

Review

Alternative Carbon Sources as Foaming Agents for Electric Arc Furnace Steelmaking Slags: A Comprehensive Review

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Abstract

The steel industry contributes to approximately 7%–9% of global anthropogenic CO_{2(g)} emissions, with traditional blast furnace–basic oxygen furnace (BF–BOF) routes emitting up to 1.8 tCO₂ per ton of steel. In contrast, Electric Arc Furnace (EAF) steelmaking, especially when integrated with hydrogen direct-reduced iron (DRI), can reduce emissions by over 40%, positioning EAFs as a key enabler of low-carbon metallurgy. However, despite its lower direct emissions, the EAF process still depends on fossil carbon sources for slag foaming and FeO reduction, which are essential for arc stability and energy efficiency. Slag foaming plays a critical role in controlling the thermal efficiency of the EAF by shielding the electric arc, reducing radiative heat losses, and stabilizing the arc's behavior. This review examines the mechanisms of slag foaming, discussed through empirical models that consider the foaming index (Σ) and slag foaming rate as critical parameters, and highlights the influence of physical properties such as slag viscosity, surface tension, and density on gas bubble retention. Also, the work embraces the potential use of alternative carbon sources including biochar, biomass, and waste-derived materials such as plastics and rubber to replace fossil-based reductants and foaming agents in EAF operations. Finally, it discusses the use of new materials with a biological base, such as nanocellulose, to serve as reactive templates for producing nanohybrid materials, containing both oxides, which can contribute to slag basicity (MgO and/or CaO, for example), together with a reactive carbonaceous phase, derived from the organic fiber's thermal degradation, which could contribute to slag foaming, and could replace part of the fossil fuel charge to be employed in the EAF process. In this context, the development and characterization of renewable carbonaceous materials capable of simultaneously reducing FeO and promoting slag foaming are essential to achieving net-zero steel production and enhancing the sustainability of EAF-based steelmaking.



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1. Introduction

Global warming and climate change are the topics of many international forums and agreements, such as the Kyoto protocol, which demands controls and goals for greenhouse gas emissions to pivot their forecast [1]. In this context, data from the World Economic Forum [2] reports that 8% of the emissions from industry come from primary or secondary steelmaking. This fact is associated with the energy intensity of steelmaking and also the intense use of carbon-bearing raw materials, normally of fossil nature, which can act as

carbon sources for different purposes, such as metallurgical coke, green petroleum coke, and anthracite.

The steel industry is crucial for decarbonization, as steel production continuously rises, especially in developing regions such as South America and Asia. The World Steel Association annual report [3] shows that steel production increased from 200 million tons to more than 1.8 billion tons from 1950 to 2023. Despite the importance of steel to economics and infrastructure, it is important to consider the impact on CO₂ emissions from iron and steelmaking. The specific CO₂ emissions have risen from 1.82 to 1.92 t_{CO2}/t_{steel} over the last 10 years, highlighting the relevance of developing more sustainable routes.

In this context, regarding raw materials, it is possible to outline two different routes for steelmaking depending on the input used. The first route, also referred to as primary steelmaking, involves the reduction of iron ore and can be carried out in a blast furnace (BF) or through a smelting reduction (SR) process, using a solid carbon source and producing a liquid product (pig iron), or through direct reduction (DR) using a gaseous reducing agent (natural gas or hydrogen) and yielding a solid product of high iron metal content. The second route uses scrap metal directly, or a mix of scrap + DRI (direct-reduced iron) + solid pig iron, processed in an Electric Arc Furnace (EAF) [4].

EAF steelmaking represents one of the critical paths to more sustainable steel, combined with direct reduction (DR) as a DRI source, reducing the use of fossil fuels, especially coal and coke. BF-BOF and EAF routes represent 71% and 29% of the crude steel production, respectively, and the DRI-EAF route achieves a 41% reduction in emissions compared to the BF route [3]. This is explained by using natural gas or hydrogen (still an emerging technology) as the main reducing agents and by the lower energy intensity of the reduction process.

Besides the lowest emission of EAF routes, the refining phase of this process still requires additional charged or injected carbon inputs that act as a chemical energy source, reacting with oxygen and reducing the excess FeO in slag, generating gases and promoting slag foaming. This, by itself, is a very important efficiency indicator, as the electric arc must be covered during refining to avoid radiation energy losses [5].

Therefore, it remains important to investigate alternatives to reduce the fossil carbon demand of EAFs on the path to a net-zero steel industry. The use of different carbon sources from residues, biomass, or other biomaterials as possible slag foaming promoters, replacing coke/coal, must be continuously improved to achieve this goal.

2. EAF Operational Concepts

The EAF applies electrical energy through graphite electrodes to melt the solid raw material, which can be steel scrap, pig iron, DRI, or other ferrous material. This is possible by the ignition of an electric arc between the electrode and the metallic material, transferring energy mainly by radiation. To improve energy efficiency, side-wall oxy-fuel burners and oxygen lances are used and correspond to approximately 40% of the total energy input of the EAF [6]. The oxidation of elements such as Si, Al, C, and P during steel refining contributes to this chemical energy input, due to the exothermicity of the respective reactions [7].

The main steps in the EAF process are charging, melting, refining, and tapping. Depending on the scrap density, EAF generally demands two or three charging and melting steps before refining with high oxygen flow [8]. Figure 1 represents the overall material balance in an EAF [9]. All data in the figure correspond to 1 ton of crude steel production, and beyond the scrap and alloys (raw material), it shows the additions of fuel (natural gas), coal, and oxygen necessary to reduce electric energy demand and improve productivity.

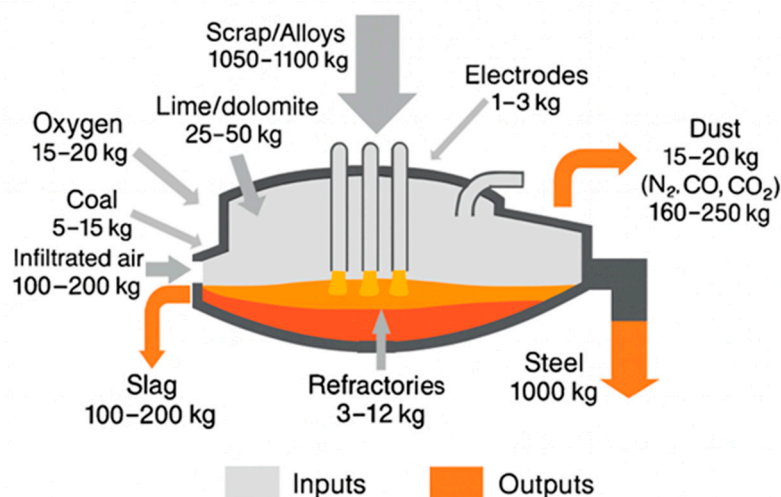


Figure 1. Typical material inputs and outputs in an EAF, adapted from [8].

Slag is formed primarily by pre-existing oxides present in the dirt of the raw material, which contains CaO , MgO , Al_2O_3 , SiO_2 , and Fe_xO_y . Another important part of slag is the SiO_2 , Al_2O_3 , Cr_2O_3 , MnO , and P_2O_5 formed by the reactions between the residual elements in steel scrap with injected oxygen. This oxygen also reacts with Fe and forms around 30% of the FeO as a consequence of the steel decarburization process.

The additions of lime (90% CaO) and dolomite (60% CaO /35% MgO) are important to feed the slag with CaO and MgO , which dissolve and create ideal conditions for refractory wear, solid phase fraction, and dephosphorization. Dephosphorization demands CaO to form a combined oxide phase ($CaO \cdot P_2O_5$), thereby stabilizing P_2O_5 in slag [10]. It is important to note that lime normally contains residual $CaCO_3$, contributing, together with the burners, to additional $CO_{2(g)}$ emissions.

Arc Stability and Total Harmonic Distortion (THD)

In the EAF, 60% or more of the total energy is transferred by the ignition of an electric arc; therefore, the behavior of the electric currents is strongly correlated to what is happening during the process, being a guide of electric arc efficiency. In the early melting phase, for example, there is a massive generation of harmonics caused by the arc instability which can be measured by the total harmonic distortion (THD) [11], voltage, or current components at frequencies that are integer multiples of the fundamental frequency (typically 50 or 60 Hz), leading to instabilities in the electric arc behavior. Grandhare, W. and Lulekar, D. [12] measured these harmonics on a 40 MVA EAF in Germany by voltage variations and noticed up to 20.9% THD on the melting phase.

