REVIEW ARTICLE



A Comprehensive Review of Secondary Carbon Carriers for Ironmaking and Steelmaking Processes: Industrial Utilization of Non-biogenic Materials in Steel Production

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Abstract

The steel industry, one of the most challenging sectors to decarbonize, is responsible for approximately 5% of CO_2 emissions in the European Union and 7% globally. Achieving the goal of climate neutrality by 2050 requires reducing the industry's reliance on carbon-based fossil resources, primarily natural gas and coal. This comprehensive review discusses the use of non-biogenic materials in the steel industry. Various types of waste play a significant role in a circular economy scenario. The circular economy approach is essential for achieving carbon–neutral steel production. The utilization of non-biogenic secondary carbon carriers, such as polymers from waste plastics and rubber from tires, serves as auxiliary reducing agents and slag foaming materials, supporting the smart carbon usage in a process integration framework. In cokemaking, replacing coal with non-biogenic materials has been identified as a cost-effective and sustainable solution. This approach aims to enhance the energy and resource efficiency of recycling processes for both post-consumer (end-of-life products) and post-industrial (materials produced during manufacturing) plastic-containing materials. Finally, the review examines methane cracking, which produces hydrogen and solid carbon. Methane cracking is a promising alternative to water electrolysis due to its lower energy demand, although it is not yet fully mature for industrial application.

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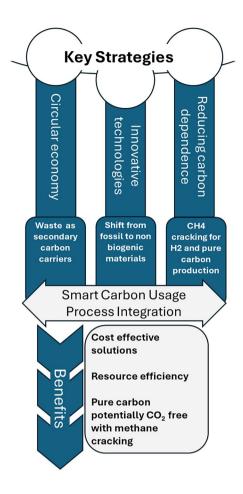
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Graphical Abstract



 $\textbf{Keywords} \ \ Steel making \cdot Iron making \ CO_2 \ reduction \cdot Decarbonization \cdot Secondary \ carbon \ carriers \cdot Polymers \cdot End \ of \ life \ tires$

Abbreviations

EAF Electric arc furnace BF Blast furnace

SCC Secondary carbon carrier

CE Circular economy

SCU-PI Smart carbon usage in a process

integration

ASR Auto shredder residue

PCDD/PCDF Polychlorinated dibenzodioxins/furans

ACI Arc covering index
SRA Secondary reducing agent
MPW Mixed plastic waste
BOF Basic oxygen furnace
DR Direct reduction
SR Smelting reduction

Introduction

Although challenging, the transition to a climate-neutral society is essential for a more sustainable world and to mitigate the impacts of climate change. In Europe, under the Green Deal scenario, all sectors of society and the economy are committed to achieving emission reduction targets.

The steel industry, one of the most difficult sectors to decarbonize, is responsible for approximately 5% of CO₂ emissions in the European Union and 7% globally [1]. The steel production relies on fossil carbon materials (e.g., coal, coke, and natural gas) as fuel and reducing agents to provide energy to the process or carbon to the steel bath. Steel production occurs via four main routes: the integrated route via Blast Furnace–Basic Oxygen Furnace (BF/BOF), Smelting Reduction–Basic Oxygen Furnace (SR/BOF) [2], Direct Reduction–Electric Arc Furnace (DR/EAF), or scrap melting in an EAF [3].



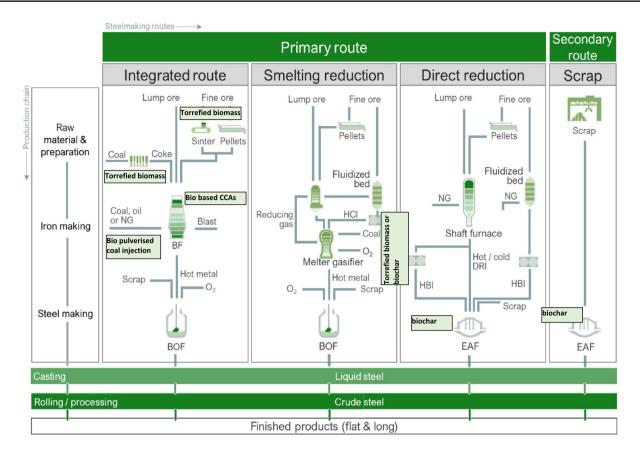


Fig. 1 Main pathways for using secondary carbon bio-carriers in iron and steelmaking routes [4]

In a previous paper [4], the use of biogenic materials (biomass, torrefied biomass, biochar, charcoal, or biocoke) was discussed, considering their benefits, technical and technological challenges, and perspectives. Figure 1 illustrates these routes using coal or coke, which can be considered for the integrated use of SCCs.

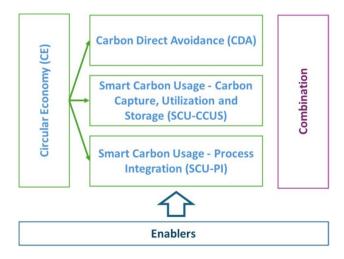


Fig. 2 Areas of intervention and their interactions [5]

In this comprehensive review, the use of non-biogenic secondary carbon carriers (SCCs), as polymers from waste plastics, rubber form tires, automotive shredder residues, is discussed as relevant topic in a circular economy (CE) and Smart Carbon Usage-Process Integration (SCU-PI) decarbonization pathways. The general scheme of decarbonization pathways of Clean Steel Partnership SRIA [5] for carbon–neutral steel production are reported in Fig. 2.

This paper describes examples of the substitution of coal with non-biogenic material, including material characteristics, technological aspects, and different ways of utilization in ironmaking and steelmaking and modeling. The innovative, cost-effective, and sustainable solution, aiming at improving the energy and resource efficiency of the recycling processes for post-consumer (after product's end of life) and post-industrial (produced during transformation processes from raw materials to final product) has also been analyzed.

The utilization of secondary carbon carriers (SCCs) is described in the following sections, reporting the main results obtained in:

1. Integrated steel production (based on blast furnace–BF) [6, 7]



2. EAF-based production route [8–10].

Adapting processes and operating practices is necessary for the utilization of SCC due to their specific physico-chemical characteristics. Table 1 below reports the main characteristics of SCC, with average values taken from:

- Average values of technical sheets from commercial products for anthracite.
- Rubber: average values from internal analysis.
- Polymers [8]
- Automotive shredder residue (ASR) [11]

Although the carbon content is generally high in all the materials mentioned above, other physico-chemical properties vary significantly:

- The volatile matter content is significantly higher in all SCC, leading to rapid devolatilization in high-temperature environments.
- Ash content is similar for rubber and polymer but higher for ASR, resulting in lower heating values for ASR compared to anthracite and other SCC.
- Polymers have low sulfur content but generally higher chlorine values.

