a large number of previous and running projects, focused on the reuse and recycling of by-products. In addition, areas with promising results will be identified and suggestions for future research will be made.

<sup>&</sup>lt;sup>1</sup> Source: World Steel Association: <u>https://www.worldsteel.org/</u>, World Steel Association: Steel industry byproducts. <u>https://www.worldsteel.org/publications/fact-sheets.html</u> : Fact\_By-products\_2016.pdf

One of the topics of the circular economy is to improve Industrial Symbiosis (IS). In this context, there are residues and by-products from sources outside the steel mill that can be used in the steelwork as secondary and recycled materials. There are virtuous examples in which the electric furnace processes have advantageously used residues from non-metallurgical contexts as alternative fuels to anthracite: these residues, such as residual plastics or biomasses, are otherwise destined to be landfilled but instead they were reused as "alternative C sources". This project will promote and scientifically and accurately spread these studies that answer the European Union of "zero waste" goal. Moreover, these materials, apart from the residual thermal value to be exploited, have a composition of oxides (often alkaline) or of metals, very useful to the steel mill (such as high value alloy elements).

The previous project results will be extracted, presented and valorised in order to provide a more homogeneous and clearer description of related benefits. A joint critical analysis will be focused on the extraction of the reasons for successes and failures, in order to provide indications and guidelines for future developments and actions. The feedback expected through discussions in planned workshops and seminars, will give important insights on the expectation of the industrial sectors, concerning research activities and industrial trends. In addition, as legislation presents some aspects for national interpretation and implementation, an integrated approach will help EU legislators to use innovative results for achieving a more homogeneous future legislation as well as a consensus in the application of laws and regulations. Also, the project would help to clear up unjustified preconceptions, as it should demonstrate and disseminate how wastes can be exploited in a profitable and environmental-friendly way.

As each past and running project presents specific characteristics and specific objectives in terms of innovation and technologies, these aspects will be analysed, and discussed in this dissemination project, in order to promote the "good outcomes". The goal is to extract general information, potentially transferable and applicable to other industrial contexts, by avoiding overlapping, duplications and irrelevant aspects. With the overview of previous and current work, it will also be possible to identify the most promising areas in which research is lacking. Thanks to the cooperation and the wide and diverse competencies of the partners cooperating in the project as well as by intensifying the contacts with interested parties also outside the steel sectors through workshops and seminars, current important issues and topics, which have not been dealt with in previous projects, will be identified.

In order to organise the topics (and sub-topics) of the dissemination project, a wide variety of results coming from the previous and running projects will be aggregated in a limited number of classes. The following list presents the most important aspects in terms of innovation, coming from the considered research projects:

- Slag internal recycling
- Slag valorisation outside the steel production cycle
- Extraction of valuable material from waste and wastewater
- Internal and external recycling of Fe-bearing by-products different from slag

- Internal and external recycling of by-product with other beneficial and valuable contents like metals, coal and lime (e.g. secondary raw materials generation for exchange in industrial symbiosis and circular economy possibilities)
- Elimination of harmful elements
- Minimisation of waste generation and landfill
- Process integration solutions for by-products management
- Modelling and simulation.

# **3.2 Objectives of the project**

REUSteel aims at developing an extensive action of dissemination and valorisation of the most important research results on the reuse and recycling of by-products, based on an integrated critical analysis of a long list of EU-funded projects, to promote the exploitation of the results and increase the synergies with other industrial sectors. The result of the above analysis will be used to identify the most urgent needs and ambitions of the European steel sector, to define a sequence of future research topics in this field, but also to highlight the non-technical showstoppers (i.e. rule, normative). This activity aims at identifying common actions expected at overcoming or smoothing the existing obstacles and at paving the way to research and implementation of innovative solutions. The target is the wider improvement of by-products reuse and recycling, which can be developed in the future years. In particular, the following intermediate objectives are expected:

- To promote the dissemination of the knowledge gained and the technological solutions introduced in relevant European projects on the reuse and recycling of by-products in the steel sector;
- To identify present merits and limitations of the various technological solutions, as well as the spread of their implementation in the European steel plants;
- To evaluate the principal reasons of success or failure in the past projects, taking into account scientific, technical, economic and legislative aspects;
- To evaluate the impact of the results on the sustainability and the competitiveness of the European steel industry;
- To identify the most promising and useful emerging development lines and to encourage the use of best results and innovative solutions, taking into account possible technological barriers;
- To identify non technological barriers (i.e. normative, authorization pathway, testing and characterization of materials, social impact etc.) to these innovations, research outcomes and other actions which can support the elimination of such barriers;
- To encourage synergies with other industrial sectors in projects promoting industrial symbiosis and circular economy;
- To identify a future roadmap and a sequence of research topics for the next years.