It is possible to use THD as a power quality indicator and as an efficiency parameter during the operation. As melting progresses and the liquid metal is predominant, the mentioned instability is expected to reduce greatly without scrap drops and harsh movements of electrodes due to the absence of cold scrap. During refining, the arc thermal efficiency will be as great as the quality of the slag formed, covering the arc length totally or partially, appreciably contributing to its stability [13]. Figure 2 clarifies the effect of the slag height on the energy efficiency, considering the increase in the height by slag foaming. On a short (submerged) arc operation, there is weak radiation but also a low power input; as the arc length increases with higher voltages, it will be as efficient as the slag foaming height, overwhelming 90% of the energy transferred to the metal.

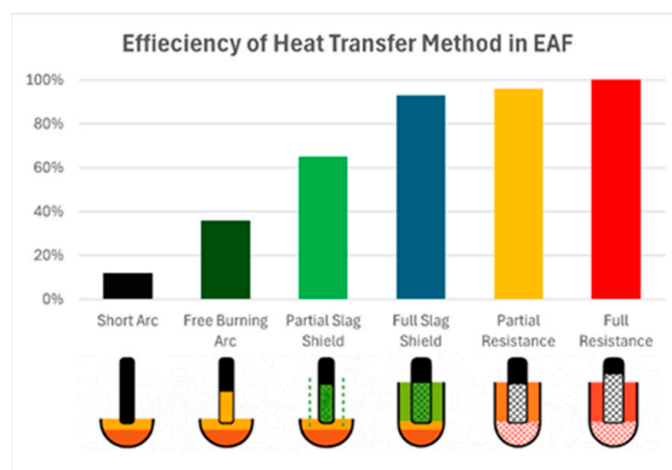


Figure 2. Arc efficiency as a function of arc length covered by slag, adapted from [13].

Based on the above discussions, it can be concluded that arc efficiency during the melting phase is lower and depends on the shielding of the arc by a solid material. On the other hand, refining is characterized by a strong relationship between slag foaming, arc coverage, and thermal efficiency. In the next section, the slag behavior will be detailed, alongside the parameters affecting its foaminess.

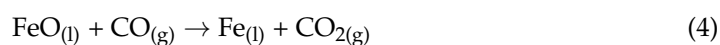
3. Slag Foaming and Carbon Injection

The slag foaming phenomenon in the EAF process has, as its main driving force, the pneumatic pressure of $\text{CO}_{(g)}$ formed during steel refining reactions within the slag layer. The reactions leading to $\text{CO}_{(g)}$ formation are described by the equations contained in Table 1 [14]. Reactions 1 and 2 occur directly in the slag and are the main contributors to foaming slag formation, while reaction 3 is complementary and less intense, as post-combustion mainly occurs at the gas outlet and is more relevant during melting, while temperatures are lower and the generated heat can be utilized to warm up the solid scrap column.

Table 1. Reactions leading to $\text{CO}_{(g)}$ formation during EAF steelmaking [14].

Reaction	Equation	Process Description
Decarburization or carbon injection.	$\text{C}_{(s)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{(g)}$, Equation (1)	Carbon reacts with oxygen to form carbon monoxide.
FeO control via carbon injection.	$\text{FeO}_{(l)} + \text{C}_{(s)} \rightarrow \text{Fe}_{(l)} + \text{CO}_{(g)}$, Equation (2)	Carbon reduces iron oxide to metallic iron and CO gas.
Post-combustion.	$\text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$, Equation (3)	Carbon monoxide is oxidized to carbon dioxide.

Additional reactions that occur on the slag-gas and carbon-gas interfaces are represented by Equations (4) and (5). The kinetics of these reactions is mostly controlled by the mass transfer of $\text{O}_{2(g)}$, $\text{CO}_{(g)}$, and $\text{CO}_{2(g)}$ through the gas shield formed between carbon and slag [15].



The nature of the added carbon source is an important factor to ensure efficiency, especially in FeO reduction, as the material application conditions may vary (batch charging or injection), but the reaction rates must be consistent to maintain good $\text{CO}_{(g)}$ generation

and consequent slag foaming. In Table 2 [16], the key properties are shown, providing guidance for reduction processes and fuel use.

Table 2. Data for the main properties of mineral carbon sources on different applications, adapted from [16].

Metallurgical Process	Grain Size (mm)	Fixed Carbon (%)	Volatile Matter (%)	Ash (%)
Blast Furnace	25–80	>90	<0.5	<9.0
Iron Ore Sintering	<3 mm, 85%–90%	>76	>2.5	<16
Basic Oxygen Furnace (BOF)	6–25	>70	<12 (if injected during blow)	<12
Pulverized Fuel Injection (PFI)	0.1–0.07	—	<0.5	<9.0 (coke)
Fe Alloys	5–25 or 10–25	—	<1	<11
Direct-Reduced Iron Production	6–15	>40	>34	5–20

It is noted that in processes using charged carbon, larger particle sizes are preferable, providing resistance and mass to reduce losses through the exhaust system. In contrast, for injection processes, finer particles are more suitable, offering better penetration and higher reactivity.

The refining objective in EAFs can be compared to that of BOFs, as both achieve high FeO levels. In addition to the reducing function, there is also a fuel function due to the direct and simultaneous injection of gaseous oxygen. Therefore, a high fixed carbon content (greater than 70%) and finer particle size (less than 25 mm) are desirable. According to Morales et al. [17], through increasing the DRI/scrap ratio from 80 to 98.2% on a 125 MVA EAF, with the addition of graphite with a 25 kg/min injection rate, good slag foaming was noticed, together with reduced energy demand—730 to 640 kWh/ton. In this case, the high fixed carbon and reactivity of graphite associated with the high FeO content from DRI were relevant to increase the FeO reduction rate, and therefore CO_(g) generation, significantly contributing to both slag foaming and EAF's arc stability.

Influence of Slag Chemical Composition and Physical Properties

Given the fact that slag foaming is a critical parameter for EAF energy optimization, it is desirable to have a comprehensive measurement of slag foaminess tendency. Ito and Fruehan [18] proposed an equation (Equation (6)) that quantifies foaminess formation tendency, defined by the foaming index (ε), where ΔL (cm) is the foam layer and V_g (cm/s) is the gas superficial velocity. The proposed Equation (6) is consistent with the physical meaning of the foaming index, representing the average gas traveling time through the slag layer in seconds. Complementary to this, it must be mentioned that the superficial gas velocity is positively affected by the gas bubble size [19]. In the same review [19], it is mentioned that there is still a gap in understanding the relations between each slag foaming reaction generating CO_(g) and the size of the bubbles released.

$$\varepsilon = \frac{\Delta L}{V_g} \quad (6)$$

The foaming index can be correlated to the physical properties of the slag, and many researchers have contributed to this topic by investigating and proposing different models. Table 3 shows some of these models already discussed in the literature. It can be stated that even the simplest one considers viscosity (η), surface tension (σ), and density (ρ) of the slag as the main physical properties for foaminess control, thereby strongly affecting gas bubble

stability and foam formation. Moreover, based on the models presented in Table 3, it can be deduced that the viscosity should have a positive contribution to the foaming index on the opposite side of density and surface tension.

Table 3. Foaming index estimation models in the literature.

Equation of Model	Variables Considered
$\varepsilon = 115 \frac{\eta}{\sqrt{\sigma \rho}}$	Viscosity, surface tension, and density of slag [20].
$\varepsilon = 115 \frac{\eta^{1.2}}{\sigma^{0.2} \rho D_b^{0.9}}$	Viscosity, surface tension, density of slag, and bubble diameter (D_b) [21].
$\varepsilon = 3950 \frac{\eta^{1.1}}{\sigma^{0.1} \rho D_b^{0.95}}$	Viscosity, surface tension, density of slag, and bubble diameter [22].

Zang et al. [21] designed experiments with argon injected through a nozzle with multiple orifices to generate smaller bubbles—7.5 mm versus 13.5 mm with a single orifice—and also evaluated the effect of sulfur on steel, acting as a modifier of the changes in surface tension of the metal phase, increasing the contact angle and therefore the bubble size. The maximum foaming index was 56, with a slag height of 16 cm, achieved with the lowest sulfur content (0.002 wt.%) and lowest average bubble diameter (0.70 mm). The results were also used to develop the second equation described previously in Table 3.