Before describing the utilization of SCCs, it is worth mentioning a technology developed for hydrogen production that does not directly release CO_2 into the atmosphere, addresses as methane cracking or methane pyrolysis [12, 13]. This process is mentioned in this paper because it also produces solid carbon, which, due to its high purity, is suitable for various applications, such as the carburization of molten steel baths.

This process is based on the reaction:

$$CH_4 \to C + 2H_2 \tag{1}$$

Table 1 Average values of physico-chemical characteristics of SCC

Analysis	Anthracite	Rubber	Polymers	ASR*
Ash (%)	2–8	2–5	5–10	12–26
C fix (%)	85–95	15-20	1–3	2-5
Volatile matter (%)	2–8	85–75	90–96	70-85
C (%)	80-90	75–80	65–75	45-60
H (%)	0.5-1.0	8–9	8-10	5-10
Cl (%)	_	0.05	0.4 - 1.0	1.2 - 2.0
S (%)	0.5-2.0	1.4-2.2	_	0.2 - 0.4
HHV (MJ/kg)	28-30	30-32	30-32	20-30

^{*}ASR automotive shredder residues



If biomethane is used, the produced solid carbon is neutral respect CO_2 emissions. Although the technology readiness level (TRL) of methane cracking is currently too low for industrial application, it presents an attractive alternative for hydrogen production due to its lower energy demand compared to methane reforming and water electrolysis. The solid carbon produced from this reaction can potentially be reused in ironmaking and steelmaking.

Secondary Carbon Carriers' Utilization in Integrated Steel Production

Integrated steel production requires a significant amount of fossil resources. Coal is used as a reducing agent and energy carrier in different steps of whole production process. It is utilized in cokemaking [14, 15], sintering, and injected as pulverized coal injection (PCI) in the tuyeres of BFs [16–18].

The utilization of waste plastics in cokemaking has been studied extensively. The results indicate that, due to the stringent requirements for coke properties necessary for BF applications, the amount of plastic that can be used is generally low. Coke quality is crucial for controlling BF performance. Adding polymers to the coal blend for coke production results in lower density of charge materials and reduced coal strength. Literature suggests that adding waste plastic to the blend for coke production in the range of 1–2% does not affect the Coke Strength after Reaction (CSR) index.

Concerning the existing experiences, a recent European project examined the possibility of using biomass in the sintering process [19]. However, no data is available regarding the utilization of waste plastics in sintering, likely due to the high volatile matter content of polymers.

Secondary carbon carriers (SCCs) can be injected into BFs, partially replacing pulverized coal and consequently reducing coke utilization. Plastic waste, due to its widespread use, heterogeneity, and common mixing with other materials, requires comprehensive pre-treatment to ensure suitable quality. Plastics are attractive due to their high heating value, high carbon content, and large availability. Low-grade plastic waste, such as mixed plastics from collection and recycling processes, can be used as coal substitutes without competing with polymer recycling. These materials can be used after specific pre-treatment, including separation/sorting, densification, milling, and grinding to produce particles with controlled density, composition, and mechanical stability.

It is important to note that the utilization of polymers in both BF and EAF routes is governed by the Italian Standard Regulation (UNI 10667), which specifies the main physicochemical properties necessary for use as reducing agents and molten bath carburizers. Table 2 reports the chemical

Table 2 Chemical parameters outlined in the technical standard UNI 10667-17:2018

Parameter	UNI 10667-17:2018 requirement
Heterogeneous plastics content	≥80% in weight in the dry matter
Low heating value (LHV)	≥30 MJ/Kg
Chlorine (Cl)	≤2%
Cadmium (Cd)	≤8 mg/Kg
Lead (Pb)	≤100 mg/Kg
Mercury (Hg)	≤0,6 mg/Kg
Moisture	Max 10% in weight

Table 3 Extracted material requirements for the waste plastic materials used in BF A of Voestalpine Stahl (Linz site) [20]

Parameter	Value
Moisture (max. wt%)	1.5
Bulk density (min. kg/m³)	300
Particle diameter (max. mm)	6
Net calorific value (min. MJ/kg)	33
Sulfur (S) (max. dry wt%)	0.5
Chlorine (Cl) (max. dry wt%)	1
Copper (Cu) (max. dry kg/kg)	1000
Zinc (Zn) (max. dry kg/kg)	500
Chromium (Cr) (max. dry kg/kg)	500
Nickel (Ni) (max. dry kg/kg)	500
Lead (Pb) (max. dry kg/kg)	125

parameters outlined in the Italian technical standard UNI 10667-17:2018.

As further experience, voestalpine Stahl receives waste plastic in a pre-processed quality ready for injection. Table 3

shows the main quality requirements for the three different types of waste plastic currently used at voestalpine Stahl: pellets and agglomerates from various waste plastic fractions (packaging waste, commercial and production wastes, and lightweight fractions from mechanical-biological treatment), and granulate from shredder residue treatment [20–23] (see also Fig. 3).

For automotive shredder residues (ASR), one exemplary method is the VW-SiCon process (see Fig. 3). The VW-SiCon process aims to recover injectable materials for the BF from end-of-life vehicles (ELV), waste electrical and electronic equipment (WEEE), and mixed scrap. The separation is performed using mechanical methods based on the detection of optical and physical properties (such as density, particle shape, magnetic behavior, and conductivity). A shredder fraction composed of hard plastics and low in PVC is prepared for subsequent BF operations. The SiCon Plant in Antwerp, Belgium, can treat approximately 100,000 tons per year of automotive shredder residues and produces granules suitable for BF use. The shredder fiber fraction can theoretically be applied in coke ovens or power plants.

