



One-, Two-, Three-Step Processing of Waelz Slag via Sequential Hydro- and Pyrometallurgical Treatments for the Iron Recovery Enhancement

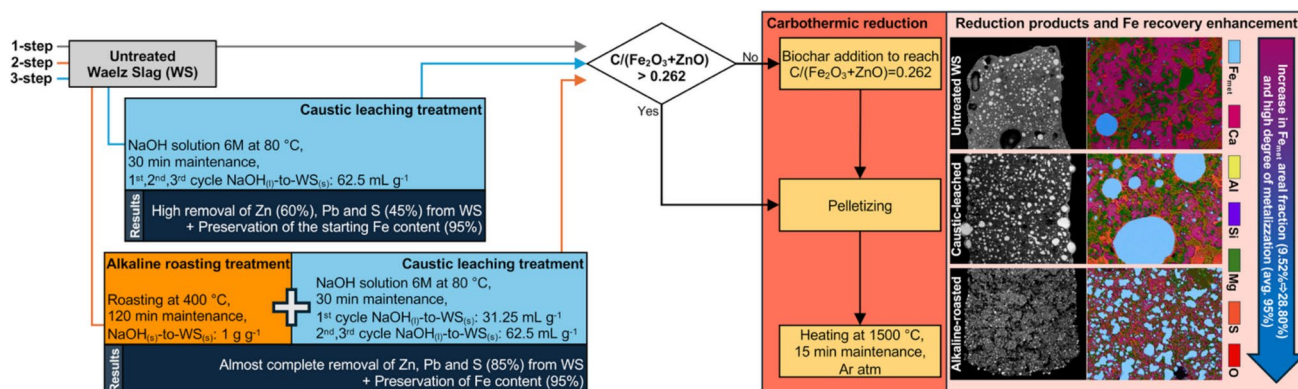
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Abstract

Waelz slag (WS) is a critical waste closely tied to the iron and zinc recycling cycles, which, thanks to its chemical composition, represents a potential secondary source of Fe. However, the presence of undesired elements (e.g., Zn, Pb, and S) poses major constraints for its direct pyrometallurgical processing (one-step treatment). To decrease the amount of these elements and increase the suitability for the subsequent pyrometallurgical processing, this study investigates the pretreatment of WS via caustic leaching (two-step treatment) and alkaline roasting followed by leaching (three-step treatment). Overall, the first pretreatment resulted in extraction degrees of over 60 wt% for Zn and 45 wt% for Pb and S, whereas the second pretreatment led to extraction degrees greater than 85 wt% for each of the three elements. Concurrently, both pretreatments preserved over 95 wt% of the initial Fe content. The pretreated WS samples were pelletized and carbothermally reduced at 1500 °C. To evaluate the effect of the alkaline treatments, the reduced pellets were characterized metallurgically and compared with the properties of reduced untreated WS-based pellets. After reduction, the pretreated WS-based pellets contained two to three times the amount of metallic iron observed in the untreated WS-based pellets (19.78–28.80% vs. 9.52%), with a consistent metallization degree of over 90 wt%. Calcium aluminates were the main constituents of the slag phase of each reduced WS-based pellet. Despite the absence of slag–metal separation, the WS processing via hydrometallurgy followed by pyrometallurgical recovery of Fe proved to be an effective waste-to-resource pathway for Fe- and Zn-bearing residues.

Graphical Abstract



Keywords Metal recovery · Slag valorization · Caustic leaching · Alkaline roasting · Carbothermic reduction · Secondary iron source

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Introduction

Waelz slag (WS) is widely recognized as one of the most critical wastes in the ferrous and nonferrous metallurgical industries. As its name suggests, WS is a residual product of the Waelz process, which is the most widely used technology for extracting the Zn contained inside electric arc furnace dust (EAFD) and/or other Zn-rich industrial byproducts [1]. About 600–800 kg of WS is produced per ton of EAFD processed [2]. In the 2000s, Barna et al. [3] estimated that about 500 kt of WS was generated per year in Europe, accounting for one quarter of the worldwide WS production (2 Mt year^{-1}) [4]. These values are expected to increase further, reaching tens of millions of tons produced per year in the coming decades due to the parallel increase in electric steelmaking and related EAFD production. Indeed, according to Brandner et al. [5], EAFD production is expected to increase to 18 Mt y^{-1} worldwide by 2050, resulting in potential WS generation of 10.8 Mt y^{-1} .

From a chemical standpoint, WS is an iron-reduced slag characterized by significant amounts of Fe (22–40 wt%) to non-negligible amounts of unreacted C (2–8 wt%), and unrecovered Zn (up to 4 wt%), as well as Ca (5–17 wt%), Mg (1.5–3 wt%), Si (3–17 wt%), and Al (1–3 wt%) [3, 6]. While the general chemistry depends on the feed mixture and composition, the relative concentration of the latter four elements depends on the kiln operating conditions (e.g., temperature and maintenance time) and, more specifically, on the nature of the fluxes used [7]. When limestone is used as a slag-forming agent, higher concentrations of Ca and Mg will be present. Conversely, when sand is used, higher amounts of Si and Al will be present. Furthermore, WS is characterized by the presence of trace amounts of toxic heavy metals such as As, Cr^{6+} , Cu, Pb, Ba, and V, as well as the occasional presence of Ag and Au [3].

To date, most WS is landfilled, thereby posing high environmental risks due to the leaching of hazardous elements [8]. In an effort to provide a valid alternative to the current end-of-life management of WS, a small number of researchers have investigated the possibility of using it as a secondary material for road pavements [9], concrete aggregates [10], cement [11], and clay bricks [12, 13]. However, complying with ever-stricter environmental regulations has limited the implementation of such practices on an industrial scale [14].

Beyond the aforementioned applications, WS is a potential source of Fe that, after its recovery, can be reintroduced into iron and steelmaking processes as a secondary feed similar to what is currently performed with direct reduced iron. This would also help to address the declining availability of high-grade iron ores that is affecting the ferrous metallurgy industry

[15]. Consequently, the development of metal recovery strategies based on pyrometallurgy and focused on WS has seen an increasing number of contributions in recent years. Grudinsky et al. [16] successfully processed WS through either reduction smelting with SiO_2 -based flux at 1650°C or after froth flotation at 1500°C , resulting in the production of a low-silicon ferro-silicon alloy and cast iron nuggets, respectively. At the same time, Dall'Osto et al. [17] and Romero et al. [18] focused on the impact of the reducing agent nature and slag viscosity on reduction process behavior. Finally, Pichler and Antrekowitsch [19, 20] investigated the use of gaseous reducing agents (e.g., pyrolysis gas or hydrogen) for the parallel recovery of Zn, Pb, and Fe at 1050 – 1150°C .

Despite the promising results achieved through pyrometallurgical approaches to WS, one of the main limitations is the presence of residual Zn and Pb. During the process, these elements can be reduced, evaporate, and react with the refractory linings of smelting furnaces (e.g., rotary hearth, rotary vessel, submerged arc, and flash smelting), triggering corrosion phenomena as well as re-condensate on the lower-temperature sections of the furnaces in the form of Zn scaffolds [21]. Additionally, it should be noted that the reduction of zinc and iron oxides, whether alone or as spinel phase, is a competing process [22]. Therefore, to achieve satisfactory metal recovery yields, the need for reducing agents should increase for the reduction of WS relative to the reduction of iron and zinc oxides alone.

To overcome these challenges, hydrometallurgical processes have gained attention as a viable solution for selectively extracting Zn, Pb, and other critical elements without affecting the Fe content. While these processes have primarily been applied to EAFD, they can also be extended to WS given the close relationship between the two materials.

Acid leaching is mostly based on H_2SO_4 [23–25] or HCl [26–28] solutions, which have proved highly effective in dissolving zinc oxides and spinels, often exceeding a 90 wt% Zn extraction degree, as well as achieving satisfactory results whenever Pb is present as an oxide. Furthermore, ultrasound-assisted leaching can reduce process time and increase the process yield [29]. However, the major drawback is the poor selectivity, as substantial amounts of Fe, Ca, and Mg can be transferred into the leachate. Ammoniacal leaching relies on NH_3 [30, 31], NH_4Cl [32, 33], or $(\text{NH}_4)_2\text{CO}_3$ [34, 35] mediums and offers improved dissolution selectivity. However, its use is limited due to the nearly null dissolution of spinel, slow kinetics, and operational challenges related to reagent stability and recycling [36]. Caustic leaching, which uses NaOH solutions, has been widely implemented for processing EAFD and other Zn-plus Fe-bearing residues due to the high degree of Zn and Pb extraction possible, the compatibility with alkaline electrowinning of Zn, the retention of Fe in the solid residue,

and the possibility of further enhancing its performance by microwave-assisted leaching [37–40]. Despite these advantages, however, the process is associated with significant reagent consumption, as solutions of 5 M NaOH or higher are required. Additionally, while it is slightly superior to ammoniacal leaching, it is also unable to fully dissolve zinc ferrite spinels. To address this last point, either alkaline roasting or calcination roasting can be performed to break down the spinel phases into simpler, more reactive and leachable forms [41, 42]. The former involves the heating of the residues in NaOH above 350 °C [43, 44], the latter in CaO above 1000 °C [45, 46]. However, increased reagent consumption and energy demand due to the additional roasting treatment must be taken into account.