# **3.3 Scope of the project**

The scope of the dissemination actions is on the one hand defined by the large number of EUfunded research projects (especially but not exclusively ECSC, RFCS and HORIZON), which will be evaluated within the project. A list of these projects is reported in **Deliverable 2.1**. Due to the high number of projects to be disseminated and the research being state of the art, to the authors' opinion a dedicated accompanying measure to circulate these results is fully justified. At the beginning of the project, this list will be reviewed and completed by the project partners, to define the scope of the projects that will be evaluated inside the project.

Additionally, the dissemination project will also take into consideration the technological status and trends in other important steelmaking countries and areas like Turkey, Japan, South Korea, China, India, USA and South America. This comparison will allow the assessment of present and future weaknesses in order to plan ad hoc actions aiming at keeping the European steel industry's competitiveness. Along with the topics defined in the section 3.1, further specific actions to define the scope of the proposal will be performed, as follows:

- Collection and organisation of information and results from the relevant projects. This will allow the verification of the possibilities of application of the main achieved results from the projects.
- Assessment of success and failure of the projects in order to analyse the critical points (possibly why the project succeeded or why it failed to achieve stated goals in a clear and easy to understand way, which cannot be always obtained from the report summary).
- Designing and preparation of a questionnaire to be shared among the coordinators or some partners of past and ongoing projects, in order to have a deeper analysis of the results achieved in the ongoing and past projects on the same topic.
- Clarifying barriers for recycling solutions by identifying and analysing common issues, as well as differences, regarding non-technical factors that exist within the EU countries regarding policies and the application of laws and regulations.
- Set-up of a user-friendly web site in order to collect all the information on the projects and to provide useful links and news to allow an easy access to this information, including downloadable files. In particular, relevant documents will be uploaded, such as the results of the project analysis, the presentations of seminars and workshops, and a road map for future developments, etc.
- Stakeholders will be involved in the evaluation by the support of questionnaires designed in order to receive feedback on topics, trends and application of findings, and the quality of dissemination events. In addition, the feedback will cover the experience of participants within the RFCS Steel Research programme or other programmes, such as H2020.
- Organisation of webinars, but also videos and animations, to support the dissemination actions will aim at presenting the most innovative technologies.

- Workshops organisation in order to share information and to provide open discussions, focused, in particular, on future developments and on the road map definition.
- Papers publications on specialised scientific and technical journals as well as international conferences participation, to spread most relevant achieved results within the scientific community. This will focus the attention of scientists and researches on these topics in order to contribute to further advancements and progresses in the field.
- Creation of a group named "REUSteel" on ResearchGate, a platform on the World Wide Web, which is very well known and widely adopted in the technical and scientific community, where researchers worldwide generate profiles describing their research work, list their skills and participate in discussions and open forums. The "REUSteel" group will be established by SSSA at the beginning of the project to come into discussion with other interested researchers and increase the visibility of publications and of all the other dissemination material produced in the project.

# **3.4 Target groups of the project**

The main target groups of the dissemination actions will be

- the steel plant technicians and production managers
- slag processors
- plant manufacturers
- external processors of steelwork residues
- Researcher of Research Institutes and Universities

Moreover, representatives from European member governments will also be included so to better address the supporting measures in the field of by-products reuse and recycling.

Finally some dissemination initiatives will be also directed toward new generations, as part of the dissemination material will be prepared taking into account the possible use in High Schools, in order to improve sensitivity of future generations (which are tomorrow's workers and stakeholders) towards the topics of recycle, reuse, industrial symbiosis and circular economy.

#### 4. Relevant literature results

Over the last few decades, ever more stringent European regulations and higher disposal costs have led the steel sector as well as all the process industry, to increase by-products and waste recycling rate [1]. On this subject, researchers have been committed to investigate methodologies and techniques allowing the enhancement of by-products management and recycling (see some examples in [2] [3] [4] [5]). In particular, in the last few years, the concept of Circular Economy (CE) has emerged among stakeholders and policy makers,