In general, the use of waste plastic in the BF combines energy recovery and feedstock recycling, reducing the demand for other fossil reducing agents such as coke, coal, or heavy fuel oil, and thereby decreasing the overall CO₂ footprint. Feedstock recycling in the BF process involves the generation of synthetic gas. Compared to complete incineration, a portion of the energy content of waste plastic is utilized as chemical energy during injection into the BF. Waste plastic use in BF is the most significant feedstock recycling process in Europe. Currently, voestalpine Stahl is the only EU steel producer using waste plastic as an alternative reducing agent in the BF (Fig. 4). However, this practice is spreading across Europe. On the other hand, Acciaierie

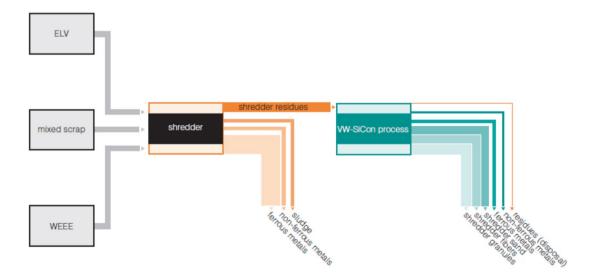


Fig. 3 Schematic of the VW-SiCon process for the pre-treatment of ASR [22]



Fig. 4 Waste plastics used at voestalpine Stahl (A = pellets, B = agglomerate, C = granulate) [22]

d'Italia has conducted experimental trials to test plastic injection in their BFs and is investing in industrial plants for polymer injections.

The plastic injection plant at the Linz site was commissioned in 2007 (Fig. 5), with permission to inject a maximum of 220,000 tons per year at their largest BF A, with a daily nominal capacity of 8500 tons of hot metal (HM). Currently, about 70,000 tons per year, corresponding to approximately 20 kg/t HM of waste plastics, are injected. Over the last 2–3 decades, other steel producers have investigated the use of plastic waste in their BFs.

Various plastic wastes are stored in five silos, each with a capacity of 800 m³. The appropriate mixing of plastic waste is achieved using weigh-belt feeders and oscillating discharge

systems. Oversized particles (> 10 mm) are removed through sieving.

At BF A, 32 injection positions are installed (6 bar absolute pressure, 25 mm pipe diameter), with the pneumatic injection system developed by E.S.C.H. GmbH (Germany). Different lance systems are used for injection, including coaxial lances, high dispersive lances, and swirl lances. In the BF raceway zone, the injected waste particles are molten and gasified at temperatures around 2300 °C, forming H₂ and CO according to the following reaction equation [17]:

$$C_n H_m + n/2O_2 = nCO + m/2H_2$$
 (2)

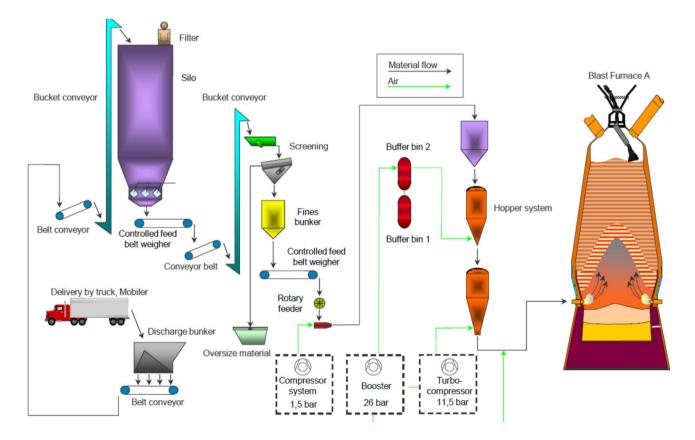


Fig. 5 Waste plastic injection process scheme of BF A at voestalpine Stahl in Linz [12]

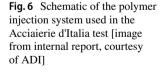


The reduction of iron ore occurs through chemical reactions with gaseous H_2 and CO, with a desired C to H_2 ratio of 8:1.

On the other hand, in 2022, Acciaierie d'Italia conducted plastic injection tests in BF number 4 at the Taranto site. Due to the experimental nature of the trials, the polymer was added to the PCI flow in the PCI production plant, located more than 200 m away from the BF (Fig. 6). Consequently, PCI and polymer joint feeding occurred along the pipelines without a dedicated injection system for polymer. The characteristics of the materials used align with those reported in Tables 1 and 2. The amount of polymer injected varied from 500 to 1700 kg/h, corresponding to 2–9% of the polymer within the PCI and polymer mix. One of the main objectives of the test was to verify the feasibility of using the current PCI injection system for polymer injection.

To minimize the risk of blockages in the transport pipe due to differences in material viscosity and density, Bluair® polymer [8] with a particle size smaller than 2 mm was used (Fig. 7). Despite this precaution, accurately controlling the injected polymer fraction proved challenging, and the delivery pressure in the transport pipe increased significantly. These issues were attributed to the intermittent descent of the polymer inside the vessel, a reduction in voids between the powder particles leading to an increased packing factor, and the temporary occlusion of some injection lances.

Apart from the pressure issues with the injection system, no significant changes were observed in the operation of the BF, except for a slight increase in the hydrogen content (0.5%) of the BF top gas. This increase did not affect the gas network operation or subsequent treatment and utilization. The preliminary trials were successful, and the polymer injection is expected to bring significant cross-sectoral benefits in terms of environmental sustainability. Consequently, Acciaierie d'Italia (ADI) is now investing



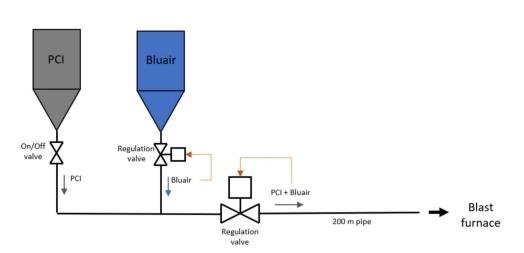




Fig. 7 Particle size on the left, reduced particle size on the right used for tests (Bluair® particle)

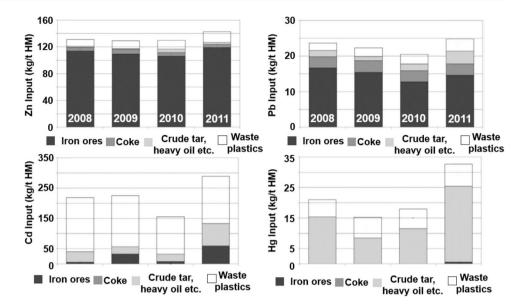
in the design, construction, and installation of a dedicated system for polymer injection in its BFs.

The issues related to the control of particles injection experienced during trials will be addressed with the erection of a dedicated injection system.

Regarding environmental aspects, polymer injection into the BF introduces additional heavy metals, such as zinc, lead, mercury, and cadmium, which can influence emissions in the BF top gas or affect process stability. For the operation at voestalpine, waste plastic contributes to 60–80% of the total cadmium input, approximately 30% of the total mercury input, and around 15% of the total lead and zinc input (see Fig. 8).