This work explores a multistep waste-to-resource route in which hydrometallurgical treatments are applied to WS, not as a stand-alone process, but as a synergistic pretreatment to maximize the metallurgical quality of the pyrometallurgical reduction products (slag and recovered iron) by decreasing the amount of undesired elements (e.g., Zn, S, Pb), thereby representing an advancement in current practices for recovering metals from critical industrial residues via pyrometallurgical processes alone (e.g., red mud [47, 48], mill scale [49, 50], jarosite [51, 52], steel dust [53, 54], and WS itself [16–20]).

Starting from industrially gathered WS, three methodologies were employed: (i) direct carbothermic reduction, (ii) caustic leaching followed by carbothermic reduction, and (iii) alkaline roasting followed by leaching and carbothermic reduction. The elemental extraction and mineralogical evolution of the WS were investigated after alkaline roasting and each leaching cycle. Concurrently, in order to define the optimal alkaline-based methodology, the consequences of the WS pretreatment on the Fe recovery via carbothermic reduction at 1500 °C was evaluated in terms of mass loss, degree of reduction, degree of metallization, and the chemistry and mineralogy of the reduction products.

Materials and Methods

Waelz Slag

The WS used in this study, hereafter referred to as untreated WS, was provided by a Waelz process plant and underwent

open-air cooling. The location and name of the company are not reported here for confidentiality reasons. Prior to characterization, the untreated WS was homogenized by grinding it in a planetary ball miller (Retsch PM 400, Retsch Technology GmbH, Haan, Germany) with zirconia balls until reaching a very fine sand (< 125 µm) granulometry.

The chemical composition of the untreated WS was analyzed by means of energy-dispersive X-ray spectroscopy (EDS) using a Zeiss Sigma 500 (Carl Zeiss AG, Jena, Germany) field-emission gun scanning electron microscope (FEG-SEM) equipped with an Oxford Instruments X-Max Ultim 65 EDS probe (Oxford Instruments plc, High Wycombe, UK). To achieve a chemical composition as close as possible to that obtained by traditional bulk analysis methods, five samples weighing approximately 2 g were taken after quartering the untreated WS and distributed homogeneously on the sample holder. Multiple areal EDS analyses were then carried out at low magnification across the entire surface of the sample, and the results were averaged. Table 1 shows the composition of the untreated WS sample.

The mineral composition of the untreated WS was analyzed via X-ray diffraction (XRD) using a Rigaku SmartLab SE diffractometer (Rigaku Corporation, Tokyo, Japan) in θ – θ configuration. The diffraction pattern was acquired between 5° and 90° 2 θ , with a scan rate of 2° min^{−1}, step size of 0.02°, sample rotation of 60 rpm, and using a Cu–K α radiation (λ = 1.54 Å) source with a one-dimensional (1D) X-ray fluorescence (XRF) suppression detector (D/Tex 250, Rigaku Corporation, Tokyo, Japan). Peak indexing was performed using the Crystallography Open Database (COD). Figure 1 shows the diffraction pattern of the untreated WS sample and the identified mineral phases.

The main elements detected by the EDS analysis were, in descending order, Fe, Ca, C, and Zn. Collectively, these elements constituted over 50 wt% of the WS chemical composition. For the sake of completeness, it should be noted that the amounts of Fe and C exhibited slightly higher standard deviations than the other elements due to intrinsic heterogeneity that remained in the untreated WS. Nevertheless, since the average percentage of each element was consistent with the XRF results of other WS streams available in the literature [4, 17, 55], the methodology was deemed reliable and used to monitor the chemical composition of WS during the pretreatments.

Table 1 Chemical composition of the untreated Waelz slag sample, wt% (standard deviation in brackets)

C	Fe	Zn	Ca	Al	Si	Na	Pb	S	K	Cl	Others ^a
16.03 (3.02)	24.71 (2.86)	10.48 (0.95)	16.41 (1.62)	1.57 (0.31)	2.80 (0.38)	2.64 (0.38)	1.51 (0.24)	0.63 (0.18)	0.67 (0.27)	1.20 (0.17)	Balance

^aO, Mg, Cr, Mn

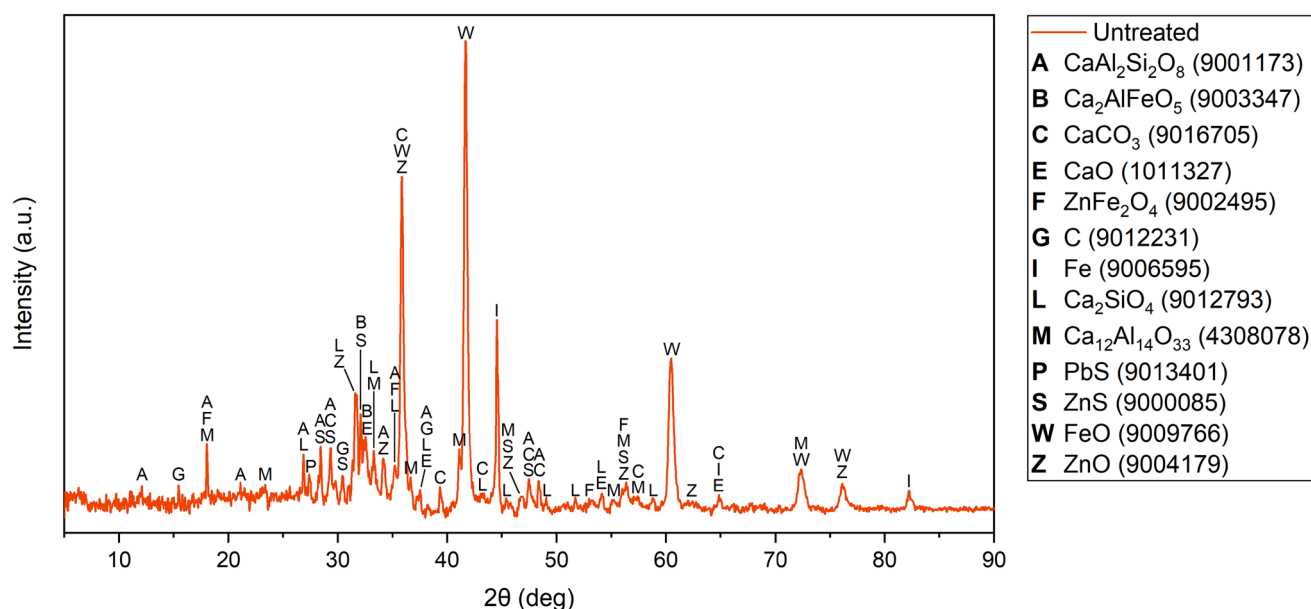


Fig. 1 Diffraction pattern of the untreated Waelz slag sample (COD card number in parenthesis)

The chemical composition results were also confirmed by the WS diffraction pattern, which showed that the peaks with the highest intensities were associated with Fe-bearing phases, specifically wüstite (FeO) and metallic iron (Fe). Zn was primarily present in the form of zincite (ZnO), and, to a lesser extent, it was bound with Fe as franklinite (ZnFe_2O_4) or with S as wurtzite (ZnS). The high Ca content led to consistent amounts of calcium silicate, aluminate, and aluminosilicate in the form of larnite (Ca_2SiO_4), mayenite ($\text{Ca}_6\text{Al}_7\text{O}_{16}$), brownmillerite ($\text{Ca}_2\text{AlFeO}_5$), and anorthite ($\text{Al}_2\text{CaO}_8\text{Si}_2$). Additionally, free lime (CaO) and calcite (CaCO_3) were present and were attributed to the addition of Ca-based fluxes during the Waelz process to control the basicity of the generated slag [7]. Similarly, the detected graphite (C) was linked to unreacted coke fines that were dragged into the WS at the end of the Waelz process [55]. Finally, in addition to the aforementioned wurtzite, galena (PbS) was observed as S-bearing phase.

