

# Lessons learned from attempts at minimizing CO<sub>2</sub> emissions in process metallurgy: Pyrolyzed secondary raw materials, bio-coke, and hydrogen as alternative reducing agents

*F. Diaz<sup>1,2</sup>, M. Sommerfeld<sup>2</sup>, G. Hovestadt<sup>2</sup>, D. Latacz<sup>2</sup>, B. Friedrich<sup>2</sup>*

<sup>1</sup>. Group Leader Automation and digital transformation for process metallurgy,

<sup>2</sup>. Institute of Process Metallurgy and Metal Recycling IME,

RWTH Aachen University, Intzestraße 3, 52056 Aachen, Germany.

Email: [fdiaz@ime-aachen.de](mailto:fdiaz@ime-aachen.de)

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## ABSTRACT

The metallurgical sector significantly contributes to the global carbon footprint and encounters the challenge of developing more sustainable production methods. This study introduces novel approaches aimed at reducing CO<sub>2</sub> emissions within the industrial sector, some of which have been developed up to the demonstration scale.

In two case studies, urban waste from the agricultural sector (corn, olives, coconut, etc.) and WEEE recycling residues (Shredder Light Fractions) were subjected to thermal treatment. The resulting materials were then used as substitutes for conventional fossil-based reducing agents in both the copper and ferroalloy industries. Furthermore, hydrogen was employed at different scales to assess its efficacy as a reducing agent for recovering metal oxides from fayalitic copper slags.

Our findings reveal promising prospects and defined specific challenges for the integration of these alternative reducing agents in the industry. The synergistic use of pyrolyzed SLF, bio-coke, and hydrogen presents a viable pathway to significantly diminish CO<sub>2</sub> emissions while simultaneously improving the sustainability of the metallurgical sector.

## INTRODUCTION

The metallurgical industry produced approximately 1.9 billion tonnes of steel, 69 Mio tonnes of Aluminium and 22 Mio tonnes of copper in 2022 (Mineral commodity summaries 2023 2023), contributing to roughly 5.2% of the total anthropogenic CO<sub>2</sub> emissions together with other Industries like cement and chemicals. In comparison to other industrial sectors, the metallurgical industry accounts for approximately 30% of these emissions, closely competing with the cement industry (Raimund Malischek, Adam Baylin-Stern, and Samantha McCulloch 2019).

Greenhouse gas emissions are a significant concern due to the climate crisis, especially within the metallurgical industry. The primary source of CO<sub>2</sub> emissions is iron production, specifically in blast furnaces, which employ carbothermal reduction, resulting in substantial direct CO<sub>2</sub> emissions. Furthermore, processes like pelletizing, coking, sintering, and steelmaking also contribute to direct CO<sub>2</sub> emissions (Cavaliere 2016). In addition to the direct CO<sub>2</sub> emissions generated during carbothermal reduction processes for metal production, there are other, less-discussed sources of CO<sub>2</sub> emissions that are also relevant. These include the production of metallurgical slags and the subsequent handling of such metallurgical waste materials, often involving high temperatures that require fuels or energy and carbothermal reduction, which requires reducing agents. This is especially significant, given that for instance in the copper sector, flash smelters can yield up to 3 tonnes of slag per tonne of copper (Gorai et al. 2003; Zhang et al. 2022), containing 1% to 5% copper by weight, equivalent to up to 10% of the copper in the input material (Gorai et al. 2003; Gonzalez et al. 2005; Roy et al. 2015), thus post-handling of such a slag is ultimately required.

The European Union has already established significant targets and signed the "Green Deal", aiming to achieve a net CO<sub>2</sub>-free economy by 2050 (European Commission 7/14/2021). This initiative creates a compelling demand for innovative process solutions within the ferrous and non-ferrous industry for the metal production and the handling of metallurgical slags.

In the context of circular economy and sustainable practices, there is extensive research underway to identify viable alternatives to fossil reducing agents. These alternatives can be broadly classified into two categories: alternative solid reducing agents sourced from "waste" materials and alternative reducing gases. The fig. 1 illustrates these alternative reducing materials in relation to their role in metallurgical applications. This, in the context of decarbonisation of the metallurgical sector.

Alternative solid reducing agents are produced through the thermal treatment or cracking of organic materials using methods such as pyrolysis, torrefaction, or hydrothermal carbonization (Alamgir Ahmad et al. 2023). These processes entail elevated temperatures and in the case of pyrolysis, the absence of oxygen. During such a process, polymers or organic structures are broken down into smaller intermediate substances, including oil, gas, and solid (Diaz et al. 2023; Alamgir Ahmad et al. 2023). The solid product of the cracking process can be referred to as "Bio-coke" when derived from agricultural waste or "Pyrolyzed secondary raw material" if sourced in the context of urban mines, from complex organic anthropogenic materials such as plastics, textiles, or electronic scrap.

In the case of alternative reducing gases, hydrogen has emerged as a primary focus in recent years. However, to be sustainable, the method of hydrogen production also plays a crucial role. For example, hydrogen can be generated through energy-intensive electrolysis, wherein water molecules are split into hydrogen and oxygen. To produce 1 tonne of Hydrogen Direct Reduced Iron, approximately 50-54 kg (545 Nm<sup>3</sup>) of hydrogen is needed, requiring between 2.5 to 3.5 MWh of energy for the water electrolysis (Vogl et al. 2018; Patisson and Mirgoux 2020). To put this in perspective, it is equivalent to the energy consumption of an individual in Germany over a span of 2 years. Therefore, it is imperative that hydrogen used for metallurgical applications is produced from renewable sources. In this case, this reducing gas can refer as "green" hydrogen.