pushing the different industrial sectors to cooperate in the valorization of their by-products toward the ambitious "zero waste" goal to be achieved at a global level. Efforts and commitments aimed at reaching this goal are found on both European and Worldwide activities (see some examples in [6] [7] [8] [9] [10]). The steel sector plays a significant role in the CE, based on the 4 "R"s [11] [12]: Reduce, Reuse, Recycle and Restore. Reduce means avoiding or minimising the environmental impact. Reuse concerns the internal recycling of by-products. For instance, reuse of sludges, through the thermal technologies, aims at eliminating or reducing its Zn content; reuse of slag aims at reducing the lime content and enabling its direct recycling. **Recycling** concerns also the creation of IS, the concept aiming at developing the synergies among different sectors, identifying new business opportunities for underutilized resources outside the boundary of the production chain [13]. In particular, by-products coming from one sector (e.g. steel industry) can become valuable inputs to other ones. Restore mainly concerns the reduction of the impact of steel products. For instance, for every ton of  $CO_2$  produced during the steelmaking process, six tons of  $CO_2$  are saved through the application of the product. Nevertheless, further improvements can be achieved [14]. These aspects do not represent a total novelty for the iron and steel sector: for instance steel slag is partially internally recycled (thanks to the high content of valuable elements like iron) or used in different fields, such as cement production, road building and restoration of marine environments, according to the national legislations. However, there is a relevant and often underestimated potential for further applications of the by-products coming from the steelworks [15], inside and outside the steel production cycle, as well as for the recycling of by-products from different applications within the steelworks [16]. Over the last few decades, steel by-products have already been recovered and used, leading to the material efficiency rate of 97.6% worldwide. For instance, in 2013 81% of production residues in ArcelorMittal were reused or recycled as by-products, and only 9% was disposed in landfills. For comparison, in mining activities, 24% of the residues were disposed in landfill in 2013 [17]. The goal of the steel industry is to achieve further improvement of by-product recovery rates and to expand its use through the increase the quality of the materials recovered, in order to achieve the 100% efficient use of raw materials and "zero-waste" [18]. Among the various by-products, slags represent those produced in greater quantity. Their worldwide average recovery rate is from over 80% (steelmaking slag) to nearly 100% (ironmaking slag). However, there are still potential improvements for increasing the recovery rate in order to reach environmental and economic benefits. On the other hand, 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 be used for providing up to 40% of the power for the steelmaking plant. In addition, ammonium sulphate can be used as fertiliser, BTX (Benzene, Toluene and Xylene) can be used in plastic products, and tar and naphthalene are used to produce electrodes for the aluminium industry, plastics and paints. In addition, dust and sludge, removed from the gases and mainly containing iron, are internally used [19]. Iron oxides and slags can be used for external applications, such as Portland cement. Zinc oxides, produced in the Electric Arc Furnace (EAF) route, can be sold to be used as a raw material mainly through the Waelz process<sup>2</sup> with over 85% of the market. Moreover,

<sup>&</sup>lt;sup>2</sup> Source: World Steel Association: <u>https://www.worldsteel.org/</u>

alternative processes are available [20] technological solutions that look promising steps forward in Zn recovery are in continuous evolution [21] [22] [23]. Furthermore, carbon bearing materials deriving from other industrial sectors (as biomass, residues from food companies, plastic and rubber wastes) can be used as partial substitute of fossil materials (coal and natural gas) [24] [25] [26], pushing toward the creation of new local economies.

Going into more detail, an overview based on the most recent studies on the management of steel industry by-products is provided.

According to EUROSLAG, about 24.6 M tons of Blast Furnace (BF) slag and 18.4 M tons of steelmaking slags are produced per year in Europe [27]. Slags are mainly used as aggregates and cement component in the building sector or in hydraulic engineering, for metallurgical use or other. Only about 9 % of steel slags are stored internally and 14 % are landfilled. In order to increase the slags reuse, it is strategic to understand their formation, composition and physical properties. A better knowledge of phase composition and the consequent application of stabilisation methods can make them suitable for reuse and/or inert disposal. Some critical aspects associated to the reuse of steelmaking slag concerning its volume instability, caused by free lime exposure to moisture, as well as its leaching behavior (due to metals contained in slag that can produce water or soil pollution), have been dealt with in recent studies [28]. In addition, land-based applications of steel slag concern replacing natural sand as aggregate in cement, often combined with its CO<sub>2</sub> sequestration properties. According to the recent literature, the slags reuse presents significant advantages; nevertheless, their internal reuse can be difficult, due to the variability of their composition and effects on the final product. A general purpose-monitoring tool was developed and exploited for the simulation and the assessment of the technical feasibility of the replacement of lime and dolime with Ladle Furnace (LF) slag with or without the partial recovery of EAF slag for the production of two steel families. Results have showed a small increase of 3–4% of the electric energy, but this is compensated by a reduction of about 14–16% of non-metallic raw materials [29].