Hydro- and Pyrometallurgical Processing of Waelz Slag

Figure 2 provides a simplified flowchart to visually represent the various treatment routes employed in this study: (one-step) direct carbothermic reduction of untreated WS, (two-step) caustic leaching of WS and subsequent carbothermic reduction of pretreated WS, and (three-step) alkaline roasting followed by leaching of WS and subsequent carbothermic reduction of pretreated WS.

It should be noted that the pretreatment parameters were derived from literature focusing on the removal of Zn, S, and Pb from EAFD and the parallel Fe beneficiation via either caustic

leaching [40, 56] or alkaline roasting [44, 57]. Indeed, as previously mentioned, the close correlation between the composition of EAFD and WS makes it theoretically possible to employ the optimal parameters for one to treat the other. This approach has also partially compensated for the lack of studies on WS alkaline pretreatments and eliminated the need for extensive experimental gradient campaigns focused on parameter optimization. Finally, it narrowed the scope of this study to gain key insights into the role of WS pretreatments on the metallurgical quality of the reduction products.

Caustic Leaching Treatment

Caustic leaching treatment was conducted in a 400 mL glass beaker containing a 6 M NaOH solution prepared by dissolving laboratory-grade NaOH pellets in double-distilled water. WS was subsequently added to the solution to achieve a liquid-to-solid ratio of 62.5 mL g^{-1} , and the solution was placed on a Falc F60 heated magnetic stirrer (Falc Instruments S.r.l., Treviglio, Italy) and maintained at 80°C for 30 min under continuous stirring at 450 rpm with a Teflon-coated stirring bar. The parameters followed the guidelines for the optimal removal of Zn from Zn-bearing dust in caustic solutions, as discussed in previous studies [40, 56]. The solution was vacuum-filtered using hydrophilic polytetrafluoroethylene (PTFE) membranes (pore size of $0.45 \mu\text{m}$) to separate and collect the solid residue. To remove any residual moisture, the residue was placed in a Carbolite HRF muffle furnace (Carbolite Gero, Neuhausen, Germany) at 90°C overnight. The dried residue was then subjected to a successive caustic leaching cycle, up to three cycles in total. To further understand the chemical and mineralogical

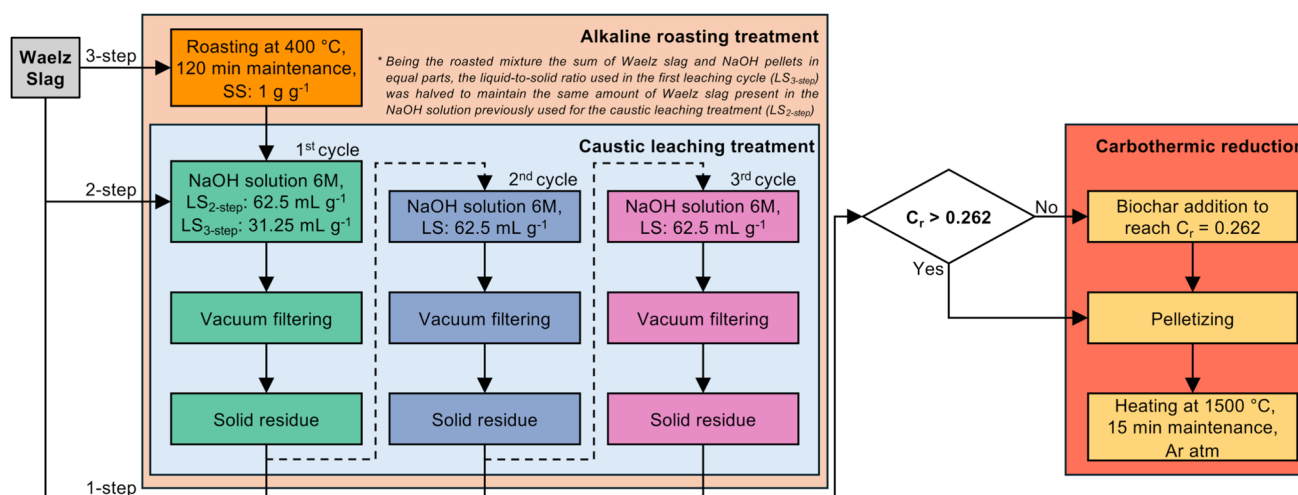


Fig. 2 Flowchart of the treatments employed on the Waelz slag (SS = solid NaOH-to-solid WS, LS = liquid-to-solid ratio, C_r C/(Fe₂O₃+ZnO) = ratio of the mixture)

evolution of the WS, a sample of dried residue was collected and characterized after each leaching cycle.

Alkaline Roasting Treatment

The alkaline roasting treatment was performed on 20 g of WS. Laboratory-grade anhydrous NaOH pellets were added at a solid-to-solid ratio of 1 g g⁻¹, and the mixture hydrolyzed using double-distilled water at a ratio of 0.25 mL g⁻¹. The mixture was homogenized through mechanical mixing, placed in an alumina crucible, and heated at 400 °C for 120 min using a Nabertherm LHT 02/17 LB lift-bottom furnace (Nabertherm, Lilienthal, Germany) in air atmosphere. As with the caustic leaching treatment, the parameters were based on previously published studies regarding the optimal range for promoting the decomposition of Zn-bearing phases [44, 57]. After cooling to room temperature, the roasted mixture was collected, crushed, and subjected to caustic leaching under the previously mentioned parameters and methodology. Since the roasted mixture consisted of the sum of the WS and NaOH pellet mass, the liquid-to-solid ratio was reduced to 31.25 mL g⁻¹ for the first leaching cycle only, in order to maintain the same amount of WS present in the NaOH solution used during the caustic leaching treatment.

Characterization of Hydrometallurgically Pretreated WS Solid Residue and Assessment of Extraction Degrees

After each caustic leaching cycle, as well as after preliminary alkaline roasting, the WS solid residues were

chemically characterized using EDS analysis, and the mineralogy was assessed using XRD analysis. Both characterization techniques were performed using the same instrumentation and parameters described previously for characterizing the untreated WS sample.

To evaluate the effectiveness and performance of the two hydrometallurgical pretreatments used in this study on the WS, the extraction degree of the primary elements of interest (e.g., Zn, Pb, S, and Fe) for the subsequent pyrometallurgical process was assessed using Eq. 1.

$$E_{j,i}(\text{wt } \%) = \left(1 - \frac{w_i \cdot c_{j,i}}{w_o \cdot c_{j,o}} \right) \times 100, \quad (1)$$

where $E_{j,i}$ is the extraction degree of the j th element at the i th treatment step, w_o and w_i are the masses (g) of the untreated WS sample and the solid residue at the i th treatment step, and $c_{j,o}$ and $c_{j,i}$ are the elemental concentrations (wt%) of the j th element in the untreated WS sample and in the solid residue at the i th treatment step, respectively. Finally, the ratio between w_i and w_o was used to determine the mass yield at each leaching cycle.

Carbothermic Reduction Process

Prior to the carbothermic reduction process, each pretreated WS solid residue was compacted into pellets 10 mm in diameter, with height of 20 mm, using a modified MTS Exceed Series 40 uniaxial tensile test machine (MTS Systems, Eden Prairie, MN, USA). Based on the C/(Fe₂O₃+ZnO) ratio (C_r) of each residue, biochar was added to reach the target value of 0.262 g g⁻¹, which has proved to offer optimal reduction efficiency for the carbothermic reduction of WS [17]. If

the pretreated WS solid residue had a C_r value greater than 0.262, no biochar was added. Specifically, the biochar was obtained by pyrolyzed wood pellets and was characterized by total carbon content of 93.51 wt%, fixed carbon content of 83.14 wt%, volatile matter content of 12.48 wt%, and ash content of 3.58 wt%. Its full characterization was discussed in an earlier work by the authors [58]. Meanwhile, the Fe_2O_3 and ZnO content was evaluated by converting the elemental values of the EDS analysis into oxides.

The carbothermic reduction process was conducted at 1500 °C under an inert atmosphere (Ar) using a Nabertherm LHT 02/17 LB lift-bottom furnace (Nabertherm, Lilienthal, Germany). Specifically, according to the authors' previous experience [17] and the literature on WS reduction [16], this temperature should be the most suitable for achieving metal–slag separation. One pellet at a time was placed in a graphite crucible, and a ceramic separator was used to avoid any pellet–crucible interaction. To ensure that the reduction behavior was not biased by the evolution of CO from the graphite of the crucible, the latter was weighed before and after each test (in the case of mass variation greater than 0.5 wt%, the test was considered invalid). The graphite crucible was then inserted into an external alumina crucible, and the whole setup placed inside the furnace. Before starting the reduction process cycle, an argon flux of 10 NL h⁻¹ was blown for 30 min inside the crucible using an alumina tube inserted inside the alumina crucible from its lid. The target temperature was then reached at a heating rate of 100 °C min⁻¹, maintained for 15 min, and the crucible was removed once the furnace had cooled naturally to below 300 °C. Throughout the thermal cycle, Ar was continuously blown to maintain the inert atmosphere.