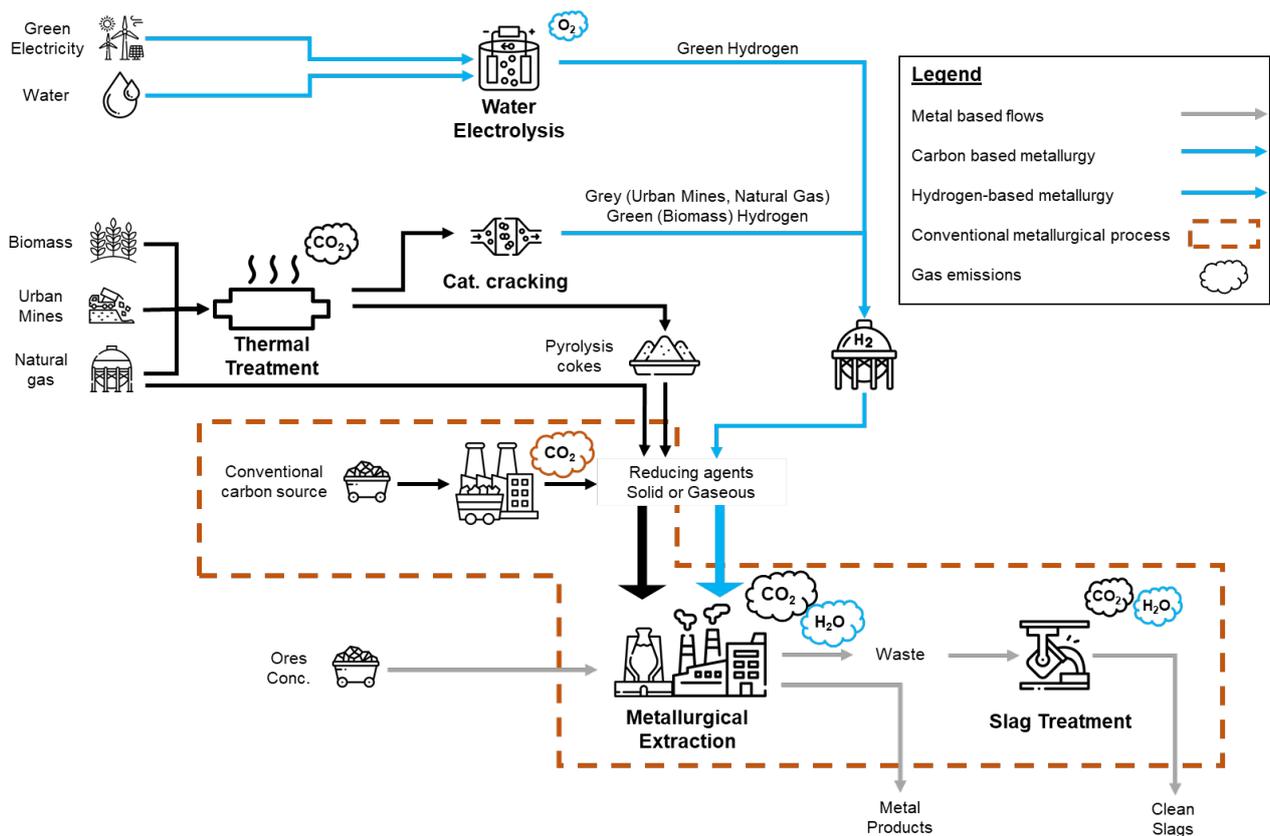


FIG 1 – Decarbonization Alternatives for the Metallurgical Industry

In addition to electrolysis, hydrogen can also be produced through the thermal treatment or cracking of organic material-rich substances such as biomass and materials from urban mines. These processes are used to generate bio-coke or to pyrolyze secondary raw materials. During such treatments, hydrogen is often produced alongside with carbon dioxide and other reducing gases like carbon monoxide, methane, and various hydrocarbons (Diaz et al. 2023). This mixture, depending

on its composition, is commonly referred to as 'syngas'. While syngas and natural gas share some similar characteristics, they are distinct in composition. Syngas, often derived from sources like coal or biomass, and natural gas can undergo different processing methods to produce hydrogen. When natural gas is catalytically cracked down to produce hydrogen, and the CO<sub>2</sub> byproduct is not captured, the hydrogen produced is typically referred to as 'grey hydrogen'. In contrast, hydrogen produced from biomass can be considered 'green hydrogen', especially when the biomass is sourced sustainably and the energy used in the process is from renewable sources (AlHumaidan et al. 2023).

This article aims to offer insights into the lessons learned, key characteristics, advantages, and the identification of essential comparative criteria in the utilization of bio-coke, pyrolyzed secondary raw materials, and hydrogen. These are considered as alternative resources to traditional fossil-based reducing agents in metallurgical applications.

## **CASE STUDY: PYROLYZED SECONDARY RAW MATERIALS AS REDUCING AGENT**

The Shredder Light Fraction (SLF) is a byproduct of the mechanical treatment of Waste Electrical and Electronic Equipment (WEEE), constituting approximately 4.2% of the output materials and containing high concentrations of primary metals like copper, tin, lead, zinc, silver, and gold (Ueberschaar 2017). The presence of valuable resources in SLF, coupled with rising disposal costs, drives pre-processing companies to seek more efficient approaches for its management. However, direct incorporation into conventional metallurgical processes introduces complexities. These include handling halogens from flame retardants, managing diverse composition, and addressing intricate morphology for charging into the smelters (Diaz et al. 2023).

In this study, SLF was obtained from a local German electronic scrap processing company, consisting of fine particles including dust, rubble, biological fragments, fibers, and plastic sheets. It has relatively low metal content, mainly fine copper wires and electronic components. SLF is carbon-rich (40.6%), with notable oxygen (17%), nitrogen (5.73%), and hydrogen (0.48%). It also contains metals like copper (1%), aluminum (3.34%), silicon (7.51%), and trace elements, resulting in a low Lower Heating Value (LHV) of approximately 18.8 MJ·kg<sup>-1</sup> (Diaz 2020). During pyrolysis, SLF transforms into pyrolysis gas (P.Gas), pyrolysis oil and water (P.Oil), and a solid product (PSLF) with metals, oxides, and pyrolysis coke, experiencing a mass loss of about 40% (Diaz et al. 2023).

PSLF can be described as a concentrated version of metals found in SLF, characterized by a black powder containing pyrolytic carbon and oxides. It is highly brittle and contains notable elements, including oxygen (24%), silicon (14.29%), aluminum (6.14%), and copper (3.3%), at higher concentrations than SLF. Additionally, it includes trace amounts of various other elements, including Precious Metals (PMs). The LHV registered for PSLF was approximately 7 MJ · kg<sup>-1</sup>. Further details about the research methods, SLF and PSLF characterization, and the pyrolysis process applied to SLF from WEEE can be found in (Diaz et al. 2023).

This case study explores an innovative recycling process for Printed Circuit Boards (PCBs), utilizing Pyrolysis Shredder Light Fraction (PSLF) as an alternative reducing agent to recover copper from oxidized slag. Fig. 2 illustrates this process, which is aligned with the principles of a circular economy, converting waste streams—SLF and PCBs—into valuable resources, such as copper and energy.

The recycling process commences with two primary inputs: SLF and PCBs. PCBs undergo an autothermal smelting, a combustion in the presence of oxygen that leverages the organic materials within the PCBs as an energy source. This results in the formation of copper-rich slag due to the oxidation of metallic components at high temperatures.

Simultaneously, SLF is processed through pyrolysis, yielding pyrolysis gas, oil, and PSLF. This carbon-rich PSLF, potentially conditioned to remove undesired metals, is then introduced into the smelter as a reducing agent. During the reduction stage, PSLF facilitates the chemical reduction of copper oxide in the slag, producing elemental copper.

The process yields three main outputs: offgas, which is managed to meet environmental standards; residual slag, which may contain non-metallic elements; and the recovered copper metal, now ready for subsequent refining and product development. By leveraging waste-derived materials for metal recovery, this process offers a more sustainable and cost-effective alternative to conventional recycling methods. The main advantage of this approach is that neither for smelting nor for the slag reduction are fossil fuels required.