Recent studies have showed that BF slags and Portland cement mixes with other steelmaking by-products, such as Electrostatic Precipitator dusts (ESP), BF sludge and Basic Oxygen Furnace (BOF) sludge, resulted in up to 90% immobilisation of hazardous constituents. Furthermore, by adding organic additives, such as citric acid, hazardous constituents can be liberated or immobilized [30]. Solid and gaseous steel by-products can be potential raw materials and reducing gases to be used for synthesizing rich iron bearing products like iron powder. The use of these by-products to produce a value-added product like iron powder can be a potential outcome. On this subject, a chemical reduction technique is suitable for synthesis of iron powders through the use of steel by-products. The aim is to optimize the process parameters of the applied techniques in order to produce pure iron powders [31]. The application of the Sequential Chemical Extraction (SE) analysis is particularly important, as it can provide information on the composition of solid steel processing by-products, and, consequently, the possibility to their classification process in order to improve the environmental protection. Recently the distribution of potentially toxic elements such as zinc, lead and copper between sensitive and immobile phases can be reliably obtained. In addition,

SE can give more refined classification by providing information for potential reusing and then reducing hazardous materials [32].

Steel slag contains iron oxides that could be recycled by reduction method and metallic iron could settle down to bottom of the reactor. Metal recovery and metallization rate could achieve 96.45% and 87.30% respectively. In addition, a good stability of the treated slag can improve its use. Furthermore, the energy of molten slag could be used effectively, and, consequently, process cost could be reduced [33]. The recovery of metals can be also achieved by using the bioleaching, depending on the slag composition. A recent test on BOF slag has been carried out for bacterial leaching and recovery of aluminum (Al), chromium (Cr), and vanadium (V). In the batch tests, Al, Cr, and V were bioleached significantly more from steel slag than in control treatments. The results showed that the culture supernatant could be used in an effective way for an upscaled industrial application to recover metals. On the other hand, the removal and recovery percentages of metals from the leachate were relatively modest, because of the high concentration of competing ions ( $SO_4^{2-}$ ,  $PO_4^{3-}$ ) in the culture medium. On this subject, other methods, such as selective precipitation, could improve the performance of the resin [34]. Concerning BOF slag, the mineralogy and element availability, such as chromium (Cr), molybdenum (Mo), and vanadium (V), could provide information to understand its possible environmental impact. This has been carried out through a Sequential Extraction Procedure (SEP), four-fraction-based, combined with X-Ray Diffraction (XRD), of two BOF slags. The results have showed that Cr and Mo primarily occurred in F4, than rather immobile elements under natural conditions, strongly bound into/onto Fe minerals. On the other hand, V has been more mobile with proportional higher findings in F2 and F3, and, through the X-ray diffraction, V has resulted bound into Ca minerals (larnite, hatrurite, kirschsteinite, and calcite) as well as to Fe minerals. However, the total amount of recovery did not represent an indicator of the availability of considered elements and, in addition, it did not correspond to the leaching of elements from BOF slag [35]. The possibility of Induction Furnace (IF) steel slag-based application in removal of Cr(VI) ions (hexavalent chromium) from aqueous solution in laboratory conditions at room temperature has been investigated. The alkali activated steel slag can induce the rate of adsorption of Cr(VI) on the surface of the adsorbent and Cr(VI) can be effectively removed from aqueous solution [36]. Furthermore, a recent study aimed to find a suitable application of the water-spray (WS-EAF) slag. After collection, crushing, milling and characterization in terms of chemical composition, morphology and phases, this slag has showed the following main phases: magnetite ( $Fe_3O_4$ ), wustite ( $Fe_{0.94}O$ ), beta-calcium silicate ( $Ca_2SiO_4$ ) and mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>). Results showed that WS-EAF slag appears to be a promising material for removal Cd (II) and Mn(II) from aqueous solutions and from industrial wastewater by adsorption [37]. In addition, BF slag, dust from the bag filters in the coking installation and dust from the liquid sludge from the scrubber have been tested to remove tricholoroethylene (TCE) from the groundwater. According to their composition and porosity, BF slag has showed the highest catalytic activity to degrade TCE by using hydrogen peroxide [38]. Recently, it has been found that some industrial by-products (steel slag, iron filings, and three recycled steel by-products) exhibited phosphate adsorption capacities higher than three natural minerals (limestone, zeolite, and calcite). In particular, the strong chemical bonds

between phosphate and steel by-products avoided the release of adsorbed phosphate to the solution. Consequently, these by-products represent alternative, low-cost effective adsorption media for phosphate removal from subsurface drainage [39].