Characterization of Reduced WS-Based Pellets

The reduced WS-based pellets were physically, chemically, and mineralogically characterized to evaluate the effect of hydrometallurgical pretreatments on the reduction process and to assess its effectiveness. Visual observation was used to identify macro-morphological differences. Meanwhile, the mass loss (Δw) and the degree of reduction (DR) were evaluated according to Eqs. 2 and 3, respectively.

$$\Delta m(\text{wt } \%) = \left(1 - \frac{w_i}{w_o} \right) \times 100, \quad (2)$$

$$DR(\text{wt } \%) = \left(\frac{\Delta m}{\Delta w_{th}} \right) \times 100, \quad (3)$$

where w_o and w_i are the mass (g) of the WS-based pellet before and after the carbothermic reduction process, while Δw_{th} is the theoretical mass loss (g) evaluated as the sum of the expected losses due to (i) the complete reduction of

all reducible oxides in the pellet at 1500 °C by C and CO, (ii) the conversion of elemental C into CO and its release, and (iii) the removal of volatile or low-melting compounds present in the WS or biochar.

To conduct the metallographic analysis, the reduced pellets were cut in half to expose the cross section, mounted using a phenolic resin, and polished up to 1 μm . The cross section was then reconstructed using a Zeiss Sigma 500 FEG-SEM (Carl Zeiss AG, Jena, Germany) equipped with an Oxford Instruments Unity backscattered electron and X-ray (BEX) detector (Oxford Instruments plc, High Wycombe, UK), whereas elemental distribution and mineral phase identification were performed using BEX imaging and EDS analysis, respectively.

Finally, the degree of metallization (DM) and the areal fraction of metallic iron (AFe_{met}) were evaluated using quantitative metallurgy of the reconstructed microstructure. Specifically, the reconstructions were post-processed in ImageJ (version 1.53t) by converting them to grayscale, which gave pixel intensity values ranging from 0 (black) to 255 (white). Then, the area occupied by metallic iron, unreduced iron, slag, carbon, and porosities was extracted according to the pixel intensity. Metallic iron was generally identified within the range of 255–190, unreduced iron oxides and slag within 190–20, and carbon and porosities within 20–0. Nevertheless, it must be emphasized that these ranges can vary based on the SEM parameters used to acquire the micrographs. The DM and the AFe_{met} were thus calculated according to Eqs. 4 and 5, respectively.

$$DM(\%) = \left(\frac{Fe_{met}}{Fe_T} \right) \times 100 = \left(\frac{n_{Fe} \cdot \rho_{Fe}}{n_{Fe} \cdot \rho_{Fe} + n_{FeO} \cdot \rho_{FeO} \cdot \chi} \right) \times 100, \quad (4)$$

$$AFe_{met}(\%) = \left(\frac{Fe_{met}}{n_T - n_p} \right) \times 100, \quad (5)$$

where Fe_{met} is the metallic iron, Fe_T is the total iron, n_{Fe} is the number of pixels attributed to the metallic iron, ρ_{Fe} is the metallic iron density, n_{FeO} is the number of pixels attributed to the oxide iron, ρ_{FeO} is the oxide iron density, χ is the weight percentage of iron in the specific oxide observed, n_T is the total number of pixels attributed to the reduced pellet cross section, and n_p is the number of pixels attributed to the porosities.

Results and Discussion

Chemical and Mineralogical Evolution Induced by Caustic Leaching

Figure 3 shows the effect of each leaching cycle on the WS chemical composition.

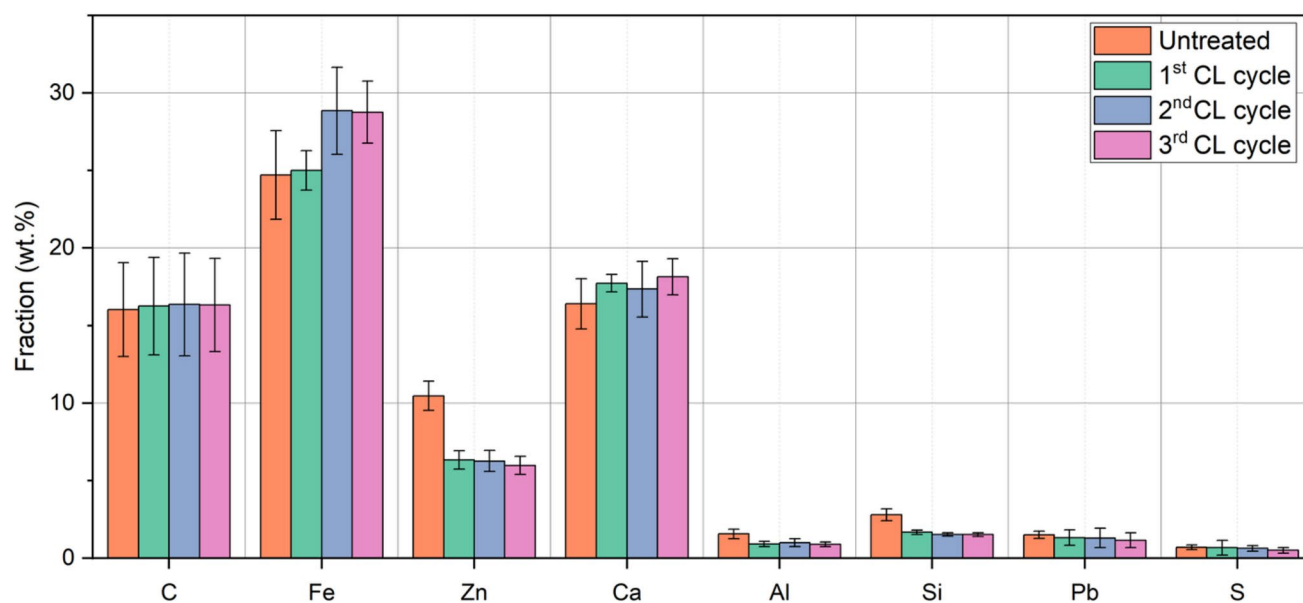


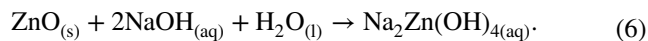
Fig. 3 Chemical composition of Waelz slag at each caustic leaching (CL) cycle

Zn, along with Al and Si, exhibited a clear decrease, reaching a final average concentration of 5.99, 0.90 and 1.52 wt%, respectively. Interestingly, their concentrations were nearly halved after the first cycle yet remained almost unchanged in subsequent ones. At the same time, although not affected by the first leaching cycle, the Fe concentration increased during the second leaching cycle and stabilized at 28.76 wt% after the final cycle. Similarly, Ca exhibited a slight upward trend, reaching an average concentration of 18.14 wt% after the final leaching cycle. Contrary to what is often reported in the literature regarding the dissolution rates of Pb in caustic solutions [40, 56], only a minor decreasing trend was observed throughout all the leaching cycles. Specifically, the elemental concentration decreased from the initial 1.51 wt% to 1.16 wt% after the third leaching cycle. Similarly, the S content decreased slightly, from 0.71% to 0.51% by the end of the caustic leaching treatment. Nevertheless, the low initial Pb and S content in the untreated WS, combined with the high variance in the data, makes confirming these results difficult from a statistical perspective. Finally, no major effects on the C content were observed, remaining stable at approximately 17 wt% after each leaching cycle.

To gain insight into the observed trends in the elemental composition of the WS after each caustic leaching cycle, the main mineral constituents were identified by means of XRD and the results are provided in Fig. 4.

For each leaching cycle, the main constituents of WS were Fe-bearing phases, specifically wüstite (FeO), franklinite (ZnFe_2O_4), and metallic iron (Fe). Furthermore, in accordance with the evolution of the chemical composition,

the respective peak intensities increased after the second cycle. Zn-bearing phases were present either as zincite (ZnO), franklinite, or wurtzite (ZnS). The detailed observation of the peak intensities revealed that the primary ZnO peak ($32.0^\circ 2\theta$) decreased progressively with each leaching cycle, becoming almost undetectable after the second cycle. This was due to the reaction of zincite with the aqueous NaOH solution and subsequent dissolution of the sodium zincate inside the latter (Reaction 6) [38].