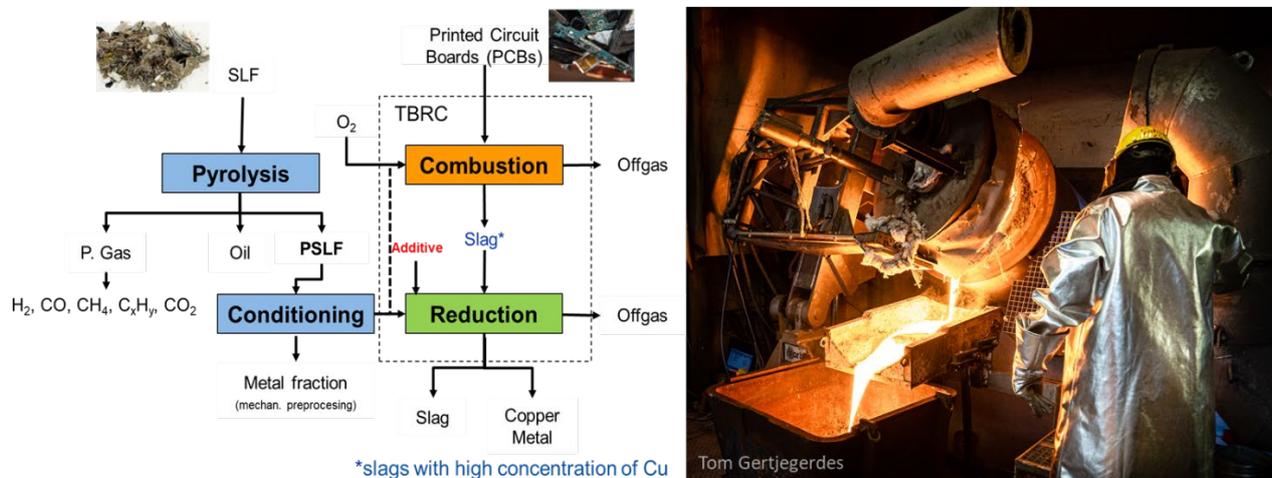


FIG 2 – Sustainable PCB Recycling Process Using PSLF as a Reducing Agent (Diaz 2020)

## Experimental work and main results

The experimental work involved the use of a demo scale Top Blown Rotary Converter (TBRC) for upscaling. The TBRC located at IME institute of the RWTH Aachen University is a cylindrical reactor with a 240L volume, capable of processing up to 100L of molten material. It utilizes an Oxyfuel burner that uses natural gas and pure oxygen for heating, providing the advantage of adjustable lambda ( $\lambda$  0.7-1.3) to control the atmosphere inside the reactor during experiments. The TBRC can rotate at speeds ranging from 0 to 10 rpm and tilt at angles from 0 to 110°, making it versatile for various applications. It is lined with Cr-magnesite (MgCr) material, suitable for copper-based materials and corrosion-resistant up to 1600°C.

The TBRC includes an offgas cleaning system with two main pathways: hygienegas and process gas. The system has a maximum suction capacity of 10,000 Nm<sup>3</sup>/h and utilizes fabric filters and electrostatic filters for dust collection. The offgases are transported to a scrubber with a pH value of 10 for removal of halogens and heavy metals like As, Cd, Pb, among others, before being released into the environment.

In the trial, 120 kg of Cu-slag was charged into the preheated TBRC at around 800°C. The furnace was heated to 1350°C using the Oxyfuel burner, and the TBRC was set to rotate at 2 rpm. The reduction experiment occurred in two phases: manual charging and injection of the PSLF. Copper concentration in the slag was monitored throughout the trial.

The stoichiometric amount of carbon needed to reduce copper oxide in the slag was calculated, resulting in the manual charging of PSLF in three periods: 72.5%, 100%, and 145% of the required amount. Rotation speed was increased to 8 rpm during manual charging to enhance turbulence. After manual charging, the injection of PSLF took place using the same molten slag. The idea was to evaluate the effect of injection and obtain some insights on the kinetics using PSLF as reducing agent.

During the injection phase, the TBRC was placed vertically, rotation speed initially set to 2 rpm, and PSLF injected at a speed of ~2.75 kg/min using nitrogen as the carrier gas. The first injection period involved injecting 50% of the required PSLF, and subsequent injection periods varied the quantity. After each injection, a gas flushing period occurred. The second injection setup used a lower  $\lambda$  value to enhance reduction conditions and included an extra stirring period. More details about the experimental setup can be found in (Diaz 2020).

The results indicated that manual charging led to poor copper reduction efficiency (7.1%) due to inadequate turbulence and surface burning. On the other hand, injection trials achieved up to 48% efficiency during the first injection period. By optimizing PSLF dosification and extending stirring periods, the efficiency increased to 82%, using PSLF equivalent to 93% of the required amount. Besides the outstanding performance, further PSLF charging was hindered by technical problems and clogging of the injector device caused by very small Cu-wires present in PSLF.

Fig. 3 illustrated the relationship between Cu reduction efficiency and C:CuO ratio in the system based on the art of charging in the TBRC, showing that process efficiency with manual charging was nearly zero under the tested conditions. Injection technology and submerged gas stirring were identified as crucial factors for improving the utilization of pyrolyzed materials as reducing agents for Cu-slags.

Similar experiments were conducted for other accompanying elements, including Ag, Pb, Zn, Ni, Sn, and Sb. Manual charging resulted in poor reduction efficiencies for these elements, but injection and submerged gas stirring significantly improved their reduction efficiencies. For example, Sb reached 100% reduction, Sn achieved 63%, Ag 100%, Pb 75%, Zn 53%, and Ni 17%.

Thermochemical simulations (FactSage™) identified four key reduction stages when using PSLF as a reducing agent for copper-rich slags: initial copper reduction, metallothermic reduction involving less noble metals, a copper co-reduction phase with metals like Ni, Sn, and Pb, and eventual iron reduction. The limited copper reduction efficiency did not result from chemical limitations but rather from challenges related to melt handling. Future improvements may involve adapting the injector to handle small wires in PSLF or enhancing mechanical conditioning of PSLF to remove some undesired metals.

In the slag system, the addition of PSLF would increase viscosity due to its SiO<sub>2</sub> content, primarily present in glassy structures from WEEE. A suggested slag design included the addition of CaO and Na<sub>2</sub>O to improve viscosity and reduce liquidus temperature. A more detailed publication on the slag design considering PSLF as reducing agent for copper slags is currently under review.