Emissions to wastewater, cleaned top gas, and BF sludge remained almost constant despite increasing heavy metal input. Thus, no environmental impacts were observed due to feedstock recycling of plastic waste in the BF. Regarding emission containing chlorine, hydrogen chloride (HCl) is primarily formed during the BF process. The generated HCl is removed by charging limestone additives into the BF, and most of the HCl is eliminated during top gas treatment (scrubber). Since Cl can cause high-temperature corrosion of walls and pipes in the exhaust system and gas cleaning, the waste plastic injection rate of materials with an average Cl concentration of 1 wt% is set to a certain limit.

Fig. 8 Input sources on the metals Zn, Cd, Pb, and Hg into the BF during the observation period 2008–2011 at Voestalpine [24]



During the tests at the Acciaierie d'Italia plant, particular attention was paid to environmental emissions, which were monitored throughout the trials. The results showed no worsening of emission conditions (organic pollutants such as IPA and PCCD/PCDF were monitored without significant variation compared to standard conditions, according to the company's internal report).

To sum up, the following main advantages can be mentioned when using waste plastic as alternative reducing agents in the BF:

- Recyclability of materials is unsuitable for mechanical recycling,
- Prevention of dioxin formation during BF operation when using Cl-containing plastic waste,
- Only minor modifications to the BF gas scrubber parameters are necessary to maintain emission levels comparable to standard BF operation without plastic (based on long-term experience from Voestalpine results),
- Partial replacement of fossil coke and coal, leading to lower CO₂ emissions due to co-reduction using the H2 generated from waste plastic gasification in the BF raceway.

Secondary Carbon Carriers Use in EAF

Steel production by EAF currently represents 28% of global production and reaches 46% in Europe. A trend is expected where the EAF share will reach, at least, 45% worldwide [25]. The EAF melting process is generally a batch process, divided into charging materials (scrap by basket), melting solid materials, refining (removing metallic species such as Si and Al and P by oxygen injection and capturing them in

the slag phase), de-slagging (removing slag), and final tapping (preparing steel for subsequent metallurgical steps). During refining, the metallurgical operations include carbon injection through lances to achieve the desired carbon level in the steel and promote slag foaming.

Fossil coal is used to promote slag foaming [26]. Lump coal is charged in the basket, while pulverized coal is usually injected through specially designed lances. Anthracite or petroleum coke are typically used for these purposes. Slag foaming occurs naturally by CO/CO₂ gas bubbles formed through the oxidation of carbon in the molten steel by oxides in the slag. Injected carbon can directly react with iron oxide (3) or reduce iron oxide indirectly (4, 5) via gasification:

$$(FeO) + C(s) \rightarrow Fe + CO$$
 (3)

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

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$
 (5)

The foam formed submerges the electrodes and has several beneficial effects on the process, including:

- Reducing heat losses (by radiation) of the molten steel bath, improving process efficiency.
- Lowering noise emissions.
- Reducing electrode and refractory consumption.

Using carbon from secondary non-biogenic sources to replace fossil carbon represents a viable solution for carbon-neutral production in a CE scenario. A review of studies on alternative carbon sources in EAF steelmaking has been conducted by Echterhof. The utilization of polymers (plastics and rubber waste) and blends of



these materials with coke in the EAF has been analyzed in several studies. These mixtures exhibit significantly increased reduction and carburization of the metal compared to coke alone. The hydrogen introduced by organic waste and side reactions involving hydrogen lead to faster gasification of solid carbon and faster reduction of iron oxide in the slag. The volume ratios during slag foaming increased with polymer additions, improving slag foaming. Due to high process temperatures in the EAF, polymers decompose into basic hydrocarbons, especially CH4 (reaction 6), and into carbon and hydrogen (reaction 7).

Polymers
$$\rightarrow C_n H_m$$
 (6)

$$C_n H_m \to n < C > + mH_2 \tag{7}$$

The proper materials preparation and the availability of tailored injection systems are key factors to allow polymers utilization in EAF.

As examples of investigations targeted on direct application on-field, two demonstration projects, ONLYPLAS-TIC and POLYNSPIRE, [8, 9, 27-29], were developed within the EU supporting Programs (Horizon and RFCS, respectively). Both projects were aimed at substituting all the fossil carbon sources—injected and charged—with a polymeric reducing agent deriving from the recycling of post-consumer plastics, i.e., from plastic waste selection and sorting plants (mixed plastic waste—MPW). MPW is particularly difficult to recycle. A suitable valorization is its application in steelmaking operations as a secondary reducing agent (SRA in UNI10667-17), substituting fossil coal. This maximizes recycling, avoiding both landfilling and incineration. The material used was prepared and delivered for tests by IBLU, The production of polymer particles starts with sorting and selection before the postconsumer plastic feedstock reaches the recycling site.

Manual and automatic sorting solutions maximize plastic content and minimize non-relevant materials and chlorine-containing plastics. Selection processes ensure compliance with technical standards and required physical and chemical characteristics. Production phases include shredding, flotation, densification, milling/grinding. The latter includes requirements concerning a range of parameters, including chlorine, mercury, lead, cadmium, low heating value, and moisture. In general, for the same foaming purposes, other materials such as rubber particles and Automotive Shredder Residues can be used. Table 4 below reports the analysis of the polymer particles, rubbers, and ASR used in the tests described in the following paragraphs, as well as the average values of anthracite, collected from commercial technical sheets of materials used in steel factories.

Table 4 Non-biogenic materials: materials type and characteristics for EAF tests

Analysis	Anthracite	Rubber	Polymers (BLUAIR®)	ASR
PCS(MJ/kg)	28-30	30–34	30–32	20–30
ASH (%)	5-10		5-10	12-25
Cl (%)	_	0.05	0.4-0.6	1.2-1.8
S (%)	0.5-1	1.4-2.2	_	0.2 - 0.4
H (%)	0.5-1	8–9	10	6–9
C (%)	80-90	75–80	65–75	48-58
C fix (%)	80–90	15–20	1–3	3–5

Anthracite values are averages from commercial product sheets; rubber data are from internal analysis; polymers from [8] and ASR from [11]

Secondary Carriers in EAF: Injection Issues and Testing

Injection technology plays a crucial role in promoting slag foaming in EAF [9], as mentioned before. It involves addressing feasibility issues, operational aspects, and thermo-fluid-dynamics challenges [28, 29].

Tailored injection systems have been developed in the mentioned projects Polynspire (by HTT Engineering [8]) and ONLYPLASTIC (by Tenova [27]).