In a similar way, Son et al. [22] determined different coefficients for acid slags with higher FeO content, but were still in agreement with the negative effect of the bubble size. The foaming index obtained was between 4 and 6, and the slag basicity (CaO/SiO₂) was near to 1, with MgO close to 10 wt.%. The FeO concentration was close to 25 wt.% in the slags used for the trials, positively affecting the fluidity of the slag, in agreement with the lowest foaming index found and confirming that the foaming stability is dependent on slag viscosity.

It is important to point out that the viscosity, density, and surface tension of the slags have a direct dependence on the overall slag chemical composition, not just FeO wt.%. Chang et al. [23] defined EAF slag as a multi-component (CaO–SiO₂–Al₂O₃–MgO–FeO) system and evaluated slag foaminess as a function of binary basicity (CaO to SiO₂ ratio), with 5 or 10 wt.% of Al₂O₃, and concluded that increasing SiO₂ and Al₂O₃ mass fractions enhanced slag viscosity and led to improved foaming. On the other hand, CaO and MgO content is particularly responsible for the formation of solid phases like MgO_(s) and (CaO)₂.SiO₂, whose presence significantly contributes to slag foaming.

Roscoe et al. [24] proposed a model of apparent viscosity that considers the effect of solid spherical particles emulsified on a liquid phase, described by Equation (7), which can be applied for EAF slags. Under conditions of MgO saturation, foaming is expected to improve due to the formation of an additional solid phase (MgO(s)) and the consequent increase in apparent viscosity. In this context, apparent viscosity does not represent the intrinsic viscosity of the liquid alone, but rather a mathematical parameter that incorporates the resistance to flow caused by the suspension of solid particles within the molten matrix. Thus, it reflects the combined rheological behavior of the liquid phase and the entrained solids, which directly impacts slag stability and foaming efficiency.

$$\eta_a = \eta(1 - 1.35\theta)^{-5/2} \quad (7)$$

Pretorius, E. and Carlisle, R. [25], based on previously published thermodynamic data for the MgO solubility at different B₃ (CaO/(SiO₂ + Al₂O₃)) ratios and FeO weight contents, calculated the liquid phases and solid phases on equilibrium and correlated them with the foamability of slag. The different slag compositions, in terms of B₃ (ternary basicity) ratio,

and MgO and FeO wt.%, were investigated through isothermal diagrams. They provided an important graphical representation of the expected foaming index as a function of these key oxides. This relationship is illustrated in Figure 3, which shows how the foaming index varies with basicity, FeO content, and MgO content.

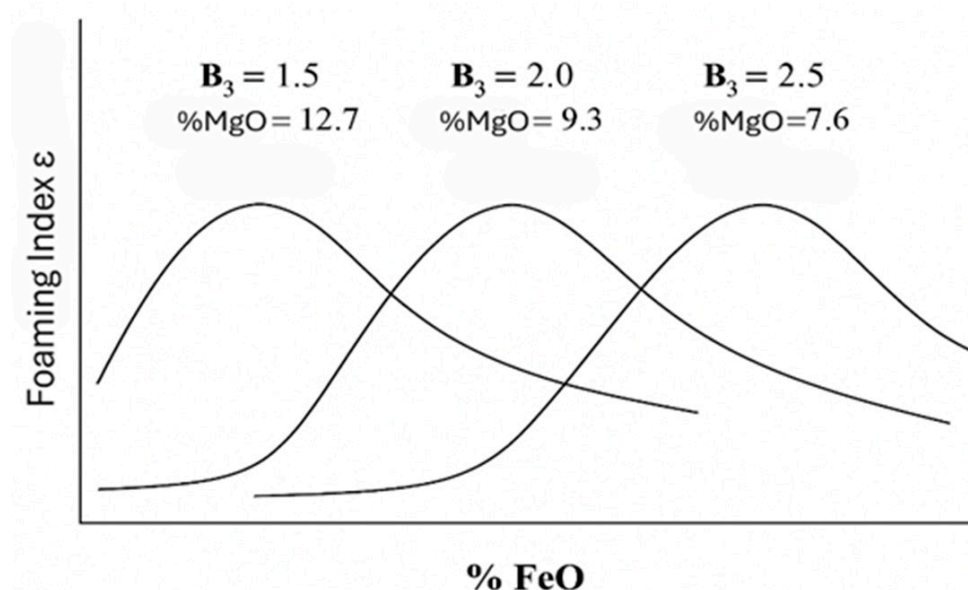


Figure 3. Foaming index as a function of basicity, and FeO and MgO wt. %, adapted from [25].

It can be seen from Figure 3 that there is an ideal FeO wt.% for slag foaming for each B_3 and MgO concentration. FeO acts as the dominant fluxing oxide, significantly lowering the liquidus temperature and increasing the liquid fraction of the slag. While moderate FeO promotes the necessary CO generation through its reduction by carbon, excessive FeO drives the slag into the fully liquid region of the CaO–MgO–SiO₂–FeO system, reducing the apparent viscosity and eliminating second-phase particles, which are essential for foam stability. Conversely, CaO and SiO₂ concentrations govern the basicity ratio (B_3), which controls the solubility of MgO and the formation of solid phases such as magnesiowustite (MgO(s)) or calcium silicates ((CaO)₂SiO₂). These phases act as nucleation sites for gas bubbles, increasing the foaming index. At lower basicity (low CaO and/or high SiO₂), MgO solubility rises sharply, requiring higher MgO additions to achieve saturation, while at higher basicity, MgO solubility decreases, and the slag becomes less sensitive to FeO variations, widening the foaming “window”.

Figure 4 shows the results of isothermal simulations (simulations on Gerdau Brazil Steelmaking Slag Simulator) of slag 1 ($B_2 = 2.4$) and slag 2 ($B_2 = 1.8$) at 1600 °C, with the MgO and FeO wt.% fixed at 8.5% and 26.7%, respectively. The results exhibited the lower content of the second phase (MgO_(s) = 0.021%), and therefore the lower effective viscosity (0.0989 Pa.s) and foaming index (1.79 s) of slag 2, with lower basicity (B_2). These results corroborate the relevance of slag saturation conditions (precipitation of MgO_(s)) with FeO maintained below the liquidus boundary, ensuring a balance between fluidity for bubble formation and sufficient solid fraction for foam stability.

Slag Chemical Composition	Point [1]	Point [2]
CaO (%)	36.2	32.165
SiO ₂ (%)	15.1	17.869
MgO (%)	8.5	8.5
Al ₂ O ₃ (%)	5.8	6.864
MnO (%)	5.3	5.3
P ₂ O ₅ (%)	1	1.183
Cr ₂ O ₃ (%)	1.3	1.3
S (%)	0.1	0.118
Weight (kg)		
Weight (kg/ton)	93.37	78.9

Basicity	Point [1]	Point [2]
B2 = CaO/SiO ₂	2.40	1.80
B3 = CaO/(SiO ₂ +Al ₂ O ₃)	1.73	1.30
B4 = (CaO+MgO)/(SiO ₂ +Al ₂ O ₃)	2.14	1.64

Temperature	Point [1]	Point [2]
Slag temperature (°C)	1600	1600

Slag Properties	Point [1]	Point [2]
Density (kg/m ³)	3282.74	3304.20
Surface Tension (N.m/s)	0.9378	0.9221
Viscosity (Pa.s)	0.0889	0.0920
Effective Viscosity (Pa.s)	0.1194	0.0989
Foaming Index (s)	2.149	1.790
f (second phase particles fraction)	0.082	0.021

References	
Input Data	Calculated Data

Figure 4. Data generated by Gerdaug Slag Simulator using real data for two EAF slags at 1600 °C.

4. Alternative Carbon Sources

Carbon injection is used to recover iron by controlling FeO formation, and, through its reduction, generate CO or CO₂ molecules, therefore contributing to satisfactory slag foaming, as explored in the previous sections. On the other hand, it results in CO₂ emissions during EAF steelmaking. For example, with an injection of 5 kg of calcined petroleum coke per ton of crude steel (minimum of the coal range presented on the mass flow at Figure 1), with a fixed carbon content of 98.63% [26], approximately 18.1 kg of CO_{2(g)} is generated on full stoichiometric combustion with gaseous oxygen (details in Table 4). Because of this, many studies nowadays have been directed to search for alternatives to fossil carbon sources such as biomasses, which could minimize the greenhouse gas emissions of the EAF process [27]. Some promising initiatives are discussed in the following topics.

Table 4. CO_{2(g)} emissions calculations of 5 kg of calcined petroleum coke with 98.63% of fixed carbon weight content [27].