### Validation Trials in Demo-scale

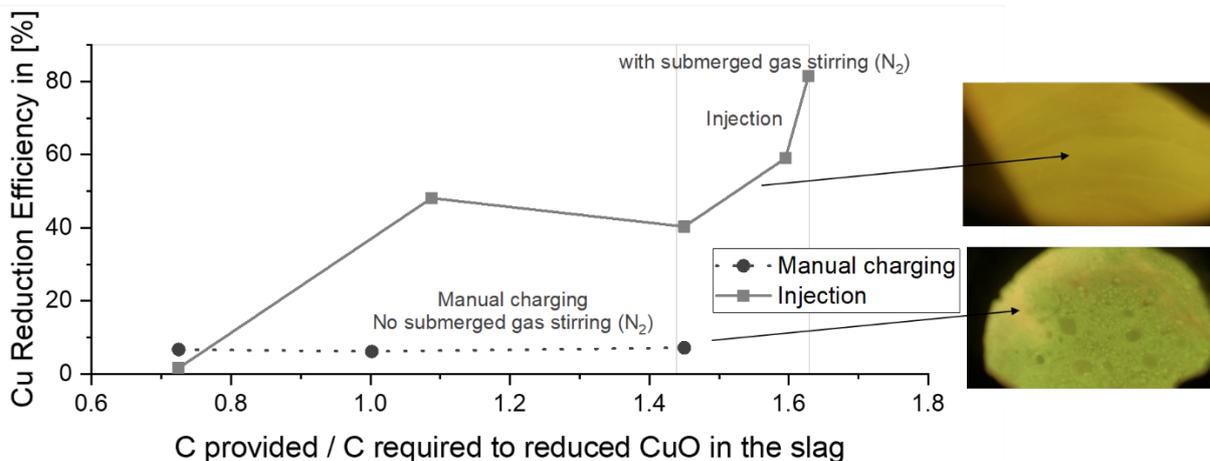


FIG 3 – Cu reduction efficiency Vs C:CuO ratio in the system according to the art of charging in the TBRC (Diaz 2020)

### CASE STUDY: BIO-COKE AS REDUCING AGENT

The production of metals, including ignoble ones like chromium, manganese, and silicon, has long relied on submerged arc furnaces, with fossil carbon serving as the primary reducing agent. However, this conventional practice contributes significantly to direct CO<sub>2</sub> emissions, urging the exploration of more sustainable alternatives. Bio-based carbon or Bio-coke has emerged as a promising candidate to replace fossil carbon in metallurgical processes.

Bio-coke, in contrast to traditional metallurgical coke, exhibits distinct proximate analysis characteristics. It is characterized by a lower fixed carbon content and a higher volatile matter content, making it more responsive to temperature changes during high-temperature processes.

Additionally, bio-coke boasts a lower ash content and a higher moisture content, which impacts its combustion and reactivity properties (Sommerfeld and Friedrich 2021).

Accompanying elements in bio-coke also diverge from metallurgical coke, with higher alkaline, chlorine, and phosphorus content, while sulfur content remains notably lower. Furthermore, the ash produced by bio-coke is characterized by increased acidity (Sommerfeld and Friedrich 2021).

Bio-coke's physical properties further differentiate it, featuring a lower density, higher CO<sub>2</sub> reactivity, and somewhat inferior mechanical stability. More details on general characteristics of bio-coke can be found in the review (Sommerfeld and Friedrich 2021).

Bio-coke, derived from sources such as coconut, corn, olive, and bamboo, is an emerging carbonaceous material that has been rigorously evaluated in comparison to conventional coke. This exploration has opened doors to its potential applications in metallurgy, particularly in the production of environmentally sustainable ferroalloys (Sommerfeld and Friedrich 2021).

In the area of metallurgy, bio-coke exhibits promise in several key processes. As it is shown in Fig. 4, its versatility allows for applications in pre-reduction, agglomeration, and direct smelting, each demanding specific attribute such as fixed carbon content, mechanical stability, purity, reactivity, and electrical conductivity. By meeting these varied requirements, bio-coke has the potential to drive the development of greener and more eco-friendly ferroalloy production methods, contributing to the reduction of carbon emissions and the promotion of sustainable practices in the metallurgical industry (Sommerfeld and Friedrich 2021).

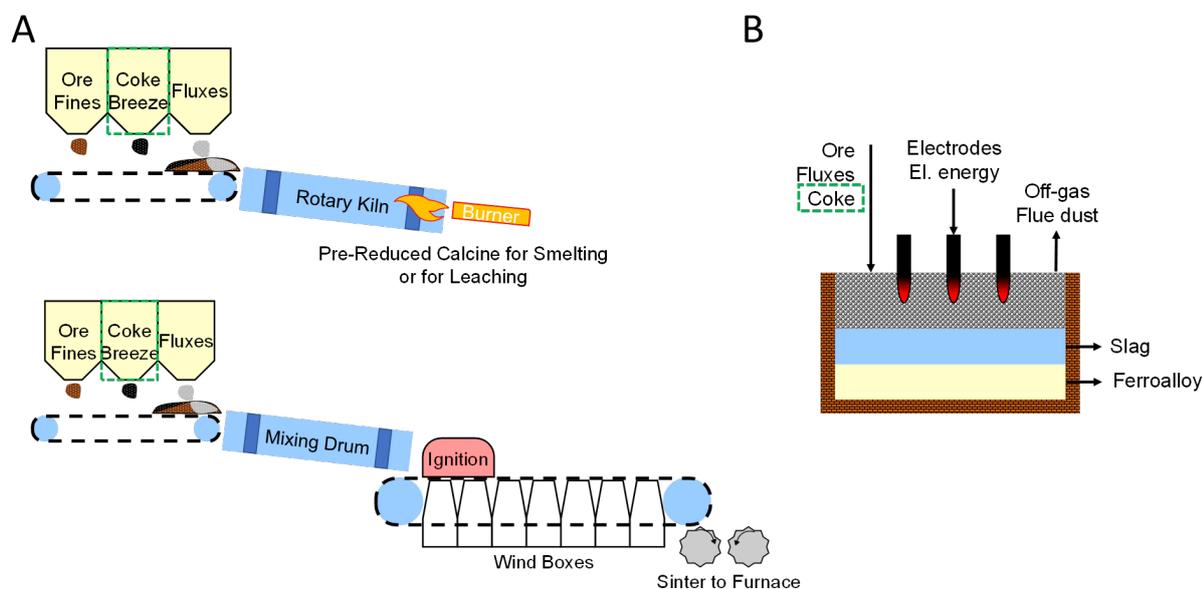


FIG 4 – A) Prereduction and Agglomeration using Bio-coke in Solid State, B) Bio-Carbon for Ferroalloy Production via Submerged Electric Arc Furnaces

## Experimental work and main results

Experiences gathered in this case study are focused on two primary aspects. In the first stage, the study explores the pre-reduction of iron ore containing chromium in solid state. In the second stage, it involves a comparison of melting operations using pre-reduced ore and co-smelting with bio-coal (biomass).