Currently, significant improvements in recycling and reuse of BF and steelmaking slag have been achieved, such as the exploitation of slag from waste heat recovery to high value added applications (e.g. cutting edge surface coating technologies). Slag is used for waste heat recovery but it is not only possible through its direct use. Lately the improvement of the recovery of waste heat in steelmaking process has been studied by introducing a Slag Carbon Arrestor Process (SCAP), which uses slag for catalyzing conversion of tar and Coke Oven Gas (COG) into hydrogen-rich fuel gas. A multi-stage system has been proposed for effective recovery of the waste heat from BF slag as well as the environmental and economic impacts of the method. 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 looks at the use of slag as energy storage material in Thermal Energy Storage (TES) systems, used in concentrated Solar Power Plants (CSPs) to collect energy [40].

The increased demand of cement has led to environmental issues and to the reduction natural resources, by also increasing costs. For this reason, in the last few years, alternate materials have been tested, such as the slag reuse in cement production.

After a rapid cooling by water quenching, BF slag results in a glassy and granular form and, consequently, it becomes an excellent substitute material for the production of Portland cement. However, new methods for treatment of molten slag have been developed (e.g. dry granulation) in order to provide a material with higher properties compared to slag cooled by water quenching, that can be inefficient for the heat recovery and can produce harmful wastes such as H<sub>2</sub>S, heavy metals and SO<sub>2</sub>. In order to improve the hydraulic activity of slag blended Portland cement, the use of insoluble chemical activators has been tested, resulting in the improvement of the compressive strength of slag blended Portland cements, by applying optimum proportions of chlorine chemical activators and quality improvers. In addition, the temperature effect on the binders of BF slag and metakaolin (MK) has been tested [40]. Furthermore, the study of alkaline activated alumino-silicate precursors, also known as geopolymers, as alternative cementing material to Portland cement, has recently been carried out, due to their high mechanical characteristics and durability. In addition, BF slag mortar activated with Olive-stone Biomass Ash (OBA) presented lower zeolite content and average pore diameter than commercial costly industrial reagents and processes that result in high CO<sub>2</sub> emissions. Not only in Europe but also in China, the increasing amount of industrial byproducts linked to the increasing steel production has led to investigate the production of a novel green cement containing superfine particles with high volume fly ash and BF slag addition. This resulted in a novel green cement with better mechanical properties compared to commercial blended cement as well as better hydration properties than Ordinary Portland Cement (OPC) [41].

Recently, recycling of EAF slag as a green source in ceramic tile production, due to its chemical composition, has been considered. In addition, the exploitation of slag has been extended to biomedical applications, because of the bioactivity and biocompatibility of Fluorapatite-based glass ceramics for some applications (e.g. bone replacement, dental and orthopedic applications) as well as for optoelectronic applications, due to their chemical and crystallographic structure similar to the apatite structure of the bone [40]. In China also hotpoured converter slag has been used for ceramic materials. Fly ash, microsilica, and quartz have been mixed and, after heating at 1100–1200 °C, the ceramics have been sintered [42].