Reaction	Carbon—C _(s)	+	Oxygen—O _{2(g)}	=	CO _{2(g)}
Stoichiometry	Mass C(s) = 12 kg		Mass O _{2(g)} = 32 kg		Mass CO _{2(g)} 44 kg
Formulas	WCs = IC × FC, where WCs is the total weight of carbon injection, IC is the carbon source injection, and FC is the fixed carbon weight content of the chosen carbon source.		WO ₂ = $\frac{32 \times WC}{12}$, where WO ₂ is the weight of O _{2(g)} consumed.		WCO ₂ = $\frac{44 \times WC}{12}$, where WCO ₂ is the weight of CO _{2(g)} generated.
Results	WC = 5 × 0.9863 = 4.9315		WO ₂ = $\frac{32 \times 4.9315}{12}$ = 13.1507		WCO ₂ = $\frac{44 \times 4.9315}{12}$ = 18.0822

4.1. Agricultural Wastes as Coke Blends

Using biomass as a C source in the EAF is interesting, mainly because it is renewable; however, due to the large amount of oxygen present and the presence of inorganic residues (ash content), additional challenges arise. However, treated biomass in the form of hydrochar (after hydrothermal carbonization) or biochar (after pyrolysis of biochar), or even after simple roasting (pyrolysis at a relatively lower temperature), can improve these scenarios with ash removal, volatile matter removal, energy density increment, C content increment, O content decrease, etc. [28–30].

Agricultural and forestry residues have been widely investigated as partial substitutes for fossil carbon in coke production and EAF operations. Rejdak et al. [31] evaluated the addition of raw and carbonized biomass, based on beech and alder woodchips, pine sawdust, olive kernels, and hazelnut shells into coal blends for coke-making. Carbonization tests at 500 to 520 °C under nitrogen significantly improved biomass properties, reducing volatile matter from 73%–80% to below 13%, and increasing fixed carbon content to over 80%, surpassing the coal blend baseline (61.9%). Despite these improvements, the addition of biomass negatively impacted relevant coke-making indices (fluidity and the ROGA index). The Gieseler fluidity test is a standardized method for assessing coal fluidity using a constant-torque stirrer immersed in a heated coal sample (temperature = 550 °C), and carbonized biomass performed better, maintaining fluidity within acceptable ranges (255–347 ddpm) at low substitution levels (5%–10%), though it still exhibited marked deterioration at 20%. Similar patterns were observed for the Roga Index (RI), which is a prescribed drum test that measures the mechanical strength of coke produced under standard carbonization conditions. Raw biomass caused severe reductions in these indices, while carbonized biomass had a more moderate impact. These findings highlight the potential of biomass for decarbonization, if the physical and chemical limitations are addressed by the correct characterization pre-processing of the raw material.

Abd Rashid et al. (2014) [32] reported that replacing 20% of the fossil carbon with palm kernel shells (PKS) reduced CO₂ emissions by 18.69% and carbon consumption by 19.78% for the reduction of a low-grade iron ore (40% iron) pellet. PKS pyrolysis generated H₂, CO, and hydrocarbons, which are additional reduction gases and energy sources for ironmaking.

Fidalgo et al. (2015) [7] compared two industrially sourced chars derived from grape seed and pumpkin seed with four types of commercial coals used for charging or injection in EAF steelmaking. TGA tests at 850 °C under CO_{2(g)} atmosphere revealed that pumpkin seed is much more stable and comparable to regular coals, with a maximum weight loss around 95% after 150 min. On the other hand, grape seed char revealed a much higher reactivity, possibly associated with the different pyrolysis conditions, physical structure, and chemical composition of this char (27.1 wt.% volatiles, 12.4 wt.% ash content, and 72.9 wt.% fixed carbon). Relative combustion reactivity, measured by TGA, confirmed the reactivity of grape seed char, achieving 13.5%.min^{−1} weight loss against 0.5%–2.0%.min^{−1} measured for other samples (coals and pumpkin seed char). From these results and by considering the high temperature and oxygen-rich atmosphere of EAFs, it is expected to have a premature reaction on the grape seed char if charged, being more suitable for the injection method.

The results of different researchers point to the technical viability of chars and biocokes originating from agricultural waste residues, and indicate the necessity of a continuous investigation into alternatives, comparing the results of the fixed carbon and volatile contents to the performance on application and the final char properties. In the case of EAF, controlled reactivity has a great impact on avoiding premature combustion and uncontrolled reactions. This problem can be managed by reducing the surface area by briquetting the final chars, which also improves the mechanical properties [30].

4.2. Polymers and Rubber

Polymeric wastes (HDPE, PP, and PET) and end-of-life tires have emerged as effective alternatives for slag foaming in EAF steelmaking. Kongkarat et al. (2011) [33] investigated carbon/slag interactions using blends of metallurgical coke with waste polymers (polyethylene terephthalate (PET) and polyurethane (PU)) at 1550 °C. The researchers used a horizontal furnace and prepared a pressed substrate of coke and polymer/coke blends to

compare the bubble size of a melted EAF slag with 30.5% FeO mass content, placed over the substrate. The slag droplet was placed over the substrate on an alumina sample holder. The experiments aimed to evaluate slag/carbon interactions, and revealed that polymer/coke blends improved slag foaming compared to coke alone, with PET/coke achieving a stable volume ratio of ~1.2 and PU/coke fluctuating between 0.8 and 1.2, versus coke's decline to 0.7–1.0. Despite generating lower cumulative CO volumes (~0.9 L for blends vs. ~1.2 L for coke) due to their lower fixed carbon and higher volatile and hydrogen content, the blends exhibited better gas entrapment due to slower gas release rates, which favored foam stability and indicated a good forecast of slag foaming on application in EAF steelmaking. Off-gas analysis on a gas chromatography (GC) analyzer (SRI 8610C Chromatograph Multiple Gas #3 GC configuration) confirmed that volatiles such as H₂ and CH₄ from polymer decomposition participated in FeO reduction, as evidenced by their higher H₂O peaks (PET/coke: 14.06% vs. coke: 7.76%), and contributed to the understanding of the good foaming behavior presented on the droplet's tests. Table 5 summarizes the chemical analyses of polymers compared to rubber and coke, highlighting the presence of hydrogen from hydrocarbons and oxygen from volatiles [34,35].

Table 5. Main chemical characterization of polymers compared to other carbon sources, adapted from [34,35].

Carbon Source	Carbon (wt.%)	Hydrogen (wt.%)	Sulfur (wt.%)	Nitrogen (wt.%)	Oxygen (wt.%)
PET Polymers	62.5	4.2	-	-	33.3
Rubber	85.5	7.0	1.7	0.2	6.7
Metallurgical Coke	77.7	1.1	0.3	1.2	-
Biochar	89.2	0.8	0	0.5	3.2

Zaharia et al. (2009) [36] demonstrated that rubber/coke blends interacting with slag droplets significantly enhance foaming behavior by accelerating FeO reduction and generating large volumes of CO and H₂ gases. These gases originate from the rapid devolatilization and pyrolysis of rubber, which contains 63% volatile matter and 7.6% hydrogen compared to metallurgical coke (3% volatile matter, 1.1% hydrogen). The presence of hydrogen provides a kinetic advantage, as FeO reduction by H₂ is one to two orders of magnitude faster than by CO, promoting vigorous gas evolution and improved slag–metal reactions. Thermogravimetric and drop-tube furnace tests revealed that combustion efficiency nearly doubled for 30% rubber blends, with burnout values increasing from ~40% for coke to ~80% for rubber-rich blends. SEM and XRD analyses confirmed structural modifications: micropore surface area increased significantly with rubber addition, while bulk density decreased to 0.77 g/cm³ for 30% rubber blends, enhancing oxygen penetration and char reactivity. Indeed, industrial trials confirmed these findings, reporting reductions in electrical energy consumption of 2 to 4% and injected carbon up to 15%, without compromising steel quality [37]. Sessile drop experiments in a horizontal tube furnace with the rubber/coke blends at 1550 °C showed that slag volume ratios increased up to 2.2 times when rubber was blended with coke in a 20%–30% concentration, indicating higher gas entrapment and foam stability [38].

However, operational challenges persist as rubber can increase sulfur (up to 2%) and chlorine input, affecting slag stability and off-gas treatment. Sulfur tends to enlarge CO bubbles, reducing foam stability, while chlorine from PVC additions requires strict feedstock control. Additionally, combustion kinetics must be managed to prevent overheating in off-gas systems. Life cycle assessments indicate that tire recycling offers intermediate

environmental benefits compared to disposal using its calorific potential, and reducing fossil fuel consumption, such as coal or coke [39].