Conversely, the principal franklinite peaks (33.0° and $42.9^\circ 2\theta$) remained unchanged throughout the leaching cycles, highlighting the limited ability of caustic leaching to dissolve zinc ferrite spinel [38, 39]. The intensity of the wurtzite primary peak ($30.5^\circ 2\theta$), as well as that of the other S-bearing phase, galena (PbS , $28.2^\circ 2\theta$), remained fairly constant in each diffraction pattern. This is consistent with literature studies indicating that zinc and lead are poorly leachable in caustic solutions when they are present as sulfides rather than oxides [59, 60]. Furthermore, it explains the limited decrease in Pb and S concentrations observed even after three caustic leaching cycles. Among the Ca-bearing phases originally present in the untreated WS (Fig. 1), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) was the most affected by caustic leaching. In accordance with previous experimental observations [61], the reaction of anorthite with the aqueous NaOH solution led to the formation of hydrogarnet ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$), as confirmed by the presence of hydrogarnet diffraction peaks (19.8° and $31.8^\circ 2\theta$) as early as the first leaching

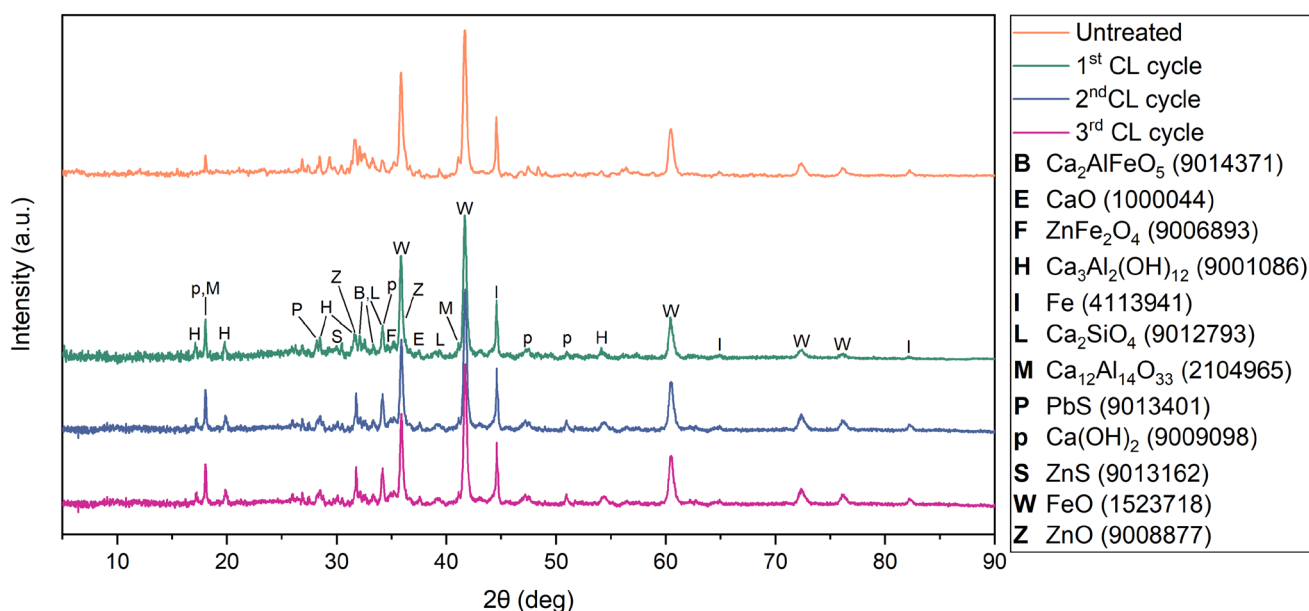


Fig. 4 Diffraction patterns of Waelz slag at each caustic leaching (CL) cycle (COD card number in parenthesis, indexing of untreated Waelz slag presented in the “Waelz Slag” section)

cycle. Concurrently, the reaction most likely generated soluble sodium aluminates ($\text{NaAl}(\text{OH})_4$) and metasilicates (Na_2SiO_3) [62], explaining the rapid decrease in Si and Al observed after the first leaching cycle. Similarly, calcite (CaCO_3) and lime (CaO), both of which were present in the untreated WS diffraction pattern, were converted into portlandite ($\text{Ca}(\text{OH})_2$), as evidenced by the increasing intensity of the corresponding primary peaks (18.0° and 34.2° 2θ). For completeness, a small amount of residual CaO was still present throughout each leaching cycle. Finally, both the calcium aluminates, present as mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and brownmillerite ($\text{Ca}_2\text{AlFeO}_5$), and the calcium silicates, present as larnite (Ca_2SiO_4), were observed after each leaching cycle, with the intensities of their respective diffraction peaks (18.1° , 32.1° and 39.2° 2θ) remaining unchanged.

Chemical and Mineralogical Evolution Induced by Alkaline Roasting Followed by Caustic Leaching

Figure 5 shows the chemical composition evolution of the WS samples after alkaline roasting followed by three cycles of caustic leaching.

A substantial increase in Na content was observed immediately after alkaline roasting. This was expected due to the SS ratio used for the treatment and the direct characterization of the roasted mixture. Indeed, during the subsequent leaching cycle, the Na content decreased and stabilized at 6.50 wt% by the second cycle. The amount of

Zn significantly decreased to 2.16 wt% after the alkaline roasting, achieving a value of 2.06 wt% at the end of the caustic leaching treatment. The behavior of Si and Al was comparable to that observed with caustic leaching alone, reaching final values of 0.94 and 1.01 wt%, respectively. Concurrently, a sudden drop in the Fe and Ca content was observed after alkaline roasting. Nevertheless, this was attributed to the significant amount of Na. Indeed, after the first leaching cycle, an increase in Fe and Ca was observed relative to the untreated WS, followed by stabilization of their concentrations over the next two cycles. The final WS had a concentration of 31.26 wt% of Fe and 20.89 wt% of Ca. Although the C content was stable after alkaline roasting compared with its initial value, it decreased to about one third after the first leaching cycle. Moreover, given the high variance, it was assumed that its content remained stable at 6.11 wt% throughout the caustic leaching cycles. Finally, alkaline roasting followed by caustic leaching was confirmed to be highly effective in removing Pb and S, as both elements were undetectable already after the first leaching cycle [36, 44].

Figure 6 shows the diffraction patterns and main mineral constituents of the WS after alkaline roasting and at each caustic leaching cycle performed.

Consistent with the significant amount of Na introduced for the alkaline roasting, most of the compounds identified immediately after the treatment were based on this element or had been affected by the alkaline environment itself. Fe-bearing compounds were present as goethite ($\text{FeO}(\text{OH})$),

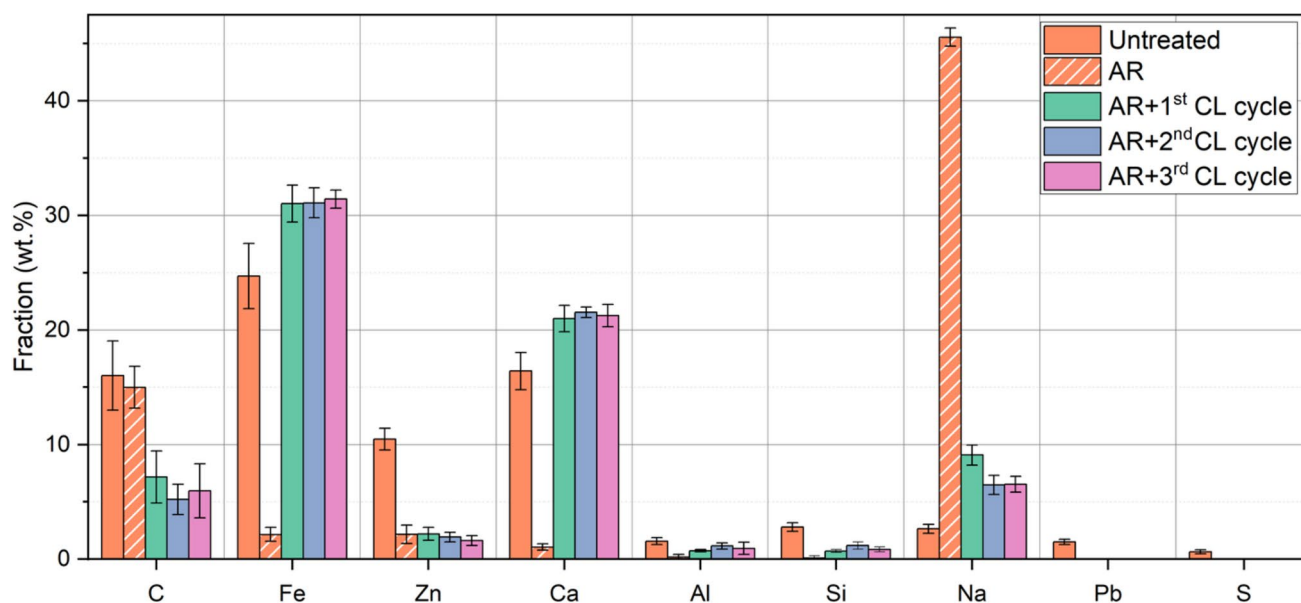


Fig. 5 Chemical composition of Waelz slag directly after alkaline roasting (AR) and at each subsequent caustic leaching (CL) cycle