Large amount of blast furnace flue dust are generated, mainly containing iron oxides and coke fines. The potential use of flue dust as a substitution to the traditional fuel and raw materials in a cement plant in India has been analysed. This can result in advantages for both steel and cement industries. The reduction of the iron content in the flue dust, by applying the magnetic separation, has been assessed, but it does not effectively segregate the iron in the flue dust and neither increases the energy content. However, the cost analysis has showed that flue dust can be used effectively by the cement industry [43]. In the last few years, alternate materials have been experimentally tested for use in preparing concrete (e.g. steel fibre, asphalt, slag, asbestos, lead, dry sludge, wet sludge, fly ash, bagasse ash, red mud, plastic, glass, etc.). A detailed study of compressive strength, flexural strength and slump value has been carried out in order to find out the most suitable by-product as an alternative of natural materials [44]. BOF slag, EAF slag, and LF slag can be useful in many fields, such as road construction, asphalt concrete, agricultural fertilizer, and soil improvement. In addition, from the environmental and economic perspective, they can potentially be used in cement clinker production. Nevertheless, in order to achieve a better use for value-added purposes in cement and concrete products, recent challenges of using steel slags as cement replacement and aggregate in cement concrete have been carried out. In particular, as the cementitious ability of steel slags in concrete is low and it requires activation, it has been found that suitable aging/weathering and treatments can improve the hydrolyses of free-CaO and -MgO in order to mitigate the instability [45]. It has been also shown that the use of steel slag aggregate with wastewater in concrete is possible without any significant deterioration in fresh and hardened concrete properties [46]. Ground Granulated Blast furnace Slag (GGBS) has good structural and durable properties, that make it suitable to be used in cement concrete. The use of GGBS in concrete construction will be eco-friendly and economical and the optimum percentage of replacement of cement by GGBS lies between 40-45 % by weight. The ultrafine GGBS can improve strength and durability properties. In addition, new materials can be added to GGBS for getting better strength and durability [47]. A study of the mechanical properties in Self-Compacting Concretes (SCC), replaced by Granulated Blast Furnace Slag (GBFS) in the limestone aggregate from 0% to 60%, has been carried out. Replacing 50% of cement by ground GBFS in mortar has achieved a compressive strength, similar to that of the reference mortar, with 100% cement. In addition, the formation of new compounds, introducing chemical bonds between the GBFS and the paste, has been obtained. The formation of strong bond, thanks to the paste richer in Si, can improve the mechanical properties. On the other hand, because of the reactivity of the slags, the substitution of sand with the slag can lead to higher compressive strength of the concrete, and, consequently, to the increase of the compressive strength. These can result in reducing the energy and raw material consumptions and the greenhouse gas emissions. Furthermore, part of the destruction of natural quarries is avoided, due to the use of by-products instead of the required raw materials [48]. Usually BF slag has been used as a substitute for cement in concrete while steelmaking slag is mostly used as a filler material in embankment construction, as it has relatively low hydraulicity and a problem with volumetric expansion. Nevertheless, due to recent improvements in the slag quenching process, also the steelmaking slag properties have improved. For this reason, a comparative study assessing the mechanical properties of concrete containing EAF oxidizing slag, steelmaking slag, and GBFS has been carried out. The results have shown that replacing cement with EAF oxidizing slag delayed the hydration reaction at early ages, without founding significant issues in setting time, shrinkage or strength development [49].

The utilization of industrial by-products in road construction not only reduce their disposal to the landfills but also to encourage their use without compromising quality and performance of the road. On this subject, some industrial by-products can be also recycled as substitutes for conventional natural aggregates for producing hydraulically bound mixtures for road foundations. In particular, the combination of Foundry Sands (FS), EAF steel slags and bottom ash from Municipal Solid Waste Incineration (MSWI) in five different proportions could be applied for road foundations [50]. Concerning the Asian countries, also in Vietnam, under local regulations, steel slag was considered as a solid waste which should be processed and landfilled. Nevertheless, in the last few years, steel slag has been considered as a normal or non-deleterious solid waste. For this reason it has been studied for its reuse in the construction sector, as a replacement for mineral aggregate, in hot mix asphalt. Two hot mix asphalt mixtures using steel slag have passed the Marshall stability and flow test requirements. Moreover, its skid resistance for the surface course satisfied the national specification for asphalt. In addition, the pavement sections with the surface course of steel slag hot mix asphalt has showed a significant higher modulus than that of the conventional one. Only the roughness of the surface course paved did not meet the requirement of the specification [51]. Aramid fiber is a synthetic fiber chemically produced through the reaction between amine group and carboxylic acid group and used as a reinforced material to enhance the performance asphalt mixtures. The assessment of the replacement of natural coarse aggregate with EAF steel slag in the asphalt mixture reinforced by aramid fiber has been carried out in order to reduce asphalt layer thickness and transportation costs. Furthermore, steel slag aggregate has been immersed in the water for 6 months to reduce (by 68%) the content of free lime and free magnesia, which can cause the expansion volume [52]. A further investigation concerns the combination of steel slag and bottom ash to be utilized as aggregate in asphalt pavement. The characterization of physical, chemical and morphological features has been carried out to compare the bottom ash and the steel slag to the conventional granite aggregate. The bottom ash has showed weaker characteristics in terms of strength compared to the steel slag which has been much stronger than the granite, due to the presence of iron oxide. In addition, the content of lower silica in steel slag and bottom ash provides potential to resist moisture damage compared to granite [53]. Also the use of BF slag as an alternative substitute of natural crushed aggregate has been recently studied. Three asphalt concrete types with different maximum aggregate particle size and one stone mastic asphalt mixture for low noise surface layers have been selected. It has been shown that, on one hand, the use of BF slag aggregates in asphalt mixtures have not influenced the quality or durability of the mixture, but, on the other hand, sometimes it could even improve the properties [54]. BF slag presents interesting physical properties and mineralogical and chemical composition, useful as granular aggregate in the production of Hot Mix Asphalt (HMA). The evaluation of the effect on the resistance of a HMA, when the coarse fraction of a natural aggregate are replaced with BF slag, has been carried through different tests. The results have showed a significant enhancement in the properties of the HMA mixture after the replacement in volume of the coarse fraction of the limestone with BF slag. However, with the total replacement of the limestone, the adhesive properties of the asphalt-aggregate system will be worse [55]. In order to improve the reuse efficiency of steel slag, especially in expansive soil modifications, the composition adjustment and activation of steel slag have been studied resulting in an optimal slag-based composite with improved cementation efficiency. After adjusting and activating the composition, the cementation of the slag has significantly improved, resulting in the suppression of the swelling potential and improved strength. In addition, the requirement of the Chinese standard for first-class road/highway has been satisfied [56]. Furthermore, a developed work has been focused on the use of BOF slag as coarse aggregate and the alternative of using Blast Furnace Dust (BFD) as a fine aggregate in order to manufacture asphalt hot mixes for pavements. The evaluation of the physical characteristics and the susceptibility to water and plastic deformation of each type of mixture has been carried. The results confirm the use of BOF slag and indicate the feasibility of BFD use as fine aggregate in order to partially replace conventional aggregates in road paving [57]. In a recent study, waste foundry sand and BF steel slag from Indian factories, have been tested for gradation, specific gravity, morphology, chemical composition, and compaction as well as engineering properties, shear strength, and permeability. Furthermore, leachate studies have been carried out in order to assess the environmental impact of their use. Compaction behaviour of both the materials has resulted to be similar to granular soils and the two products considered in the study have been assessed for fill applications [58].