4.3. Biologically Based Materials

Biochar has gained attention as a renewable carbon source for slag foaming. DiGiovanni et al. (2023) [35] ranked biochar samples based on slag foaming performance under simulated EAF conditions. Bio-briquettes produced from densified biochar and bio-oil achieved a maximum slag foaming height increase of 158%, outperforming loose biochar (20%) but remaining below nut coke (369%). The briquettes' superior performance is attributed to higher volatile matter content (~31%) and improved particle integrity, which favor gas release and slag interaction with appropriate surface tension. Thermogravimetric analysis revealed that biochar exhibits higher reactivity with CO₂ and air, initiating gasification at 274–303 °C versus >400 °C for coke. While this property accelerates FeO reduction, it also raises concerns about premature combustion during injection, which might be an operational warning due to excessive blast and liquid slag and steel splashing.

Beyond environmental advantages such as carbon neutrality and low sulfur content, biochar offers opportunities for property engineering. Adjustments in the pyrolysis process (e.g., heating rate control, biomass content), addition of binders, and particle size control can optimize reactivity and foaming capacity. Bianco et al. (2013) [40] developed charcoal applications for EAF, and after industrial trials, proposed the briquetting of biochar fines to have better control of reactivity and therefore a more stable foam due to the improved density of the particles. In agreement, Demus et al. (2016) [41] reported that compacted biochar blends improved slag-metal contact and sustained foaming for longer durations, with CO generation rates up to 40% higher compared to non-densified samples. Both studies emphasize that briquetting not only enhances mechanical strength but also stabilizes volatile release, reducing operational variability.

Kieush and Schenk (2023) [42] evaluated the impact of biochar, coke, and their mixtures on slag foaming behavior in EAF steelmaking under varied slag compositions. Experiments demonstrated that biochar alone achieved stable foaming only within a basicity range of 1.2–3.4, with foam heights up to 10.0 cm and volumes of 311.6 cm³, but its performance was generally lower than coke. Biochar's high volatile matter content (~41 wt.%) and porosity contributed to its rapid reactivity, causing uncontrolled foaming at FeO contents above 30 wt.%. Conversely, coke provided optimal foaming for slags, with basicity between 1.2 and 2.7 and FeO contents of 15–30 wt.%, reaching foam heights of 11.0 cm and volumes of 342.7 cm³. The most significant improvement occurred when using a 1:1 mixture of coke and biochar, which extended the foaming range to FeO contents of 15–40 wt.% and maintained stability even at low basicity (1.0). This mixture achieved foam heights of up to 10.6 cm and volumes of 330.3 cm³, with longer foaming times (6–9 min) compared to biochar alone (3–4 min), indicating synergistic effects from combined carbon sources. The findings confirm that partial substitution of coke with biochar can avoid uncontrolled reactions and enhance slag foaming height and stability, broadening operational flexibility and supporting the transition toward renewable carbon sources in EAF steelmaking.

In summary, biochar shows significant potential as a slag foaming agent, but still presents challenges related to density, thermal stability, and operational control. Future research should continuously focus on standardized protocols for evaluating foaming capacity, the development of biochar–polymer–coke blends to maximize gas generation, and modeling studies to predict behavior at an industrial scale.

Nanocellulose-Derived Materials

Cellulose is the most abundant renewable compound obtained from the biosphere, and it can be found in plants, algae, tunicates, and some bacteria [43]. It contains carbon, which can be considered as a potential biomaterial, replacing regular fossil carbon sources in EAF steelmaking. Nanocellulose is a sustainable nanomaterial derived from cellulose, characterized by its high crystallinity, large surface area, and tunable surface chemistry. Its production can follow different routes:

1. Sulfuric acid hydrolysis: A widely used method where α -cellulose is treated with concentrated H_2SO_4 at a controlled temperature ($\sim 60^\circ\text{C}$), producing sulfated cellulose nanocrystals with rod-like morphology and surface sulfate groups that improve dispersion in water [44].
2. TEMPO-mediated oxidation: This route introduces carboxylate groups (COO^-) on cellulose nanofibrils, enhancing their reactivity and adsorption capacity. The process uses NaBr and a TEMPO catalyst under alkaline conditions, followed by mechanical disintegration [45].
3. Alternative green methods: Recent studies have explored ionic liquids, deep eutectic solvents, and subcritical water hydrolysis to reduce environmental impact and improve scalability [43].

Teixeira et al. (2021) [44] reported that sulfated nanocellulose (S-CNC) and TEMPO-oxidized nanocellulose fibers (TCNF), used to recover Co^{2+} from aqueous solutions, provided 87% and 90% metallic recovery, respectively, at pH 6 and 25°C , with equilibrium reached in less than 30–45 min, suggesting prominent adsorption kinetics. Moreover, TCNF also demonstrated significant adsorption capacities of $167\text{ mg}\cdot\text{g}^{-1}$ for Cr^{3+} , $1104\text{ mg}\cdot\text{g}^{-1}$ for Ni^{2+} , and $66\text{ mg}\cdot\text{g}^{-1}$ for Zn^{2+} [46]. A recent publication [47] demonstrated that expressive recovery values can also be achieved for other cations of considerable toxic effect, such as Hg^{+2} . According to these authors, recovery is strongly influenced by the nature of the type of functionalization employed. For Hg^{2+} , TCNF performed much better for an adsorption process conducted at pH 5.0 and ambient temperature, in comparison to SCNC, with recovery values, respectively, equal to 89.3% and 35.2%.

Also, the authors demonstrated that the nanofibers' thermal behavior under an inert atmosphere, as observed through careful TGA experiments, can be significantly influenced by the metal's presence. In the case of TCNF, no variation was observed, but in the case of SCNC, a change in the thermal degradation mechanism was evidenced by the appearance of a new thermal event around 300°C . Moreover, it was evident that both nanocellulose types are thermally more unstable than the α -cellulose sample used as a raw material for synthesis, which can be attributed to their significant nanometric nature, as depicted in Figure 5, which was derived from atomic force microscopy (AFM).

The expressive affinity of the carboxylate groups from TCNF (R-COO^-) for transition metal cations in aqueous solutions can be explored in the synthesis of advanced nanometric oxidized materials, as exemplified recently for zinc ferrite spinel (Fe_2ZnO_4) containing samples of expressive pseudo-capacitance ($2031.81\text{ F}\cdot\text{g}^{-1}$) [48], which exhibited excellent chemical and morphological control (Fe_2ZnO_4 globular nanoparticles, Figure 5). In the images contained in Figure 6, both crystallinity (crystalline planes) as well as the expressive nanometric nature of the Fe_2ZnO_4 phase can be clearly seen. Also, in the inlet diffraction plot, diffraction rings associated with specific planes of the zinc ferrite cubic structure are shown.

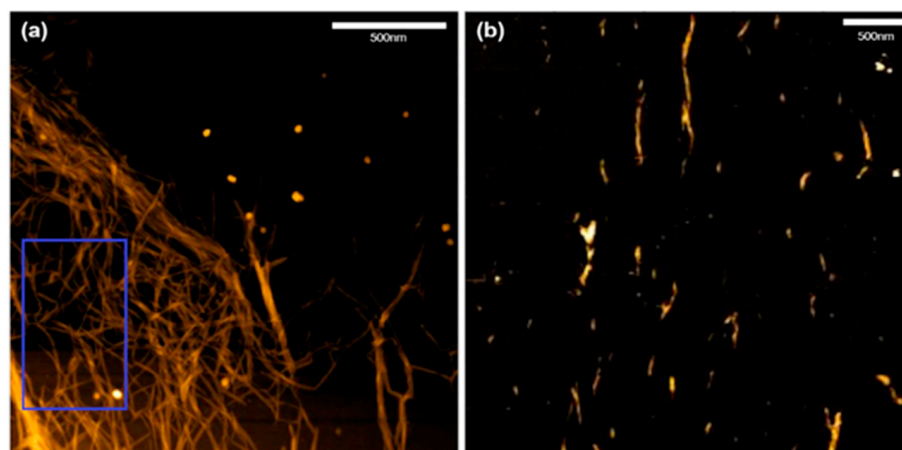


Figure 5. AFM images of TCNF (a) and SCNC (b) [44].