During the initial phase, laboratory-scale experiments were conducted to investigate the pre-reduction process using bio-coke as an alternative reducing agent. A resistance heating furnace was employed for these trials, with each starting with an initial sample mass of 35 grams. Different combinations of ore and reductants were explored at varying ratios. Mass loss measurements following each trial assessed chemical reactions, and individual heating of ore and reductants helped isolate their respective mass losses. Samples were charged in 99.7% pure alumina crucibles (50mm diameter, 75mm height) and continuously flushed with 5 NI/min of argon to prevent oxidation. The 16-liter volume furnace chamber accommodated a maximum of six crucibles, ensuring uniform

sample temperature. The experiments varied the maximum temperature and duration at that temperature, with a 3.5-hour heating process and uncontrolled cooling. Results are illustrated in Fig. 5.

Fig. 5 provides a comprehensive comparison of various carbonaceous materials as reducing agents for chromite pre-reduction, categorized by operational temperatures. The degree of reaction on the graph represents the portion of carbon involved in reducing the chromite ore.

At the lower temperature of 1000 °C, bio-carbons like corn exhibit a moderate degree of reaction after 60 minutes, reaching up to 17.4%. Olive, another bio-carbon, demonstrates similar modest reactivity at this temperature. Coke, Coconut and Bamboo performed poorly at this temperature with less than 10% degree of reaction.

Elevating the temperature to 1150 °C significantly alters the reaction landscape. Within a 60-minute window, all materials, particularly Olive and Coconut, show increased degrees of reaction. Coke as reference stands out with the lowest degree of reaction, indicating low reactivity within this intermediate temperature range and conditions.

Prolonging the duration at 1150 °C to 180 minutes incrementally raises the degree of reaction for all materials. Although olive's performance improves slightly, it suggests a potential plateau in reactivity at this temperature. Coke improved the degree of reaction, indicating a poor kinetic performance compared to bio-coke at these conditions.

The most striking results are observed at the upper threshold of 1300 °C. Here, bio-carbons, while still exhibiting increased reactivity for all materials, are surpassed by Olive, reaching around 60% of the degree of reaction. Coke performs the worst, reaching only 30% of the degree of reaction.

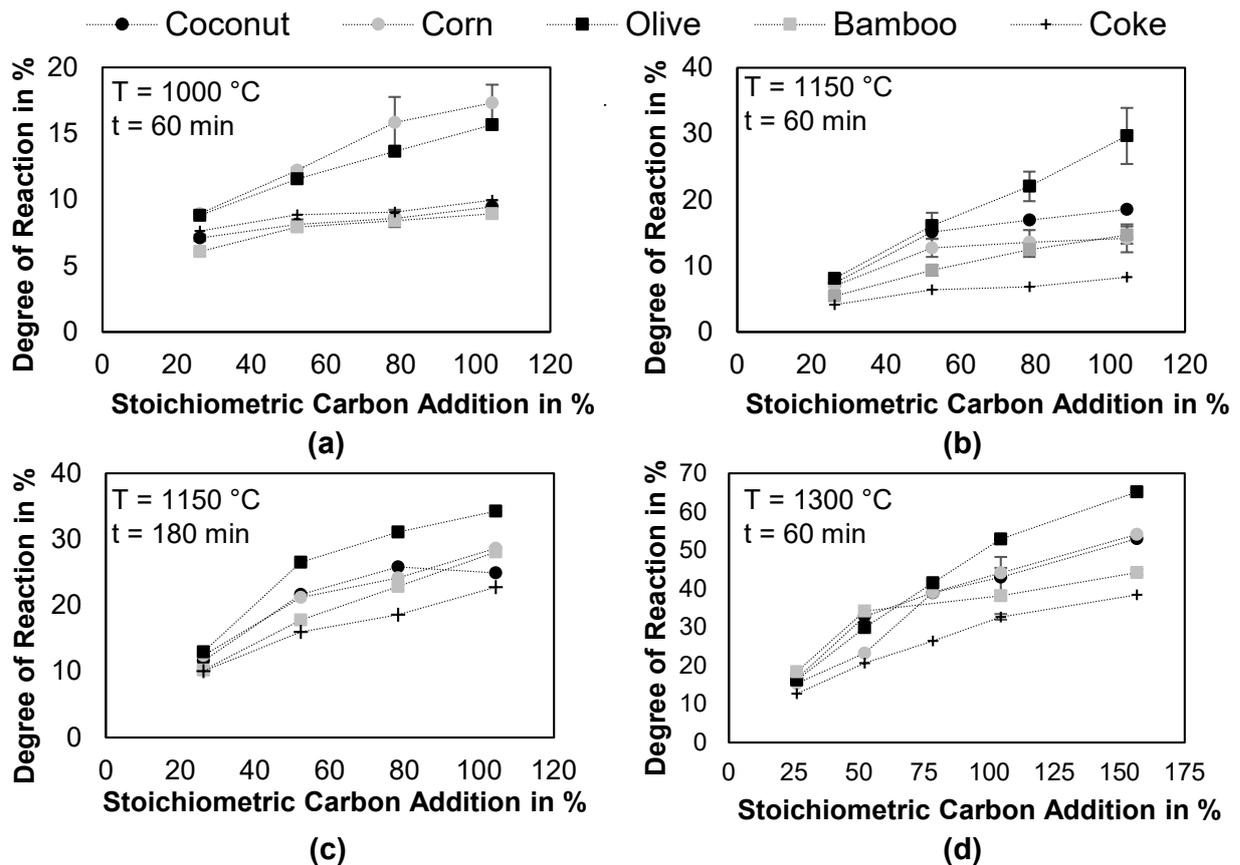


FIG 5 – Degree of reaction dependent on the carbon addition for various reducing agents and temperatures. a T = 1000 °C, t = 60 min, b T = 1150 °C, t = 60 min, c T = 1150 °C, t = 180 min, d T = 1300 °C, t = 60 min (Sommerfeld and Friedrich 2022)

In the second stage of the investigation, various reducing agents were employed for ferrochrome production, involving pre-reduction for different durations and operations without pre-reduction. Notably, both coke and bio-coal (biomass) yielded comparable chromium output during the smelting

process. However, the use of bio-coal led to phosphorus content in green ferrochrome exceeding ASTM and DIN standards, whereas lignite coke met these standards. Sulfur content remained consistent regardless of the chosen reducing agent.

Thermochemical simulations were conducted to assess relative energy demand and off-gas production. The base-case scenario involved the use of unreduced material with coke. The results indicated an increase in specific energy demand when bio-based carbon was employed. Nevertheless, pre-reduction effectively mitigated the heightened energy demand associated with bio-based carbon, resulting in reduced energy requirements for the smelting process, thanks to enhanced pre-reduction. A similar trend was observed for off-gas production, with bio-based carbon contributing to increased emissions, but pre-reduction successfully mitigated this effect. It is important to note that the details of this work are currently under review.