Furthermore, the application of steel slags as a liming material to raise the pH in acidic soils as well as to improve the physical properties of soft soils has been deepened in the last few decades [59]. For instance, the application of BOF slag to alkaline soils, affected by excess sodium, can decrease the exchangeable sodium content of saline sodic soil irrigated with saline water [60]. In addition, thanks to some properties, such as high porosity and large surface area, slags are successful used in marine environment for coral reef repairing [61] and for building artificial reefs. Furthermore steel slags can be used for H<sub>2</sub>S and metalloids adsorption from marine environments [62]. However, the application of the BOF slag as liming material presents some critical aspects, due to its content of trace amounts of heavy metals. In particular, chromium (Cr), which, 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 oxidized to CrVI by manganese (hydr)oxides (MnO<sub>2</sub>). The liming properties of BOF slag reduce the production of CrVI, while the added synthetic Mn<sup>IV</sup>O<sub>2</sub> promotes oxidation of CrIII. In general, the oxidation risk of CrIII present in BOF slag to CrVI, due to MnO<sub>2</sub> contained in the soil, is expected to be very low, because of the

low solubility of CrIII in soil [63]. Other recent results reported that the Linz-Donawitz (LD) converter slag amendment at a rate of 2.0 Mg ha<sup>-1</sup> in submerged rice cropping systems has significantly (p < 0.05) increased grain yield by 10.3–15.2%. In addition, it has mitigated CH<sub>4</sub> emissions by 17.8–24.0%, and decreased inorganic As concentrations in grain by 18.3–19.6% as well as has produced higher yield (due to the increase of photosynthetic rates) and the increase of availability of nutrients to the rice plant. The decrease in CH<sub>4</sub> emissions could be due to the higher Fe availability in the slag amended soil, that works as an alternate electron acceptor and, consequently, suppresses CH<sub>4</sub> emissions. The decrease in As uptake by rice with LD slag amendment could be due to the more Fe-plaque formation which could adsorb more As and the competitive inhibition of As uptake with higher availability of Si [64]. In addion, Iron (Fe) materials can be used for immobilizing arsenic (As) in soils, resulting in As concentration reduction in rice grains. The effect of by-product Fe materials coming from the casting industry on the As mobility in two soils by a long-term (about 100 days) flooded soil incubation experiment has been assessed [65].