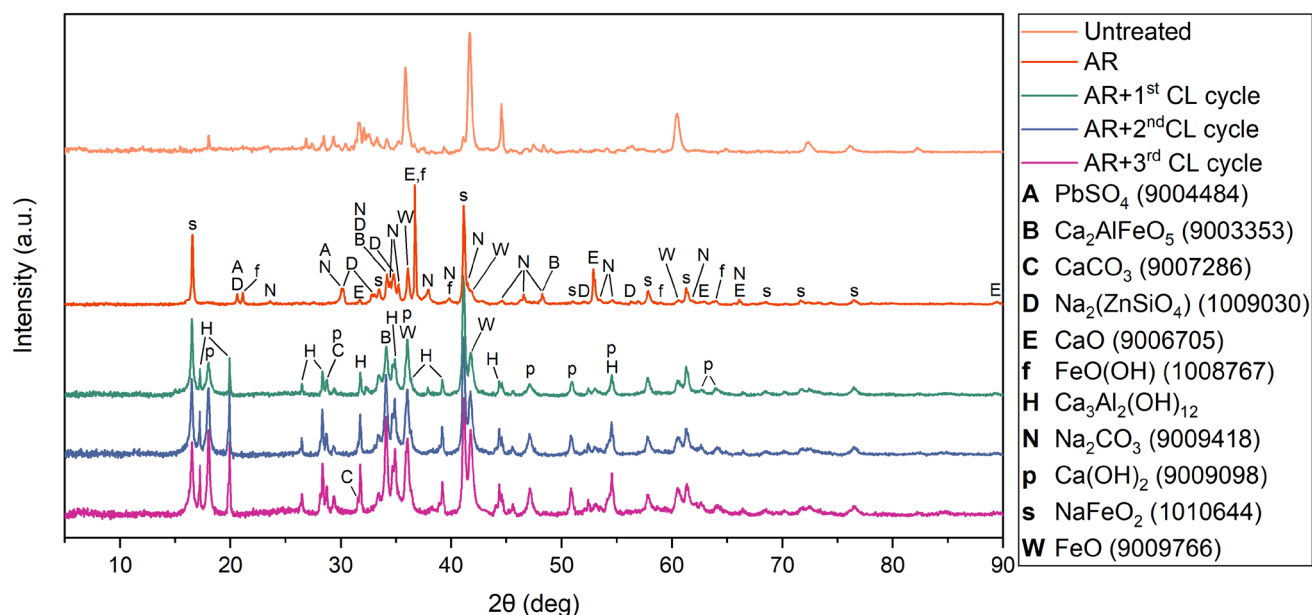
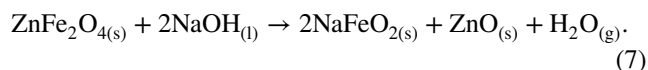


Fig. 6 Diffraction patterns of Waelz slag directly after alkaline roasting (AR) and at each subsequent caustic leaching (CL) cycle (COD card number in parenthesis, indexing of untreated Waelz slag presented in the “Waelz Slag” section)

sodium ferrite (NaFeO_2), and wüstite. On the one hand, goethite originated from the hydroxylation of either the metallic iron or wüstite. On the other, the presence of sodium ferrite was thermodynamically expected, being the most stable phase in the Zn-Fe-Na-O-H system at temperatures above 100 °C [63]. In the context of this study, sodium ferrite most likely originated from the franklinite

decomposition and its reaction with molten NaOH during the roasting (Reaction 7).

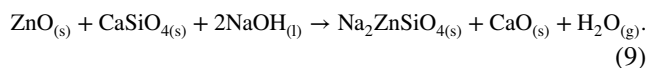


Throughout the subsequent caustic leaching cycles, the intensity of the main peak of sodium ferrite (41.1° 2θ)

decreased progressively in favor of the main diffraction peak of wüstite, though it never disappeared entirely. This reflects the previously observed steep decrease in Na concentration and constancy in Fe concentration. On the other hand, the absence of the main goethite diffraction peak ($36.7^\circ 2\theta$) after the first caustic leaching cycle makes it unclear whether sodium ferrite regenerated in parallel (Reaction 8) and then dissolved in the aqueous NaOH solution [57].



Similarly, Zn-bearing compounds originally present in the untreated WS (Fig. 1) underwent complete transformation during the alkaline roasting treatment, resulting in the formation of disodium zinc silicate ($\text{Na}_2(\text{ZnSiO}_4)$). The latter originated from the reaction of zincite and the ZnO released from the franklinite decomposition (Reaction 7) with the SiO_4^{4-} groups released from larnite lattice disruption. This formed an intermediate zinc silicate (ZnSiO_4), which after reacting with the molten NaOH led to the formation of disodium zinc silicate and lime (Reaction 9) [64, 65].



Consequently, the disodium zinc silicate dissolved in the solution during the subsequent leaching cycles, which can be associated with the decrease in Zn and Na content [66]. Still, in this regard, the appearance of natrite (Na_2CO_3) diffraction peaks ($29.7^\circ 2\theta$) after alkaline roasting and its subsequent disappearance during leaching due to its higher

solubility in aqueous solutions than other carbonates (e.g., CaCO_3), can be associated with the drop in the concentration of both Na and C [67]. After roasting, the main Ca-bearing phases, including anorthite, larnite, and mayenite, were absent, while hydrogarnet and portlandite appeared after caustic leaching, most likely originating from the decomposition and hydroxylation of the aforementioned mineral phases [68–70]. During the following leaching cycles, brownmillerite-related peaks were detected at constant intensities, and residual amounts of lime and calcite were observed as well. Finally, the temperature of the alkaline roasting treatment, together with the air environment in which it was conducted, allowed for the oxidation of galena and the subsequent formation of anglesite (PbSO_4). The latter was easily dissolved during the following caustic leaching cycle, which is in accordance with the null amount of Pb previously observed [71]. Wurtzite most likely underwent the same process, which explains the absence of S after leaching [60]. However, the specific process that occurred is unclear because no zinc sulfide or related mineral phases were observed in the diffraction pattern immediately after alkaline roasting. This could be because they were below the instrument detection limits.

Assessment of Extraction Degrees

In accordance with prior research results [39, 40, 44, 56], the use of alkaline treatments allowed for the selective removal of undesired compounds for the following carbothermic reduction, while preserving Fe-bearing phases. In this regard, Fig. 7 shows the extraction degree of Zn, Pb, S, and

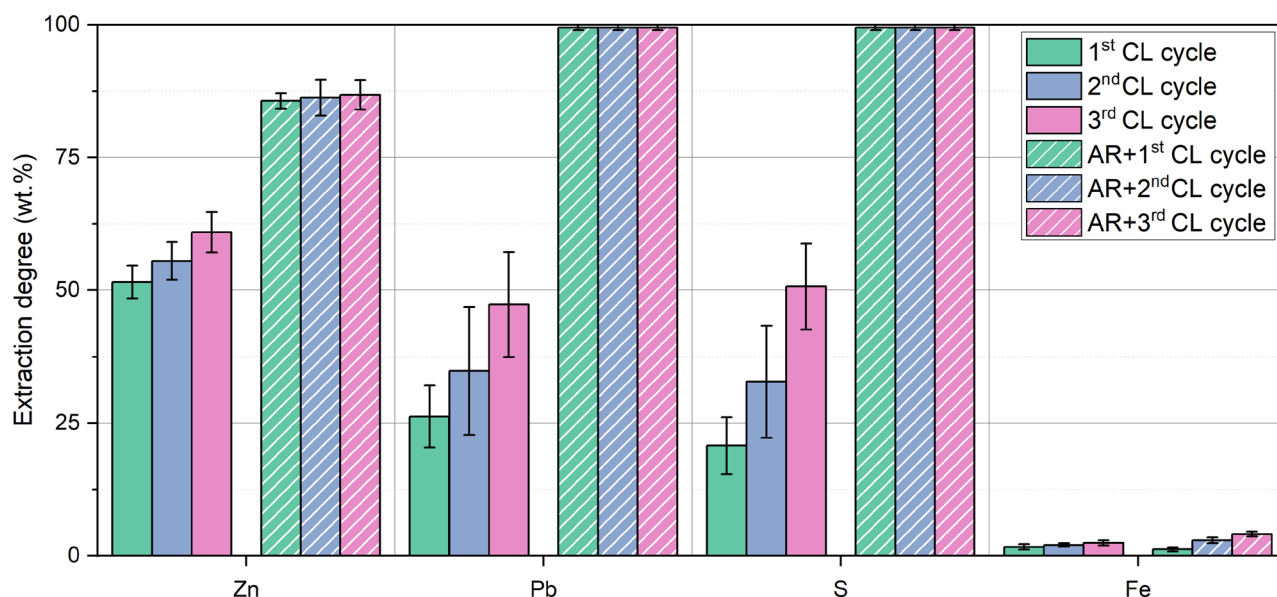


Fig. 7 Extraction degree of Zn, Pb, S, and Fe achieved by caustic leaching (CL) and alkaline roasting (AR) treatments

Fe from WS at each caustic leaching cycle either as single treatment or after the alkaline roasting.