To give an idea, regarding the injector developed in Polynspire project, a preliminary Computational fluid dynamics (CFD) study was conducted to identify the most reliable injection conditions. The bulk density of the plastics used was low (around 0.3 t/m³, while coal density is about three times greater) and had a low gasification temperature. This required design and testing of a dedicated system:

- To maximize the energy of injected particles,
- To control the temperature in the injection zone to prevent premature reactions before particles properly mix with slag and steel, and
- To ensure efficient mixing of steel and slag with the injected material to promote effective reactions when particles are used as carbon substitutes.

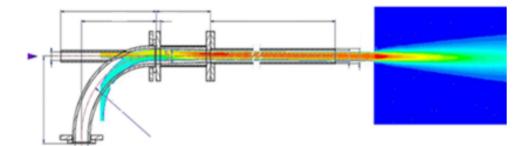
Additionally, it was important to inject particles at an efficient angle and distance to the liquid steel.

The final option identified was a lance where injected plastic particles were blended with recycled 'white slag' to reduce reaction temperature and increase kinetic energy impact. Figure 9 shows examples of velocity maps in and outside the injector.

This basic injection lance was combined with an oxygen injector to promote reactions in the furnace and enhance bath mixing. The design process was supported by both water model tests and CFD analysis. The basic concept of



Fig. 9 CFD analysis of the plastics/slag mixed materials injector; CFD simulation model results showing the fluid flow field from the injection system



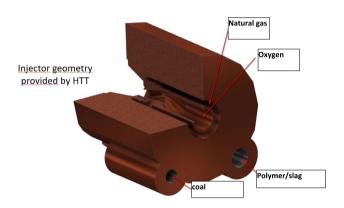


Fig. 10 Sketch of a dedicated injector developed and applied in the Polynspire Project (courtesy HTT) [8]



Fig. 11 EAF steel bath reduced scale water model with simplified lances equipment [8]

the combined injector, which integrates both plastic particle injection and oxygen injection, is illustrated in Fig. 10.

In the system shown in Fig. 10, the plastic particles are injected via the central part of the lance. These particles are then shrouded by high-velocity oxygen to increase their speed within the envelope around the particles. Another ring of nozzles is used for natural gas as the primary burner fuel, and the final ring consists of nozzles for combustion oxygen. All these nozzles are co-centrically assembled and installed in a water-cooled copper jacket to enable operation within the EAF environment.

The lance injection behavior was tested using both physical and numerical modeling. Due to the time-consuming nature of numerical simulations of jet behavior in a multiphase system, the impact of injected particles and their penetration into liquid steel was simulated using a simplified reduced scale (1:3) water model. Since water has a similar ratio of viscosity and density to steel, a water model can provide indications of real behavior according to Froude's similarity.

Figure 11 shows the simulated EAF steel bath water model with simplified lance installation. The lance operated with compressed air at a 45° angle, creating a cavity by injecting compressed air with plastic particles. Plastic particles (1–3 mm) were added to the lance air stream to simulate injection (Fig. 12). A comparison with the efficiency of the

pulverized coal injection was carried out in terms of particle penetration in the bath.

Information was also provided on the splashing effect above the bath level induced by the injection lance, the cavity formation in the liquid due to gas penetration, and the trend versus jet angle impact. The tests with the physical model showed that the penetration of the injected particles was acceptable for the purposes of foaming practice, comparable to the penetration cavity with fossil particles.

Within the Onlyplastic project, injection devices were developed by Tenova. A sketch of the first version is shown in Fig. 13. A supersonic oxygen lance and a coal lance are coupled together in a single device mounted on the furnace wall. This design allows the supersonic jet to penetrate the slag layer and allows solids release to the steel-slag interface by entrainment effect.

The solution was then optimized by Tenova, in a first step with a version suitable for injecting low-density materials (KT® Twin SRA), to maximize the entrainment effect by making the two streams encounter outside (or very close to) the slag layer. Its preliminary testing on the Feralpi Lonato EAF (Fig. 14, penetration on the left, sketch on the right)



¹ Tenova KT® Twin injection system.

Fig. 12 Image of the EAF water model testing with injection of polymers and penetration into the bath [8]



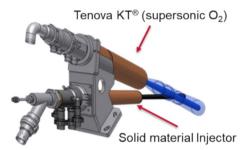


Fig. 13 Tenova KT® Twin injection system [9]

gave encouraging results for injecting solid material into modern EAFs.

The next step was a KT® Multi injection system (Fig. 15), where multiple solids are injected from a unique lance to favor advanced process control practices and installation in complex layouts. This solution was used to test advanced production practices in IP 2 (single configuration) and IP 3 (twin configuration) by coupled lime and BLUAIR® SRA injection as described next. The objective was to optimize the slag foaming process by controlling the different heat releases of the materials.

From Design to Industrial Testing

Mentioned EU projects, whose tailored injection systems, have utilized the same polymer particle (Bluair® particle). Trials to apply the injection solution, shown in Fig. 10, were carried out in the frame of the Polynspire project, at the Ferriere Nord EAF Plant. Long-term trials were systematically performed. Different operational conditions were analyzed to assess the effect on the process of various parameters, such as the quantity of utilized polymers leading to a reduction of fossil coal and the substitution percentage. In detail, two campaigns were carried out. At first, about 2000 test heats were carried with 30% less anthracite, replaced by

plastics as a right compromise among available material and quantity significant enough to assess process parameters variations. Once achieved encouraging results, a further 200 test heats followed with a 50% replacement.

The furnace metallurgical performances were evaluated by collecting and analyzing more than 40 different variables as representative indicators. The most interesting indicators are described below:

- Anthracite usage: amount of fossil coal; a negative value indicates resource saving.
- Calorific value: a measure of heating power (anthracite plus polymers contribution).
- Total harmonic distortion: higher values indicate better energy transfer to the metallic bath, avoiding dispersions and excessive wear of refractories, and are related to foaming slag formation.
- Sound pressure level: recorded near the EAF; lower sound levels reflect better foamy slag formation.
- Average active power: higher values indicate more efficient energy transfer to steel.
- EAF specific electric consumption: electricity consumption per ton of liquid steel produced; a negative value indicates energy saving.
- Metallic yield: amount of liquid steel produced versus the amount of charged scrap, expressed as tapped steel/ charged material amounts. Furnace loss is complementary to 100.
- O₂ consumption: a negative value indicates resource
- CO₂ emissions: considering only the quota affecting the use of anthracite and polymers; a negative value indicates resource saving.
- Exported power from furnace water-cooled panels: higher temperatures indicate higher heat loss inside the furnace. Less radiation means better foaming slag.