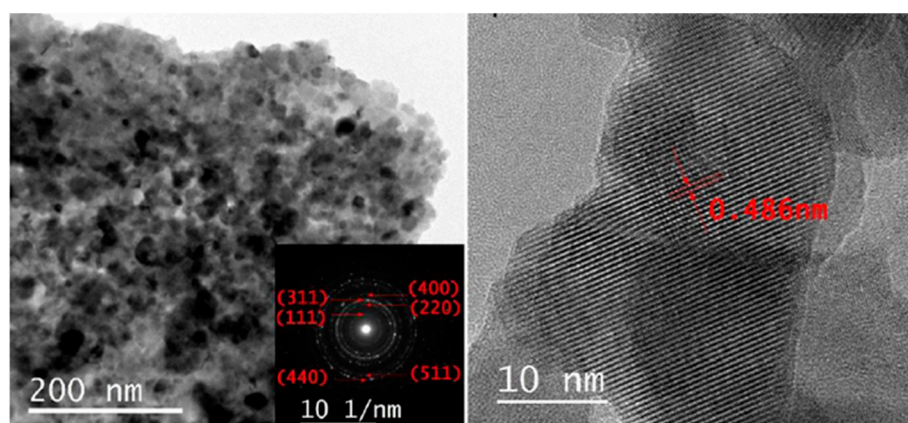


Figure 6. TEM (left) and HRTEM (right) bright-field images of zinc ferrite nanocrystals [48].

In another recent application of the same new synthesis strategy, cobalt ferrite spinel (Fe_2CoO_4)-containing samples were successfully synthesized using TCNF as a reactive template [49]. The globular-shaped spinel nanocrystals (mean particle size of 19 ± 0.2 nm, Figure 7) showed promising catalytic activity toward hydrogen generation through sodium borohydride (NaBH_4) hydrolysis under basic media, with an HGR (hydrogen specific generation rate) of $1.89 \text{ L.g}^{-1}.\text{min}^{-1}$ at 25°C , a very competitive value compared to nanocatalysts of similar nature reported earlier in the literature.

Through changing the atmosphere's chemical nature from oxidant (atmospheric air) to inert (argon), it is possible to synthesize a new class of materials, where a carbonaceous matrix is present together with oxidized nanocrystals. This can be demonstrated in the case of iron-oxide-containing samples [50], which were synthesized through iron cation (70 g.L^{-1} initial concentration in aqueous solution) adsorption over TCNF nanofibers, followed by thermal treatment under argon atmosphere at 800°C for 2 h. According to X-ray diffraction Rietveld analysis, metallic iron, wustite (FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3), and maghemite (Fe_2O_3) crystals were detected. Also, a significant amount of a carbonaceous phase was observed (Figure 8), which was considered to be graphite during the Rietveld fitting procedure.

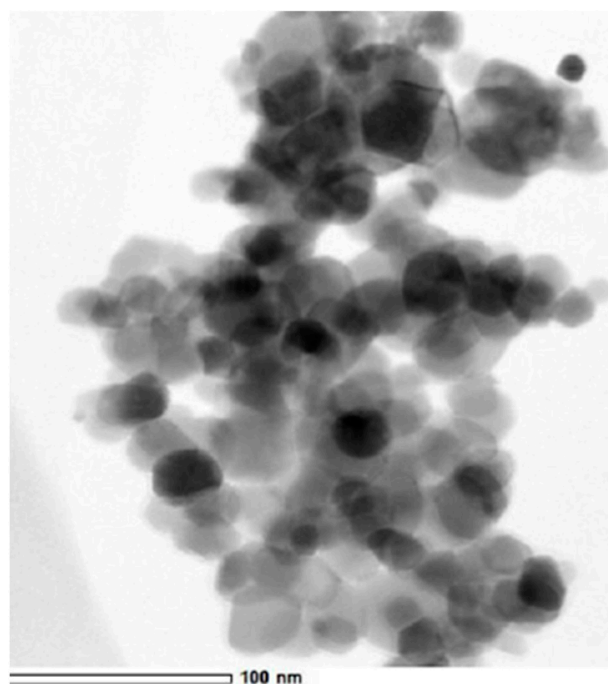


Figure 7. TEM image of globular-shaped cobalt ferrite nanoparticles synthesized with TCNF as a reactive template [49].

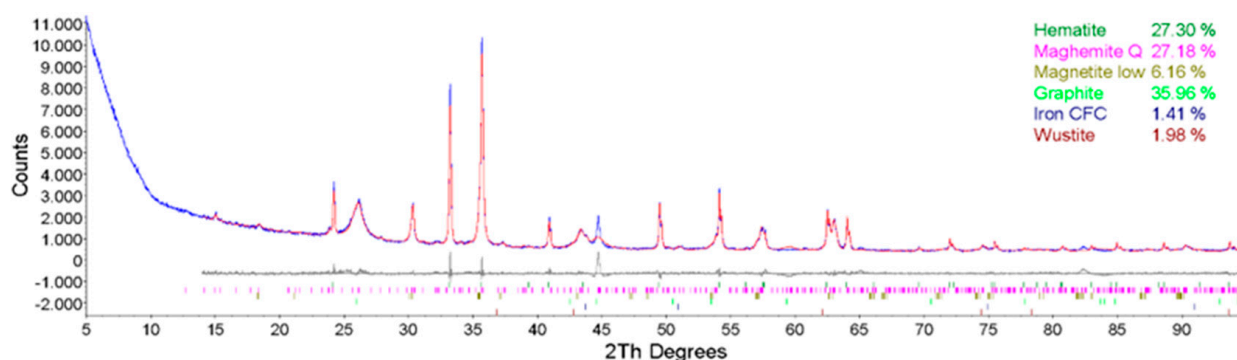


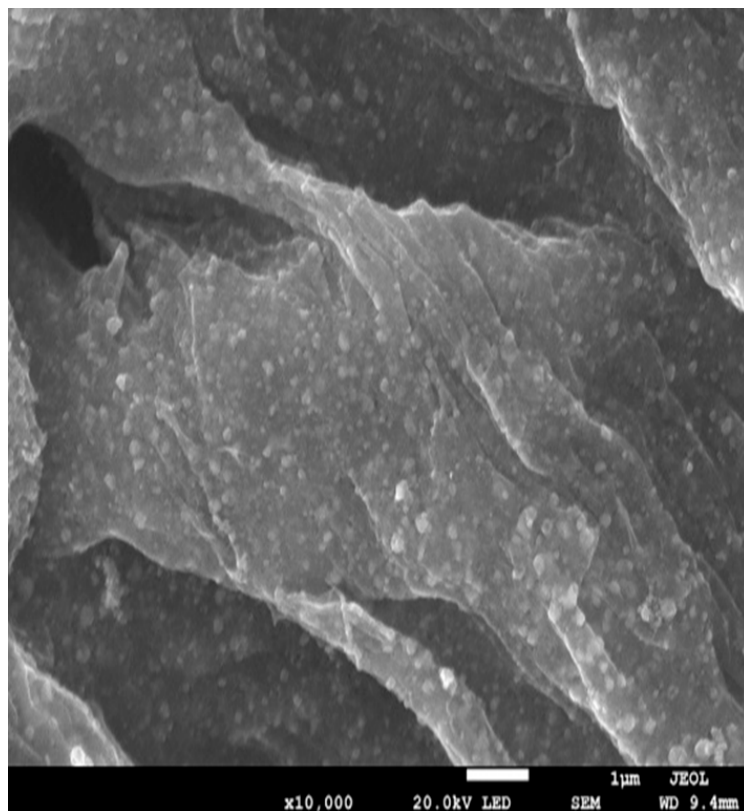
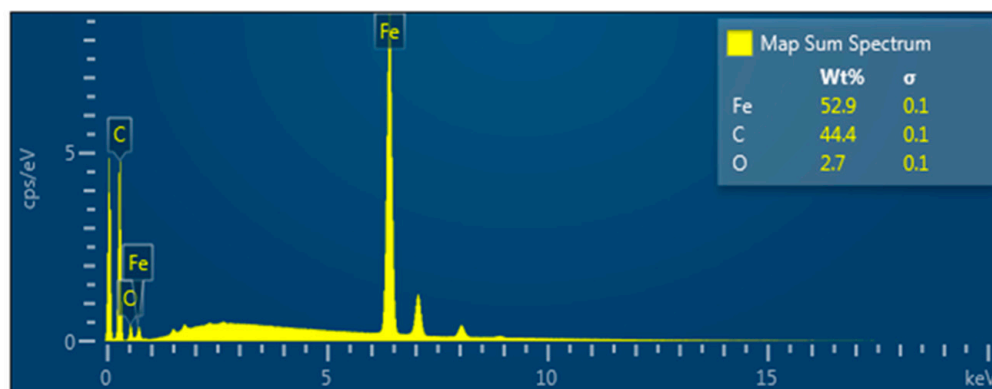
Figure 8. Rietveld fitting result for an iron-oxide containing nanohybrid sample synthesized at 800 °C for 2 h under inert (argon) atmosphere [50]. Grey line represents the difference between experimental data (blue curve) and model (red curve).