A direct comparison of the two treatments revealed that, although caustic leaching alone achieved a remarkable Zn extraction degree of 51.53 wt% after the first cycle and 60.92 wt% by the final cycle, in the case of carrying out a preliminary alkaline roasting, this can increase the Zn extraction degree by approximately 1.5 times. Specifically, alkaline roasting was characterized by an almost constant Zn extraction degree of 86.25 wt% along the subsequent three leaching cycles performed. This difference was primarily due to the limited extraction of franklinite in the caustic leaching treatment alone, as opposed to the alkaline roasting treatment, which transformed the zinc ferrite spinel into more leachable sodium ferrite and zincite [63, 72]. The superior performance of the alkaline roasting treatment was even more pronounced in the Pb and S extraction degrees, with nearly complete removal already after the first leaching cycle for both elements and related mineral phases. Conversely, caustic leaching alone achieved relevant extraction degrees of 47.31 wt% for Pb and 50.73 wt% for S only after the third cycle. The slightly higher S extraction degree was associated with the removal of wurtzite after the last caustic leaching cycle rather than with the removal of galena, which is commonly known for its stability in caustic solutions, which also explains the partial extraction of Pb [59]. No major differences were observed in the Fe extraction degree trends. Despite a small relative increase from one leaching cycle to the next, both treatments were able to preserve the Fe in the WS as noted by the extraction degree below 5 wt% at the end

of the respective leaching cycles. For the sake of completeness, the mass yields at the first, second, and third leaching cycles of the caustic leaching treatment alone were 83.78%, 75.71%, and 68.59%, respectively, while after the alkaline roasting treatment, the mass yields at the first, second, and third leaching cycles were 82.27%, 67.20%, and 66.29 wt%, respectively. In both cases, the progressive decrease in solid residue was related to the progressive dissolution of mineral phases in the NaOH aqueous solution discussed above.

Carbothermic Reduction of Pretreated WS-Based Pellets and Product Characterization

Table 2 provides the mixture used for the WS-based pellets. Specifically, the WS samples, whether untreated or pretreated, were quartered and the homogenized fractions chemically characterized once again. This allowed us to evaluate the specific composition of the WS fraction used to manufacture the pellets and determine whether adding biochar was necessary. Indeed, both the untreated WS samples and those subjected to caustic leaching were characterized by higher C_r than the target value (0.262). Consequently, biochar was only added to the WS samples that underwent alkaline roasting followed by leaching.

Figure 8 shows the visual appearance of the WS-based pellets after heating at 1500 °C.

Regardless of the pellet-specific mixture, and in line with the preliminary results of reducing carbon composite agglomerates made from WS and biochar [17], each pellet exhibited good sintering properties and strong mechanical

Table 2 Waelz slag and biochar mixture characteristics

Pellet labeling	Untreated	Caustic leaching			Alkaline roasting followed by leaching		
	Un-WS	L1-WS	L2-WS	L3-WS	R1-WS	R2-WS	R3-WS
Leaching cycle	–	1st	2nd	3rd	1st	2nd	3rd
WS _{mix} , wt%	100	100	100	100	97.16	92.34	91.58
C _{WS} , wt%	15.68	14.77	15.14	14.71	7.81	5.02	5.63
C _{BC} , wt%	0.00	0.00	0.00	0.00	2.84	7.66	8.42
C _r , g g ⁻¹	0.361	0.346	0.324	0.290	0.262	0.262	0.262

WS_{mix}: relative amount of Waelz slag in the mixture, C_{WS}: specific carbon content already contained in the Waelz slag, C_{BC}: carbon amount added by means of biochar, C_r C/(Fe₂O₃+ZnO) ratio of the mixture

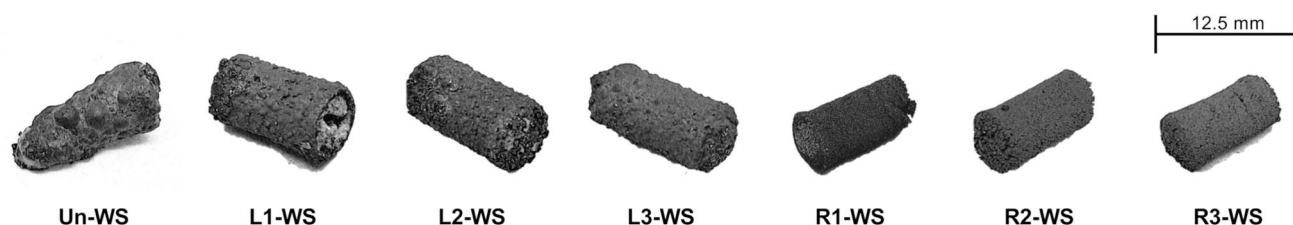


Fig. 8 Visual appearance of the Waelz slag-based pellets at 1500 °C

stability with low to null friability. Furthermore, consistent with the observations of Grudinsky et al. [16], no distinct metal–slag phase separation was observed, although the smelting process occurred. This was most likely due to the high viscosity of the slag itself, which hindered the separation [73]. Furthermore, the rough surface and occasional external cracks were related to the formation and expulsion of carbon monoxide or volatile compounds which occur during the carbothermic reduction process [e.g., $\text{FeO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Fe}_{(s)} + \text{CO}_{(g)}$, $\text{ZnO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Zn}_{(g)} + \text{CO}_{(g)}$] [74].

Figure 9 shows a summary of the DR and mass loss achieved by each WS-based pellet after heating at 1500 °C.

The lowest DR was obtained by the Un-WS (65.44%) sample, which, when expressed as mass loss (28.93 wt%), supports the consistency in reduction behavior of untreated WS [17]. Applying caustic leaching cycles either directly or after alkaline roasting significantly increased the DR values. The caustic-leached WS-based pellets showed an improvement in DR up to 27% relative to the Un-WS sample (L1-WS: 76.06%, L2-WS: 82.71%, and L3-WS: 83.15%). This increase in reduction capacity was primarily due to the lower content of non-reducible oxides in the chemistry of the caustic-leached WS. For example, the presence of SiO_2 - or Al_2O_3 -based compounds can negatively affect the reducibility of iron oxide-bearing matrices: after dissociation, the SiO_2 and Al_2O_3 can react with iron oxides to form hard-to-reduce compact silicates (e.g., $2\text{FeO}_{(s)} + \text{SiO}_{2(s)} \rightarrow \text{Fe}_2\text{SiO}_{4(s)}$) [75] and aluminates (e.g., $\text{FeO}_{(s)} + \text{Al}_2\text{O}_{3(s)} \rightarrow \text{FeAl}_2\text{O}_{4(s)}$) [76]. Conversely, an excess of free CaO has a positive effect by binding SiO_2 and Al_2O_3 into calcium silicates and

aluminates [77]. In light of this, and considering the evolution of WS chemistry during caustic leaching, it can be confirmed that the treatment enhanced the overall reducibility of WS by decreasing the amount of undesired compounds, which in turn increased the likelihood of contact points between carbon and reducible Fe- and Zn-based oxides [78].