## **CASE STUDY: HYDROGEN AS REDUCING AGENT FOR COPPER SLAGS**

The central objective is to produce copper-steel with inherent antibacterial properties using hydrogen as the reducing agent. The primary focus is on efficiently reducing valuable metal oxides, particularly copper, while minimizing the formation of undesirable byproducts. Environmental and economic sustainability considerations are essential in this study, encompassing evaluations of energy consumption, emissions, and the feasibility of scaling up the process for potential industrial applications.

Research into copper reduction from slags to produce Copper containing steel alloys has primarily utilized carbon carriers like coal and natural gas. Busolic (Busolic et al. 2011) demonstrated a two-stage reduction process, achieving significant copper recovery (up to 51%) from slags initially containing copper oxide and copper sulfide. Gonzalez (Gonzalez et al. 2005) employed carbothermal reduction, resulting in a ferrous metal phase with high purity. Sarfo et al. (Sarfo et al. 2017) and Zhang (Zhang et al. 2018) explored carbothermal and natural gas reduction processes, respectively, obtaining varying copper content in the final slag. Blenau et al. (Blenau, L., Stelter M., Charitos A. 2021) investigated graphite injection for improved kinetics, yielding copper-rich metal alloys. These studies underscore the potential for selective copper reduction within iron recovery processes.

Hydrogen-based reduction processes show promise in extracting valuable metals from slags. Qu et al. (Qu et al. 2020) investigated synthesis gas rich in hydrogen (70%) with copper-sulfur slag, resulting in the formation of a significant copper-rich matte phase. Zhang et al. (Zhang et al. 2022) reduced low-grade copper slag using hydrogen in the solid-state, achieving a metal phase with 10.4 wt.% copper. These studies introduce hydrogen treatment as a viable option for processing low copper slags, offering good insights for the current research.

In fig. 5, the process concept is introduced, aiming to utilize hydrogen as a reducing agent for treating slags generated during sulfur burning. The objective is to eliminate remaining sulfur from the slag and reduce copper oxide to produce a copper-containing steel product (Hovestadt, G., Friedrich, B. 2022).

The project, funded by the European Union under the name HARARE, aims to explore the potential of hydrogen-based reduction processes. It focuses on two residue streams from the metallurgical industry, with the goal of advancing the technology readiness level (TRL) from laboratory scale to potentially extract important technology metals in the future. This project is a collaborative effort led by Sintef AS, involving six European universities and research institutes, along with the assistance of four companies.

In the context of this project, one of the research directions is the reduction of primary copper slags, which is the subject of this report. The objective is to scale up the process from handling 1 kg to up to 3 tons of slag melt. The approach involves a two-step reduction process. In the first step, the focus is on achieving a copper-rich metal phase, followed by a second step to obtain a copper-poor iron phase and valuable metal-free slag. The primary emphasis is placed on the selectivity of the first reduction stage.

In their 2022 study, (Hovestadt, G., Friedrich, B. 2022), highlight the importance of safety during the injection of molten materials, emphasizing the need to monitor several precautions and parameters. This includes maintaining a temperature above a 1000°C for direct ignition. The protocol also involves post-combusting hydrogen before initiating the cooling process in a quenching box. Another key safety measure is to avoid cold mixtures containing less than 4 vol. % hydrogen. Lastly, it is essential to prevent the formation of explosive mixtures outside the melt at temperatures exceeding 560°C.

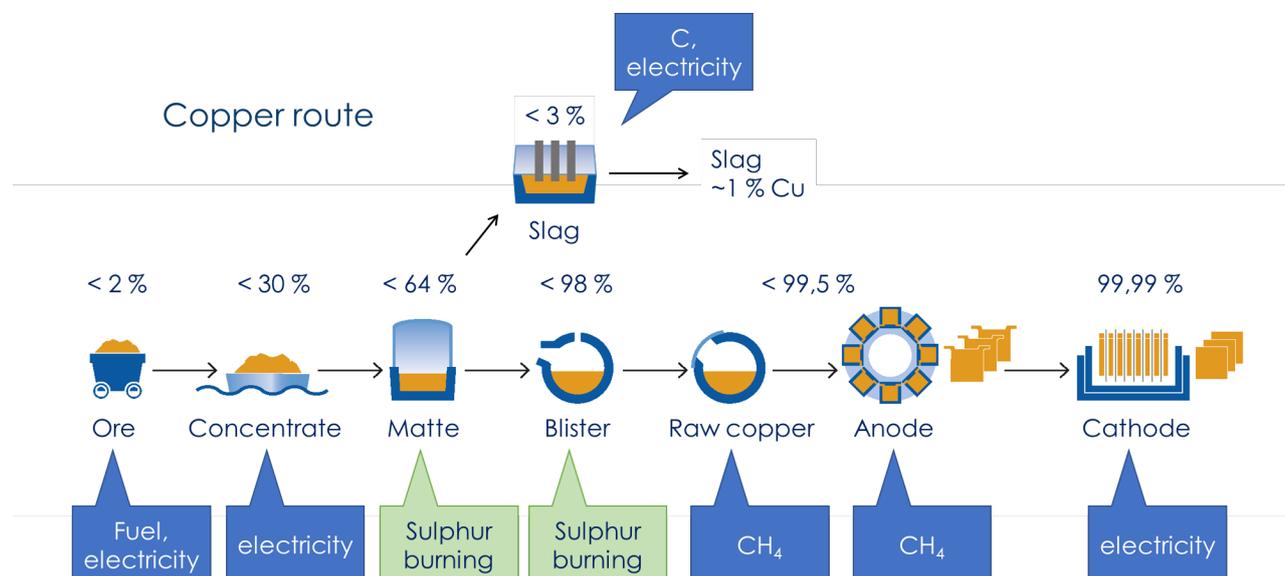


FIG 6 – Hydrogen based-reduction process for Cu-slag cleaning (Hovestadt, G., Friedrich, B. 2022)

## Experimental work and main results

In this study, the experimental setups range from lab-scale to demo-scale. The conditions for both setups are presented as follows. However, the main focus of this report is on the demo-scale experiments.

The lab-scale (Fig. 7 A) equipment includes a resistant heated furnace, refractory lining, ceramic lance, and has a temperature capability of 1300°C. It can process up to 1.5 kg of input material with a volume flow of 2 L/min of hydrogen-reducing gas, equivalent to 4.66 minutes per melt volume.

On the other hand, demo-scale (Fig. 7 B) operations handle 400 to 500 kilograms of slag, using an oxyfuel burner for heating and injecting 30 Nm<sup>3</sup>/h of gas, with hydrogen concentrations ranging from 50 to 100 vol.%. A ceramic shielded steel lance is employed in this larger-scale setup. The melting unit dimensions and off-gas cleaning system details of the demo-scale plant remain consistent with those presented in the section titled "Case study: Pyrolyzed Secondary Raw Materials as a Reducing Agent".