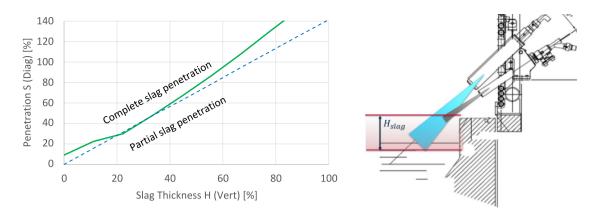


Fig. 14 Tenova KT® Twin injection system performances. Left: comparison of foaming slag penetration capability between the coal injector and the SRA injector. Right: configuration of the two jets in the Tenova KT® Twin injection system [9]

Fig. 15 Tenova KT® Multi injection system. Left: concept sketch; right: installed on Feralpi EAF [9]



Table 5 Results of heats using 300 kg/heat or 600 kg/heat polymers in substitution to anthracite

	DELTA USING 30% POLYMER (%)	DELTA USING 50% POLYMER (%)
Anthracite consumption per heat	-34	-41.93
Calorific value per heat	+4.76	+21.2
Total harmonic distortion	+0.45	+1.22
Sound pressure level	-0.47	-0.69
Average active power	+0.37	+0.49
EAF specific electric consumption [kWh/t _{liq steel}]	-1.3	+1.92
Metallic yield	-1.44	+15.66
O ₂ consumption	-0.3	-2.71
CO ₂ emission per heat	-5.6	+4.34
Exported power from furnace panels	-13	-27
Exported power from settling chamber and fume treatment	+9	+12

About CO_2 -emission, 5.6% saving refers to the averaged emission due to anthracite and polymers used for each heat. In particular, the heats with use of only coal led down to 24 Kg CO_2 /tliq steel while using polymers. That amount considers only the amount of anthracite and polymers used for that heat and their respective carbon content. Moreover, the CO_2 -emission concerning only the part of the polymer could be further reduced by 30% due to the biological origin of the portion of the material. The previous calculation does not consider this reduction. Summarising, the contribution from the coal could be quantified in 3,1 CO_2 ton for every ton injected while for polymers is about 1,9.

Exported power from settling chamber and fume treatment water-cooled panels: higher temperatures indicate higher heat loss through the fume treatment plant. This value refers to post-combustion reactions inside the pipe-

line. Temperature decreases and some reactions become possible.



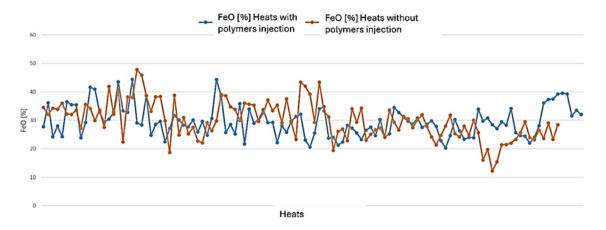


Fig. 16 Focus on FeO % in the EAF slag

Table 6 Summary of trials carried out in the Feralpi Lonato plant in the ONLYPLASTIC project [9]

Test number	Coal charged	Polymers charged	Polymers injected	Coal injected
1	No	No	Yes	No
2	No	Yes	Yes	No
3	No	Yes	No	Yes
4	No	Yes	No	No
5	Yes	No	Yes	No
std	Yes	No	No	Yes

A comprehensive overview of the performance in terms of the defined parameters for different polymer amounts injected is shown in Table 5.

Another important indicator of process stability compared to "standard conditions" is the variation in the iron oxide percentage in the slag. The experimentation showed that no significant variation of iron oxide content in the slag detected using anthracite or blend anthracite/plastic particles (Fig. 16).

Finally, confirming the positive results in terms of overall sustainability, a measurement campaign at the chimney performed both with and without polymers showed no significant differences in environmental impact (dioxins, furans, dust, and organic pollutants).

At the Feralpi EAF plant, in the frame of Onlyplastic project [9], the feasibility of polymer utilization in EAF was also confirmed. Feralpi conducted preliminary trials of charging polymer chips in the basket. The chemical composition of the particles (injected) and chips (charged) was the same. Different combinations of polymer usage were tested, including coal or polymer injections and carbon and polymer basket charging.

Table 6 summarizes the experimental matrix used at Feralpi.

Positive results with polymer injection in EAF have been obtained in terms of:

- Process stability.
- Energy consumption and steel composition.
- Slag foaming and arc covering.

The effectiveness of the plasma arc through foamed slags is detected using an acoustic sensor. Positive results have been obtained in trials with injection of polymer and antrachite and polymer alone.

Tests with Rubber Particles

End-of-life tires as a substitute for charge coal or anthracite were used in two industrial EAF steel works: the LME plant owned by Beltrame Group in France and the Acciaierie Venete plant in Italy [30]. The tires contain carbon in synthetic and/or natural rubber, textiles, and carbon black, as well as a significant amount of steel wire, which can be recycled in EAF. Natural rubber included in the tires can be considered carbon neutral. In the tests carried out by LME in France, the material was added in bulk, in big bags, via injection, and through the fifth hole. They determined a substitution rate of 1.7 kg tire per kg of carbon and found that using up to 8-12 kg/t steel is possible without detrimental effects on product quality, emissions, or process behavior. However, adding tires instead of coal requires careful handling to avoid increasing the temperature in the off gas dedusting system. Tires should be placed in the middle of the basket to avoid direct contact with the hot heel and reduce burn-off.

Tests using rubber particles have also been extensively performed outside Europe [31]. Numerous industrial trial campaigns were conducted at the OneSteel Sydney steel works, where the injection coke for slag foaming was replaced by an HDPE/coke blend. The use of the HDPE/



coke blend led to better slag foaming according to visual observations, reduced specific energy consumption (-3%), reduced power-on time, and similarly reduced tap-to-tap time, leading to increased productivity.

Tests with Auto Shredder Residues

ASR light fraction was used to produce briquettes (by pressure extrusion) to replace carbon in EAF. This material was tested within the European funded project RIMFOAM,² addressing materials characterization, densification into lumps suitable for charging in the basket with scrap, and industrial trials.