The GOF achieved after Rietveld analysis was shown to be equal to 1.95, corroborating the fitting quality. Also, the estimated mean crystallite sizes (Table 6) suggested the presence of considerable nanometric content. Scanning electron microscopy (SEM) analysis (Figure 9), together with EDS spectra acquisition and deconvolution (Figure 10), confirmed the presence of a carbonaceous matrix (carbon peak), over which iron oxide (iron and oxygen peaks) crystals are physically dispersed.

The intimate presence of these phases was also evidenced through Raman spectra (Figure 11), where characteristic peaks of iron oxide (218–489 cm^{-1}) and the carbonaceous phase (1100–3260 cm^{-1}) could be clearly identified, characterized by the typical G, D, and 2D bands. In particular, the G and 2D bands are indicative of graphitic carbon.

Table 6. Mean crystallite sizes for crystalline phases identified in the iron-oxide-containing nanohybrid sample [51].

Phase	Mass Fraction (%)	Mean Crystallite Size (nm)
Hematite (Fe_2O_3)	27.30	127.3
Magnetite (Fe_3O_4)	6.16	34.3
Maghemite (Fe_2O_3)	27.18	53.2
Iron (Fe)	1.41	33.9
Wustite (FeO)	1.98	11.7
Grafite (C)	36.54	9.1

**Figure 9.** SEM image of iron-oxide- and carbonaceous-phase-containing nanohybrid material synthesized using TCNFs as a reactive template under argon atmosphere at 800 °C for 2 h [50].**Figure 10.** EDS spectra of the area represented in the SEM image depicted in Figure 5 [50].

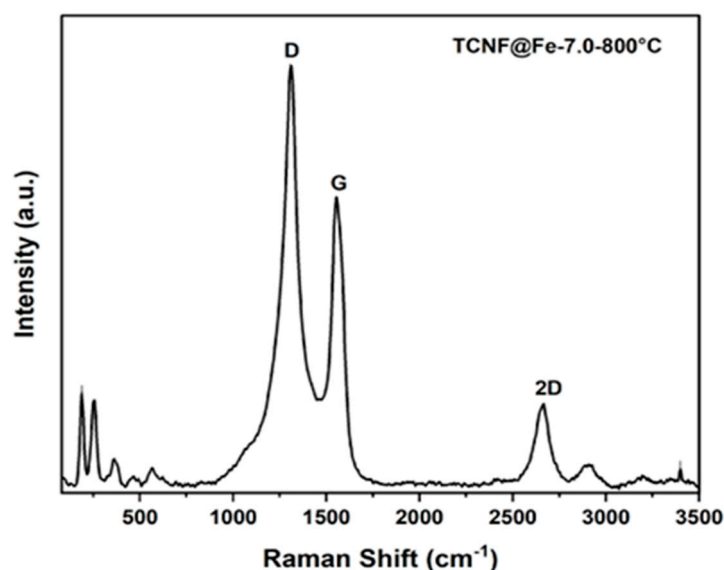


Figure 11. Raman spectra of iron-oxide and carbonaceous phase containing nanohybrid material synthesized using TCNFs as a reactive template under argon atmosphere at 800 °C for 2 h [51].

Nanohybrid Additives Using TCNF as a Reactive Template

The above results reinforce the idea that through a simple atmosphere change (oxidant to inert), it is possible to efficiently produce nanohybrid bifunctional materials, where a carbonaceous phase is present in intimate contact with oxide nanocrystals, the nanometric oxides generated through the interaction of oxygen in the gas phase with the metals adsorbed over TCNFs, and the carbonaceous phase associated with TCNF thermal degradation.

This type of technology could be explored in the future for producing efficient additives for the EAF steel production process, where a reducing agent (carbonaceous phase) is supplied together with oxides that can promote the slag physical properties (apparent viscosity and basicity). The carbonaceous phase could act as in situ reducing agent for FeO (CO generation through the reaction with injected O₂), and calcium or magnesium oxides previously presented contribute to basicity and viscosity—two vital parameters for maximizing slag foaming and arc stability. It is worthwhile to mention that regarding the reactivity of the carbonaceous phase, it could even be enhanced through a simple post-oxidative treatment, for example, through exposure to a KOH or NaOH solution [51,52]. On the other hand, regarding the oxides present, basic oxides like CaO or MgO could be interesting candidates to promote basicity, and to contribute to solid inclusion formation, both of which are very relevant aspects in considering the optimization of slag foaminess. Therefore, there is an interesting field of research in applying this type of nanohybrid material for injection in an EAF as a partial substitute for coke or coal in the steelmaking industry.

The nature of the synthesis can be exemplified by the scheme depicted in Figure 12. Considering that we want to produce a nanohybrid containing both CaO and MgO nanoparticles, we can start with a suspension containing 1 g of TCNF nanofibers in contact with a diluted solution containing similar amounts of calcium nitrate (Ca(NO₃)₂·6H₂O) and magnesium nitrate (Mg(NO₃)₂·6H₂O). After maintaining the system under constant stirring under ambient temperature for 30 min contact time, the solid phase is separated from the aqueous media through vacuum filtration, followed by washing/centrifugation steps, and finally dried in a stove at 40 °C for 24 h. Next, the dried TCNFs impregnated with the cations adsorbed in its surface are thermally treated under a constant argon flux (industrial grade) at fixed temperature. The O₂ concentration in the flux gas must be low enough to not lead to an expressive oxidation of the nanofibers, thereby hindering carbon loss through

the formation of volatile oxidized molecules—but it must be high enough to generate the necessary thermodynamic driving forces for the oxide formation (CaO and MgO) through combination with the available Ca^{+2} and Mg^{+2} cations present.

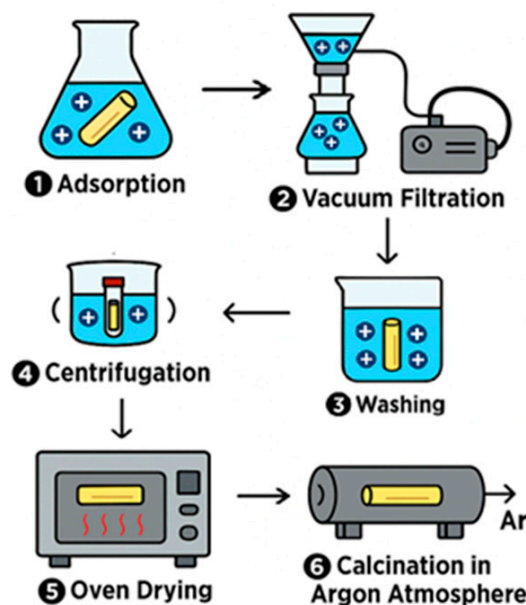
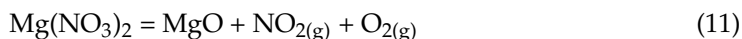
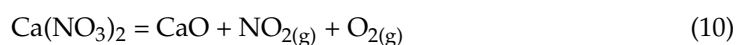
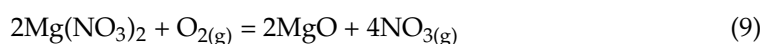


Figure 12. Synthesis procedure of the carbon-bearing nanohybrid containing MgO and CaO nanoparticles.

In order to prevent nitrate formation after drying, it is important to wash and centrifuge the TCNFs containing the desired metallic cations, thereby contributing to the removal of undesired NO_3^- anions.

The nitrate formation can impede the synthesis process by demanding higher temperatures in order to make the desired oxide formation thermodynamically viable. This could be accomplished either through the direct action of the available oxygen (Equations (8) and (9)) or through thermal decomposition (Equations (10) and (11)).