Fig. 8 depicts the trends in metal concentration during a two-stage hydrogen reduction process. The results in the left figure indicate a decrease in copper and lead concentrations, both diminishing as the hydrogen volume increases. Copper begins at nearly 1% by weight and falls sharply in the initial stage, then stabilizes in the second, suggesting that most copper reduction occurs after 90 liters of H<sub>2</sub> per kilogram of slag. Lead follows a similar pattern, starting below 0.5% by weight and decreasing to almost negligible levels, which implies a significant impact of hydrogen in reducing lead content during these stages.

Regarding zinc, its concentration starts above 4% by weight and exhibits fluctuations with a slight increase as the hydrogen volume rises, likely due to the reduction of other metals, but then decreases to below 1%. However, the second stage shows a clear downward trend in zinc concentration as the hydrogen volume increases. Iron, on the other hand, displays a contrasting behaviour; its concentration increases more steadily in the first stage and even more so in the second, indicating that iron is more reactive to the process as the hydrogen volume rises and copper reduction takes place. Overall, the process demonstrates the differential reactivity of metals during

hydrogen reduction, with increasing iron concentrations in the slag, while copper, zinc, and lead are reduced, reflecting their distinct affinities and reaction kinetics with hydrogen.

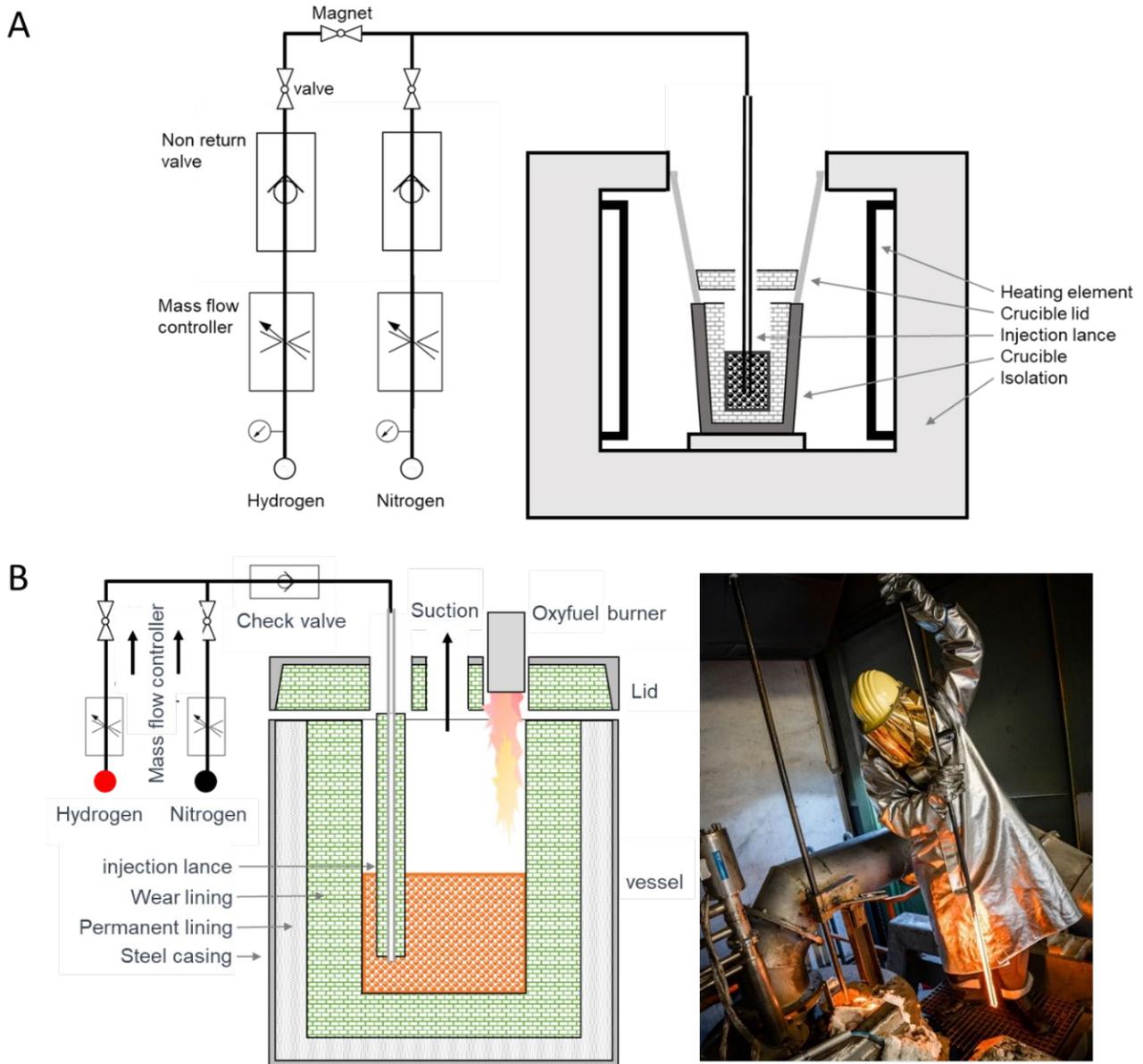


FIG 7 – A) lab-scale setup, B) demo-scale setup, for H<sub>2</sub> reduction of Cu-Slags

Table 1 indicates the overall efficiencies and end concentrations of metals in the two-stage hydrogen reduction process. As it can be seen, for copper (Cu), the recovery efficiency in the first stage is 74%, with a final concentration of 0.22 wt. %. The efficiency slightly increases to 75% in the second stage, with the final concentration remaining at 0.22 wt. %. This suggests a stable end concentration of copper across both stages.

Zinc (Zn) shows a recovery efficiency of 70% in PS1 with a final concentration of 1.32 wt. %. There's a notable increase in efficiency to 86% in PS2, accompanied by a decrease in final concentration to 0.72 wt. %. This indicates a more effective reduction of zinc in the second stage, leading to a lower residue concentration.

Lead (Pb) has a high recovery efficiency of 91% in the first stage, with a very low final concentration of 0.02 wt. %. In the second stage, the efficiency slightly improves to 94%, maintaining the final concentration at 0.02 wt. %. The consistently low final content of lead suggests a highly effective reduction process across both stages.

The data reflect the varying responsiveness of different metals to the hydrogen reduction process. The process is especially effective for lead, moderately so for zinc, with the highest reduction

occurring in the second stage, and least effective for copper, which maintains a consistent concentration post-reduction after the first stage.