ASR, also known as "car fluff," is the fraction of a shredded end-of-life vehicle (ELV) with a calorific value ranging from 20 to 30 MJ/kg, depending on the ash content. The heterogeneity of ASR, along with varying levels of contaminants (chlorine, heavy metals, PCDD/Fs), moisture, ash, and calorific value, presents significant challenges in selecting or designing an appropriate treatment process.

The chemical properties of ASR have been optimized through a combination of manual and automatic sorting solutions, maximizing plastic content and minimizing non-relevant materials, including chlorine-containing plastics and other undesired elements. The plastic mixture from the automotive recycling chain is pretreated to form dense briquettes, which can be handled similarly to fossil coal lumps and charged into an EAF basket. High-pressure densification and hot extrusion were tested to produce mechanically stable materials, with high-pressure technology proving most reliable. The resulting briquettes had a carbon content of 52% and an ash content of 34%.

In the RIMFOAM [11] project, the trials were performed in the EAF substituting 100 kg of coal with 450 kg of ASR briquettes. The main effect has been the reduced electrical energy consumption by approximately 8 kWh/t. In addition, parameters such as natural gas consumption, oxygen consumption, or tap-to-tap time have not been affected. However, ASR briquettes should not be charged at the top of the scrap basket to avoid early and rapid combustion, which increases the temperature in the off-gas duct. An increased substitution of 200 kg of coal with 900 kg of ASR led to a temperature overload in the dedusting system, which was intolerable. Emission measurements showed no negative impact on emission levels, including dioxins and furans.

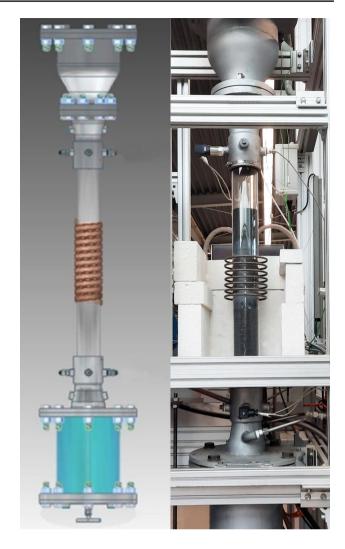


Fig. 17 Inductively heated BFI test unit

Carbon from Methane Pyrolysis for the Iron and Steel Industry

As part of the decarbonization of industrial processes, alternative raw materials and new processes are being considered. Here the experience at German smelter plants is reported. A key focus is transitioning from carbon-intensive BF processes to DR plants, where iron oxide is reduced to iron using natural gas or hydrogen. This transition eliminates the coking and sintering plant stages [19], necessitating new process stages such as smelters or EAFs.

Future iron and steel industry processes will still require carbon, which must be produced or sourced in a climateneutral manner. Methane pyrolysis, which splits methane

https://op.europa.eu/en/publication-detail/-/publication/163be3c2-7d97-11ec-8c40-01aa75ed71a1/language-en



Fig. 18 Pyrolysis carbon from inductively heated methane pyrolysis and carbon black particles collected at the end of the process. [Picture from internal tests at BFII]



Pyrolysis carbon used in the inductively heated moving bed



Carbon black particles collected after methane pyrolysis

Fig. 19 BFI-tablet press and pelletizing disk



(from natural gas or biogas) into hydrogen and solid carbon, is a promising process [32]. The reaction is as follows:

$$CH_{4,(g)} \rightarrow C_{(s)} + 2 H_{2,(g)}$$

Hydrogen from this process can be used in DR, while carbon pyrolysis can be utilized in various metallurgical applications. The suitability of pyrolysis carbon depends on its material properties, which vary based on the pyrolysis process conditions, resulting in different morphologies, chemical compositions, and particle sizes. High-purity methane pyrolysis can produce carbon with over 97% carbon content. As a relevant experience, it is worth mentioning the "Methanpyrolyse" project in Germany investigated the use of pyrolysis carbon in iron and steel industry processes.³

For these investigations, BFI generated pyrolysis carbon in an inductively heated pyrolysis test facility (Fig. 17). The facility features a vertical quartz glass reaction tube (80 mm outer diameter, 750 mm length) with inductive heating provided by a water-cooled coil. The inductively heated zone is approximately 150 mm in height.

In the BFI investigations of methane pyrolysis, carbon is deposited on pre-charged carbon particles within the reactor. During the inductively heated methane pyrolysis process at BFI, carbon is produced in the form of dust with a maximum particle size of 4 mm, depending on process parameters and the dimensions of the carbon particles used in the furnace. Additionally, methane conversion results in the formation of carbon black, a high-value product. The carbon black is collected in a fine filter and is characterized by strongly agglomerated particles. The apparent average particle diameter in the agglomerated state is approximately $15 \, \mu m$ (Fig. 18).

Direct utilization of materials containing pyrolytic carbon is limited due to their small particle sizes. Test materials to meet the chemical requirements of specific applications must generally be processed to meet physical requirements as well. Most applications require carbon-containing materials with particle sizes ranging from a few micrometers (μ m) to about 25 mm.

Currently, the largest quantities of carbon-containing materials are used in metallurgical plants for injection coal in BFs and coking coal in coking plants. However, these processes will be replaced by new hydrogen-based processes in the coming years. Therefore, the described BFI's investigations focused on the use of pyrolysis carbon in EAFs.

In EAFs, carbonaceous materials are used as charge coal, for slag foaming, or as electrode material. Traditionally, materials such as coke breeze, petroleum coke, or anthracite have been used. The requirements for pyrolysis carbon



https://www.sciencedirect.com/science/article/pii/S036031992 4028027

Table 7 Selected mixtures of materials containing pyrolysis carbon with cement or molasses; figures in wt%

Trial	Pyrolysis carbon material	Molasses	Cement
V1	92	0	8
V2	92	8	0
V3	90	0	10
V4	90	10	0
V5	88	0	12
V6	85	15	0
V7	85	0	15

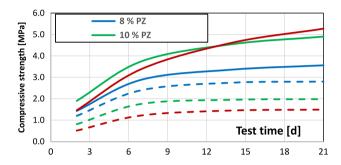


Fig. 20 Compressive strength curves of tablets from pyrolysis carbon and Portland cement or molasses binder

vary depending on the application, with particle size being particularly important. For slag foaming, carbon carriers with a particle size of 0.2 to 2 mm are injected into the liquid melt bath to improve energy input, reduce heat losses, and decrease noise. Charge carbon, added during the scrap melting phase, serves for basic carburization and additional energy input. Charge coal with a particle size of up to 25 or 40 mm, depending on the carbon material, is added via the scrap basket or cover hole. Carbon can be used directly as carburizing agent applications due to its particle size and chemical properties.