The use of another steel industry by-product, the mill scale, formed during the hot rolling of steel, as a potential material used as Bipolar plates (BPP), a component of proton exchange membrane fuel cells (PEMFC), has been studied. Mill scale, due to its high iron content, can be a source for current collector in BPP and can contribute to decrease the overall cost of PEMFC based fuel cell systems. The mill scale powder was sieved, mechanically alloyed with the carbon source, and pressed under inert gas atmosphere. The structural changes of powder particles were studied by XRD, optical microscopy, scanning electron microscopy, and microhardness measurement. The achieved results have showed that the mill scale can potentially be applied to BPP, although further investigations and evaluations should be carried out [66].

A further by-products utilization includes fly ash, a by-product from burning pulverized coal in electric power generating plants, and GGBS, obtained by quenching molten BF slag to produce a glassy, granular product that is then dried and ground into a fine powder. The use of fly ash bricks has increased in recent years, because of their long term performance and their good mechanical and durability properties. In particular, the addition of fly ash improves the strength of concrete blocks, and the maximum compressive strength and split tensile strength have been reached with 50% replacement of fly ash. In addition, the compressive and flexural strength have increased by adding 30% of glass powder [67].

Furthermore, Steel Furnace Slag (SFS), Coal Wash (CW) and Rubber Crumbs (RC) have been recently mixed and tested in order to obtain an energy-absorbing capping layer with the same or higher properties compared to conventional subballast. Seven parameters, such as gradation, permeability, peak friction angle, breakage index, swell pressure, strain energy density, and axial strain under cyclic loading, have been considered. It was found that a mixture with SFS:CW = 7:3 and 10% RC (63% SFS, 27% CW, and 10% RC) is the best mixture for subballast [68].

Another "player" that has a primary role in steel industry is what is needed in practice for all the process steps, namely the refractory materials. Indeed, these products are present from the Blast Furnace to the Casting Machine, including furnaces, converters, vessels, nozzles and so on. Cases of internal recycling of spent refractories as slag formers or conditioners or for partial substitution of raw materials in the mixtures for new refractories are present worldwide. A virtuous model concerning this last aspect is given by the case of Nippon Steel & Sumitomo Metals Corporation that developed a method to purify from iron the spent refractories in order to obtain a recycled material that can be used for on-site additions to monolithic refractories or for concretes [69]. On the other hand, the increased establishment of strategic alliances between steel producers, refractory recyclers and refractory manufacturers opens the way to a circular economy approach hence favouring the setting-up of industrial symbiosis [70]. This implies also the possibility to extend the use of recycled refractories for external use, as examples for glass and cement industries [71].

Furthermore, a good example of IS involving the steel sector has been recently provided. In particular, the mutual exchange of materials has been carried out among a steelmaking plant, vendors, and other business partners in a network of industrial companies. The involved plants were a steelmaking plant, generating by-products (slag, EAF dust, mill scale, and zinc sludge) used by a cement manufacturer and a zinc smelter plant as raw material. The sludge serves as raw material for zinc ingots used in the steelmaking plant as raw material for the manufacturing of wire rod in the galvanization process [72].

Significant examples of IS have been recently provided, 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, biomasses or residual plastics, that are usually destined to landfill, can be reused as "alternative C sources". Biomass can be used in the iron and steelmaking as a possible solution to decrease fossil-based CO<sub>2</sub> emissions (above 50% compared to the current integrated route) and the net increase of direct CO<sub>2</sub> emissions is avoided, due to the emitted CO<sub>2</sub> capture by the growing during their growth. The use of biomass as reducing agent in different iron and steelmaking processes has been shown in recent literature [73]. For instance, biomass can be used in cokemaking, sintering and in carbon composite agglomerate production, through the injection of biomass, especially charcoal, and through replacement of PCI by high carbon content charcoal. On the other hand, the simultaneous conversion and utilization of carbon dioxide and plastics into fuels/chemicals in high temperature iron and steel processing can produce significant effects [74]. In particular, the use of waste plastics in steel industry, reduces ~ 30% of CO<sub>2</sub> emissions compared to using fossil carbon sources. Carbon dioxide reformation with the CH<sub>4</sub> from the waste plastics used in high temperature processes produce fuel gases and reducing gases (i.e. hydrogen and carbon monoxide).

Acronym	Name
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
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
PEMFC	proton exchange membrane fuel cells
PI	Process Integration
RC	Rubber Crumbs
SCAP	Slag Carbon Arrestor Process
SCC	Self-Compacting Concretes
SEP	Sequential Extraction Procedure
SFS	Steel Furnace Slag
TCE	tricholoroethylene
TES	Thermal Energy Storage
WS	Water-Spray
XRD	X-Ray Diffraction

#### 5. List of symbols, indices, acronyms and abbreviations

#### 6. List of References

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