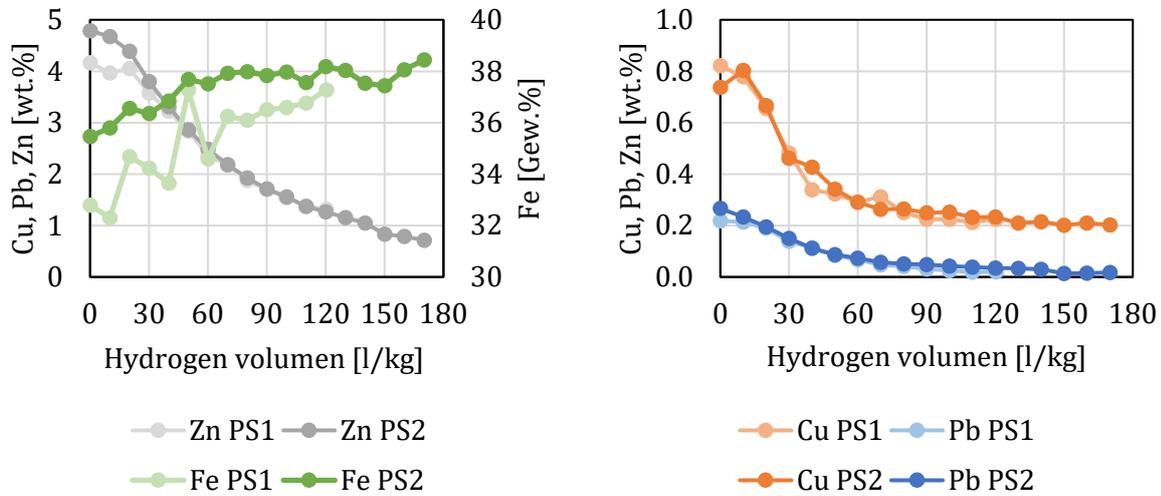


FIG 8 – Composition trends of pilot experiments based on the amount of hydrogen (1300°C, 90 vol. H<sub>2</sub>, 30 Nm<sup>3</sup>/h & 1350°C, 100 vol. H<sub>2</sub>, 36 Nm<sup>3</sup>/h).

TABLE 1 – Metal Recovery Efficiencies and Final Concentrations in a Two-Stage Hydrogen Reduction Process

Element	Yield PS1 in % (Process Stage 1)	Final Content PS1 in wt.%	Yield PS2 in % (Process Stage 2)	Final Content PS2 in wt.%
Cu	74	0,22	75	0,22
Zn	70	1,32	86	0,72
Pb	91	0,02	94	0,02

Table 2 provides a comprehensive comparative overview of three alternative reducing agents evaluated in this study: pyrolyzed secondary raw materials (Pyrolyzed SLF), Bio-coke, and Hydrogen. It highlights their source materials, production processes, carbon footprints, energy efficiency, and metal recovery efficiencies. Pyrolyzed SLF is derived from WEEE recycling byproducts, Bio-coke from agricultural waste, and Hydrogen typically from water through electrolysis or steam reforming. The table assesses each agent's carbon footprint, energy efficiency, metal recovery efficiency, final metal purity, and process compatibility, revealing distinct advantages for each. The sustainability potential, reached TLR (Technology Readiness Level), economic viability, and technical challenges are discussed, along with their environmental impact in terms of reducing landfill waste, CO<sub>2</sub> emissions, and fossil fuel dependence.

TABLE 2 – Comparative of tested alternative reducing agents

<b>Comparative Factors</b>	<b>Pyrolyzed secondary raw materials (Pyrolyzed SLF)</b>	<b>Bio-coke</b>	<b>Hydrogen</b>
<b>Source Material</b>	WEEE recycling byproducts	Agricultural waste (corn, olives, etc.)	Water (via electrolysis/steam reforming)
<b>Production Process</b>	Pyrolysis	Pyrolysis, torrefaction, or hydrothermal carbonization (from biomass)	Electrolysis/Steam Reforming
<b>Carbon Footprint</b>	Low to moderate (depends on the process and energy source for pyrolysis)	Low (considering biomass growth absorbs CO <sub>2</sub> )	Low to zero (if produced using renewable energy or biomass)
<b>Energy Efficiency</b>	Variable (dependent on pyrolysis efficiency, organic and metal content)	High (bio-coke can have high energy content)	High (especially at high temperatures)
<b>Metal Recovery Efficiency</b>	High for copper and other primary metals	Moderate to high (depending on the metal)	High for iron, variable for others (for Cu < 1wt.%)
<b>Final Metal Purity</b>	High (after metal recovery process)	Variable (affected by ash and other biomass constituents)	High (pure H <sub>2</sub> can reduce metals without contaminating)
<b>Process Compatibility</b>	Compatible with smelting processes	Suitable for use in furnaces during smelting and potentially in direct reduced iron (DRI) processes	Suitable for both smelting and DRI processes
<b>Sustainability Potential</b>	High (turns waste into resource)	High (renewable and carbon-neutral potential)	High (if produced from renewable sources)
<b>Technology Readiness Level (TLR)</b>	Up to demonstration scale (TLR 5)	Laboratory (TLR 3 - 4)	Up to demonstration scale (TLR 5)
<b>Economic Viability</b>	Moderate (influenced by the value of recovered metals)	Moderate to high (cost-effective if sourced from waste biomass)	High (long-term savings from potential carbon credits and lower emissions)
<b>Technical Challenges</b>	Handling halogens, diverse composition, intricate morphology	Lower fixed carbon content, higher volatile matter content, ash composition	Infrastructure for hydrogen production and handling
<b>Environmental Impact</b>	Reduction in landfill waste, possible emission control challenges	Reduction in direct CO <sub>2</sub> emissions, beneficial use of agricultural waste	Significant potential to reduce CO <sub>2</sub> emissions and fossil fuel dependence

## CONCLUSIONS

In conclusion, the search for an optimal approach to minimize CO<sub>2</sub> emissions in the metal production sector underscores the necessity for diverse solutions. As evolving requirements for steel and copper slag metallurgy necessitate alternative carbon sources by 2050, bio-coke and pyrolyzed materials from the urban mine sector could play a crucial role. These materials align with the industry's shift towards sustainability, offering pathways to reduce the carbon footprint of the metallurgical industry. However, relying solely on bio-coke for metal production poses technical and logistical challenges, primarily due to limited biomass availability in contrast to substantial carbon demand. An integrated approach that combines multiple strategies and materials is required to address this limitation. In this dynamic landscape, the pursuit of sustainable practices remains a primary goal in the metallurgical industry's journey towards a greener and more environmentally friendly future. Transitioning towards sustainable energy resources such as pyrolyzed secondary raw materials, bio-

coke, and hydrogen presents a promising pathway towards reducing environmental impact and enhancing energy efficiency. Given their varying technological readiness levels and environmental benefits, it is crucial to prioritize further research and development, particularly in advancing production processes and improving economic viability. Fundamental analysis on the exergy distribution of the studied systems through their incorporation in the metal production chain, scaling up technologies to improve the purity of recovered metals in pyrolysis, and enhancing the energy content of bio-coke and pyrolysis gas are key areas that could significantly impact their market readiness and adoption. Moreover, investment in infrastructure to support widespread hydrogen production and utilization will be essential. Embracing these technologies not only supports waste reduction and resource recovery but also aligns with global efforts to mitigate climate change and foster a sustainable future. Policymakers and industry leaders should consider these factors in their strategic planning to ensure a balanced and effective transition to greener energy alternatives.

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