For applications requiring finer or coarser materials, appropriate processing steps are necessary. Agglomeration is a crucial step for using fine-particle materials in specific applications. The selection and use of a suitable agglomeration process are essential. In BFI's investigations, a tablet press and a pelletizing disk were used for agglomeration. A pressing tool with a diameter of 10 mm was used to produce tablets, with a height determined by the material specification, approximately 8 mm. Tablets were produced individually at a pressure of 5 bar each (see Fig. 19).

When pelletizing the carbon-containing model substances, pellets with a particle size between 3 and 10 mm were produced. The rolling movements and the resulting

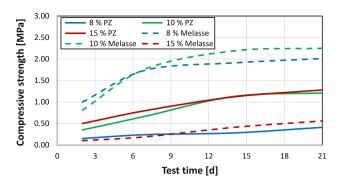


Fig. 21 Compressive strength curves of pellets with pyrolysis carbon and Portland cement or molasses binder

absorption of fine-particle material on the outer shell created a layered structure with recognizable individual particles.

In addition, to selecting a suitable agglomeration process, the choice of binder was a decisive factor influencing the strength and composition of the agglomerates. Molasses and Portland cement were chosen for the investigations on the agglomeration of pyrolysis carbonaceous materials. No major limitations were found regarding the composition of the binders. However, the fate of the binder residues in the melted products or emissions must be considered. Initially, tablets were produced using molasses or Portland cement. Table 7 shows selected mixtures used to produce tablets with the tablet press.

For later use of the agglomerates in iron and steel industry processes, the binder content should be minimized. The wide range of binder content in the formulations allowed for determining the necessary amount of binder required in each case.

After producing the tablets, their cold compressive strength is determined as a quality test using a compression testing machine. Figure 20 shows the average strength development over the test period for tablets made with pyrolysis carbon material and two different binders.

The increase in strength over the test period is evident, with higher strength observed in the first 7 days, followed by a decrease with extended storage time. This trend is more pronounced for tablets bonded with Portland cement due to hydration. The maximum compressive strength of the tablets was approximately 5 MPa after 21 days. To produce press agglomerates, a proportion of 8 wt% Portland cement is required to achieve sufficiently strong agglomerates for use in iron and steel industry processes.

The maximum strength of molasses-bound tablets was determined after about 7 to 9 days, with only slight increases in strength during further storage. The tablets bound with molasses exhibited significantly lower cold compressive strength values. A proportion of 8 wt% molasses resulted in a maximum compressive strength of approximately 2.8 MPa for the tablets. Despite this, tablets containing 8 wt% molasses



possess sufficient strength for use in iron and steel industry processes.

Comparing the chemical composition of the tablets with typical charge carbon materials shows good agreement. Tablets bound with Portland cement can be expected to have an increased ash content of up to 8 wt%, while those bound with molasses can have a higher volatile content of up to 7.5 wt%. Both values are tolerable and similar to those found in typical charge coals. A clear advantage is the higher carbon content of over 90 wt% in the tablet blends compared to conventional charge coals.

Agglomeration investigations continued with the production of pellets. Pellets were produced experimentally using molasses or Portland cement according to the same formulations as tablets. Figure 21 shows the average strength development over the test period for pellets made from pyrolysis carbon and the two binders used.

Tests on pellets with Portland cement showed poorer strength values compared to tablets. The strength curves indicate that pellets bonded with Portland cement did not achieve sufficiently high compressive strengths even after 3 weeks of storage, with maximum strengths of 1.3 MPa, approximately 25% of the maximum strength of tablets with the same formulations. Pellets with 8 or 10 wt% molasses showed similar strength results to tablets with the same formulations, achieving maximum compressive strengths of 2.3 MPa.

In principle, the initial results suggest that the use of pyrolytic carbon in iron and steel industry processes is technically feasible. From an ecological perspective, utilizing carbon from methane pyrolysis may be more favorable than fossil coal due to potential improvements in efficiency, reactivity, and feedstock preparation footprint.

General Conclusions

To achieve the CO_2 emission reduction goal of climate neutrality by 2050, it is essential to reduce dependency on fossil resources, primarily natural gas and coal. This review discusses the use of non-biogenic materials, highlighting the role of various wastes in a CE. Non-biogenic SCCs, such as polymers from waste plastics and rubber from tires, can support the decarbonization pathway SCU-PI (Smart Carbon Usage in a Process Integration frame) by serving as auxiliary reducing agents and slag foaming materials. CO_2 emission reduction is attributed to the mix hydrogen -biogenic polymer.

Concerning SCCs utilization in BF and EAF processes, particle injection in the BF process is a mature technology, used in voestalpine's integrated plant since 2007. Acciaierie d'Italia conducted preliminary trials with PCI substitution up to 9% and plans to invest in a dedicated injection facility for higher substitution ratios.

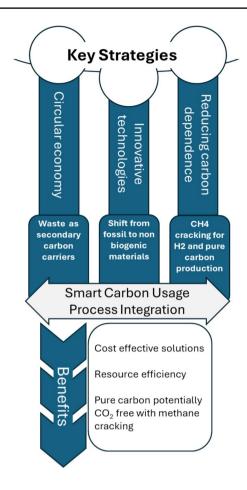


Fig. 22 Overview of key strategies and benefits from SCCs use in steel production

Utilization in EAF is more recent but has demonstrated feasibility for polymers and rubber particles, achieving a substitution ratio of 50%. Substituting coal with polymers did not affect the typical EAF profile, with traditional parameters remaining unchanged except for the use of plastic particles instead of a portion of injected coal. Long-term industrial trials confirm that polymer utilization as a coal substitute is feasible and can be adopted as standard practice. The material can be stored and injected into the pneumatic system without issues such as densification or clogging. Polymer injection technology is adaptable to various furnace sizes and plant practices, given a tailored injection system.

Complete substitution of fossil carbon sources with densified polymers has been successfully tested, overcoming previous drawbacks by using polymers produced through a new process that transforms non-recyclable heterogeneous plastic mixes into new plastic raw-secondary material. Coupled injection of supersonic oxygen and solid material is an effective strategy for both coal and polymer.

The overall scenario presented is shown in Fig. 22.

Starting from the key strategies presented, the general benefits for steel industry concur to strengthen sustainability,



both economic and environmental. Balancing economic and environmental sustainability is the main challenge for the steel industry and other hard-to-abate sectors in the coming decades.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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