Regarding the direct action of O_2 , the thermodynamic driving force should be very low, as suggested by the molar standard reaction Gibbs energy (Δg_r°) diagrams in Figure 13. In both cases (Equations (8) and (9)), the equilibrium constant should be very low for a wide temperature range (300 to 2000 K), as suggested by the observed, very positive Δg_r° values. Considering thermal decomposition (Equations (10) and (11)), the thermodynamic driving force should be higher in both cases, as suggested by the Δg_r° diagrams of Figure 14. Based on the data from Figure 14, it can be deduced that for magnesium nitrate, calcination temperature must be set to values higher than approximately 600 K, and for calcium nitrate, higher than approximately 900 K, when Δg_r° achieves negative values.

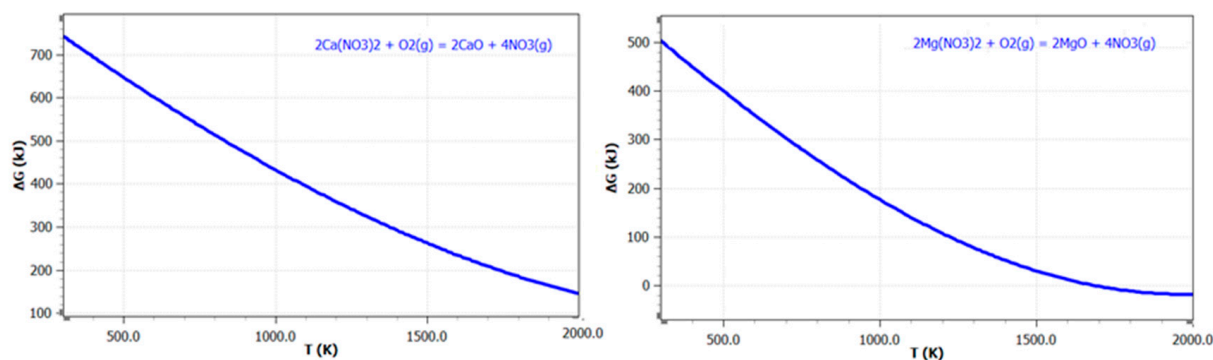


Figure 13. ΔG_r^0 as a function of temperature for Equations (8) and (9) [53].

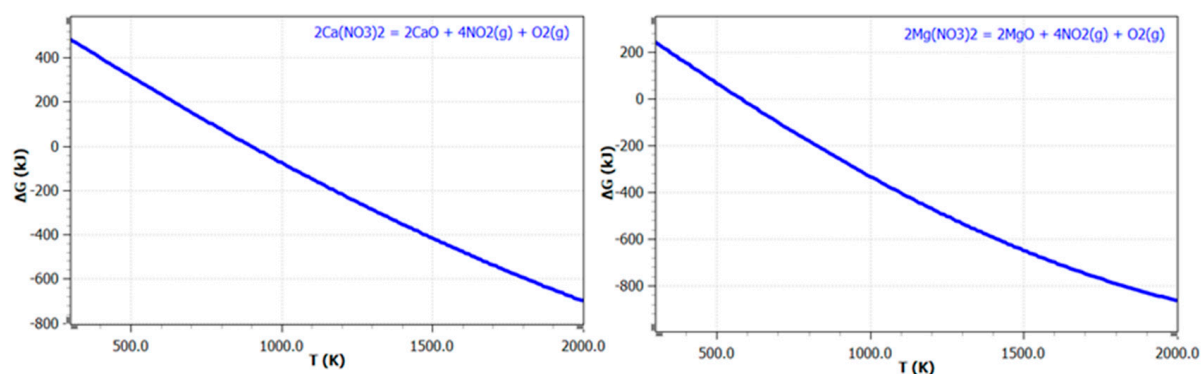


Figure 14. ΔG_r^0 as a function of temperature for Equations (10) and (11) [53].

It is worth mentioning that these temperatures could easily be achieved before the reduction stage during the EAF process, although specific chemical treatments would be required in order to eliminate the formed nitrogen oxides contained in the exhaust gas.

5. Future Research Perspectives

In this section, some future research areas are discussed regarding the application of the materials presented so far, to be explored as additives for enhancing the performance of the EAF process.

5.1. Sustainable Carbon-Bearing Additives

Numerous studies characterize carbon sources, including different biomasses or polymer residues, and compare them with coke, in addition to employing both laboratory tests on tubular furnaces to simulate EAF conditions and evaluate slag interactions and foaming capacity with different carbonaceous materials [33]. However, there remains an opportunity for the kinetic modeling of gas release and the effects on FeO reduction rates associated with the significant presence of hydrocarbons, particularly when comparing materials with varying volatile contents and carbonization levels. Such modeling enables better understanding of the trial results and advancements in processing methods, aimed at mitigating operational drawbacks such as low calorific value and premature reactivity.

Additionally, long-term tests assessing the carbon footprint of the entire process, from the treatment of the carbon source (roasting, pyrolysis, and briquetting) to its application in Electric Arc Furnaces (EAFs) are mandatory [27]. In the case of polymers and rubber waste utilization, this aspect becomes even more critical, considering the impact of atmospheric emissions in EAFs compared to incineration [38].

Finally, economic assessments are imperative to clear up the sustainability roadmap and ensure the feasibility of industrial-scale transition, since these alternative materials are often more expensive due to their processing requirements and limited availability [30].

5.2. Carbon-Bearing Nanohybrid

In order to explore the potential use of the synthesized nanohybrid materials as additives for the EAF process, it is mandatory to explore both the activity of the carbonaceous phase, as well as the possible effect of the oxide's presence on slag foaming, which is directly related to the chemical nature of the oxide phases and their concentrations in the final composite.

The reactivity of the carbonaceous phase can be appreciated both through thermogravimetry (TGA) and differential scanning calorimetry (DSC), coupled with a robust method for the kinetic modeling of CO and/or CO₂ evolution during the interaction of carbon with the available O₂ molecules. This could be accomplished, for example, by the use of a particle swarm optimization algorithm [54,55] in order to estimate the desired kinetic parameters (reaction order, activation energy, and frequency factor). It is worth mentioning that reactivity can be controlled either during the calcination stage, through the optimization of the oven temperature, or through posterior chemical treatment [51,52]. Finally, the activity of the synthesized carbonaceous phase during the EAF cycle must also be carefully appreciated through labor-scale tests, as reported for the different new carbon-bearing additives covered in this manuscript [35–37].

On the other hand, the effect of the oxide's nature over EAF slag foaming must also be appreciated, both theoretically and experimentally—on the theoretical side, through thermodynamic simulations evaluate the effect of solid phase formation, and the subsequent calculation of the foaminess index.

Moreover, for the most prominent nanohybrid compositions, the performance of the additive during the EAF process must also be quantitatively appreciated through labor-scale tests, in order to study its impact on arc stability and steel production performance.

6. Conclusions

The transition toward low-carbon steelmaking not only requires the adoption of cleaner energy sources, but also the replacement of the fossil carbon traditionally used in Electric Arc Furnace (EAF) operations as a reducing and foaming promoter agent. This review demonstrates that slag foaming remains a critical parameter for energy efficiency, and its optimization depends on both slag chemistry and the nature of the carbon source employed.

Alternative carbon sources such as biochar, agricultural residues, polymers, and rubber have shown promising results in laboratory and industrial trials. Rubber/coke blends and polymeric wastes can significantly enhance slag foaming, reduce electrical energy consumption by up to 6%, and lower injected carbon requirements without compromising steel quality. Biochar, particularly when densified into briquettes, offers environmental advantages and improved foaming performance, although challenges related to premature combustion and variability in properties persist. Recent studies confirm that mixtures of coke and biochar can broaden the operational window for foaming, achieving stability across a wider range of slag compositions.

Despite these advances, the successful implementation of renewable carbon sources in EAF steelmaking demands further research on material engineering, injection strategies, and thermodynamic modeling. Standardized protocols for evaluating foaming capacity are essential to ensure technical feasibility and environmental benefits. Future developments should also explore hybrid solutions, such as biochar–polymer composites or even

nanocomposites containing a carbonaceous phase and oxides, with both concomitantly generated through inert-atmosphere thermal treatment of nanocellulose fibers containing the desired metals adsorbed on its surface. In this last case, the strong affinity of TEMPO-oxidized nanocellulose (TCNF) toward metallic cations opens the way for the search for an optimized composition of the oxidized phase, which could contribute to both slag foaming and carbonaceous phase reactivity, stimulating CO formation at lower temperatures and under the desired rate.

In summary, replacing fossil carbon with sustainable alternatives is not only technically viable but is strategically necessary for achieving net-zero targets in the steel industry. Continued innovation is the key to unlocking the full potential of these solutions and driving the desired decarbonization of EAF steelmaking.

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