Similarly, the alkaline-roasted WS-based pellets exhibited a 43% increase in DR compared with the Un-WS sample (R1-WS: 92.03%, R2-WS: 94.79%, and R3-WS: 93.74%), as well as significantly greater mass losses than those observed for the Un-WS and caustic-leached WS-based pellets, with values ranging from 39.32 to 41.23 wt%. These increases were associated with the enhanced removal of inert elements during the WS pretreatment by alkaline roasting itself and the volatilization of Na from sodium ferrite during the carbothermic reduction process. Specifically, the most probable reaction sequence that occurred was as follows: (i) carbonation of the sodium ferrite up to 800 °C ($2\text{NaFeO}_{2(s)} + \text{CO}_{2(g)} \rightarrow \text{Na}_2\text{CO}_{3(s)} + \text{Fe}_2\text{O}_{3(s)}$) [79], (ii) melting and carbothermic reduction of the newly formed sodium carbonate above 850 °C ($\text{Na}_2\text{CO}_{3(l)} + 2\text{C}_{(s)} \rightarrow 2\text{Na}_{(g)} + 3\text{CO}_{(g)}$) [80], and (iii) parallel carbothermic reduction of hematite. In this regard, the second reaction has a key role in explaining the observed DR and mass loss increases, since the presence of sodium carbonate is deemed to provide an indirect thermodynamic driving force during the carbothermic reduction of iron oxides [81]. For completeness, from a literature comparison standpoint, similar increases were observed when sodium carbonate or other salts were used as catalysts to enhance iron recovery from industrial residues such as red mud [82–84].

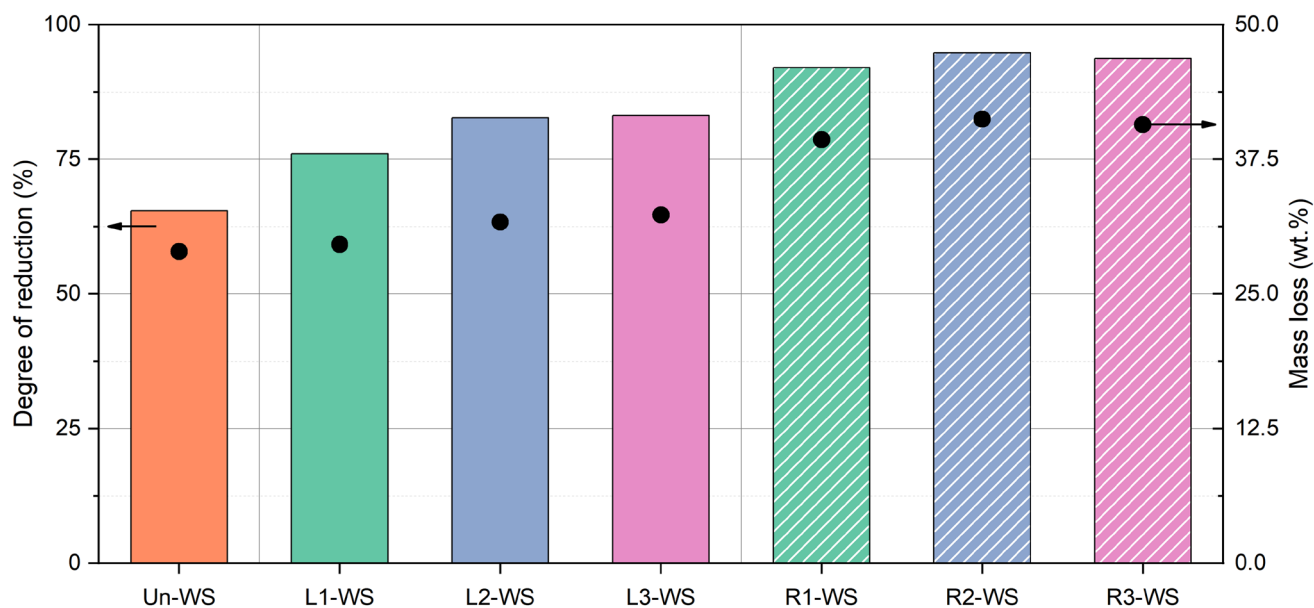


Fig. 9 Degree of reduction (bars) and mass loss (dots) of the Waelz slag-based pellets at 1500 °C

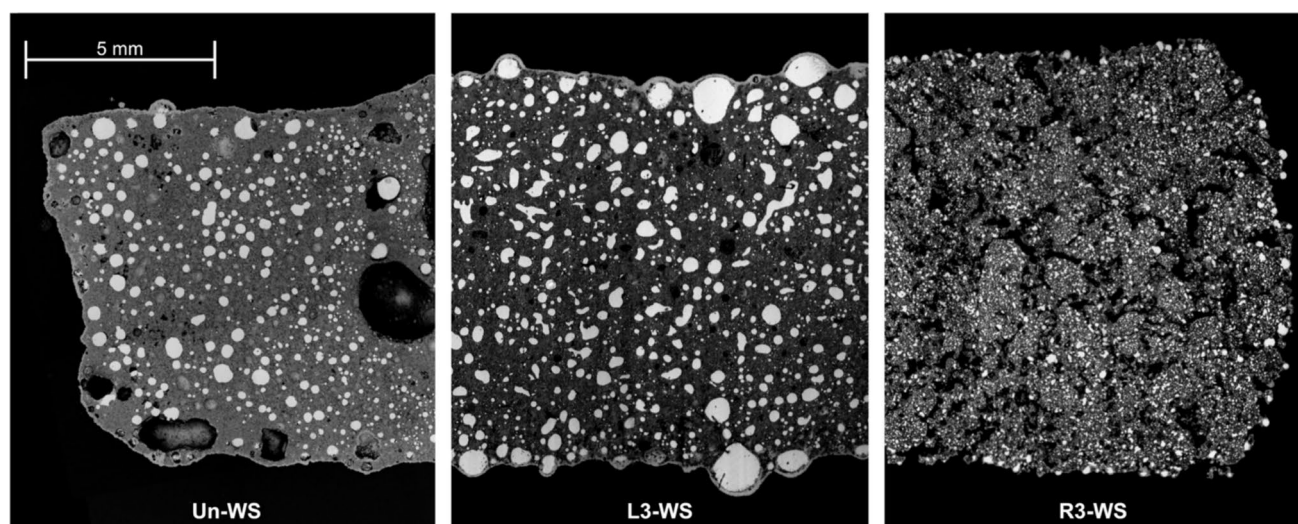


Fig. 10 SEM reconstruction of the Waelz slag-based pellet cross section at 1500 °C (white/light gray: metallic iron, gray: unreduced oxides, dark/black: porosities)

To evaluate any major differences in the microstructure and internal morphology of the WS-based pellets after heating at 1500 °C, the cross sections were reconstructed by SEM in backscattered electron (BSE) configuration. Figure 10 shows the SEM-BSE reconstruction comparison of the most relevant reduced WS-based pellets: un-WS, L3-WS, and R3-WS.

The Un-WS sample exhibited fewer and larger porosities than the two pretreated WS-based pellets, where instead the porosities were more evenly dispersed throughout the matrix. In this regard, it must be emphasized that the R3-WS sample was characterized by open and tortuous porosities, which was once again connected to the volatilization of Na-based compounds from sodium ferrite discussed above. Indeed, the release of Na as gaseous phase from molten sodium carbonate is considerably fast and, thanks to the agglomeration process, it occurs homogeneously throughout the pellet [81]. This, along with the increased amount of CO released due to the enhanced DR observed in the alkaline-roasted WS-based pellets, surely contributed to the morphological differences observed in the samples. Still, in this regard, the alkaline roasting treatment also resulted in the presence of only fine metallic iron particles (average diameter: 25 µm), which was not observed in the Un-WS and L3-WS samples, as they were characterized by the presence of both coarse and fine particles (average diameter: 150 µm). This difference can be attributed to a higher removal of non-ferrous compounds achieved with the alkaline roasting treatment, which shifted the reduction mechanism towards nucleation rather than coalescence.

To evaluate the mineralogy of the WS-based pellets after heating at 1500 °C, as well as the elemental dispersion within the phases, SEM-BEX imaging of the reduced samples was performed. Figure 11 shows the overlaid and elemental

SEM-BEX image of the most representative samples. For the detailed analysis, including the position and results of EDS spectra as well as the respective phase identification, please refer to online supplementary material Fig. S1 and Table S1.

Overall, the mineralogy of the Un-WS pellet was consistent with that of a previous study, thereby confirming the consistency of the WS carbothermic reduction process [17]. Apart from the presence of metallic iron, which was also observed in pretreated WS-based pellets and depicted by the light blue areas, the predominant phase constituting the slag matrix of the Un-WS pellet was jasmundite ($\text{Ca}_{11}(\text{SiO}_4)_4\text{O}_2\text{S}$). On the contrary, larnite (Ca_2SiO_4) was observed as predominant phase constituting the slag matrix in both pretreated WS-based pellets. Both jasmundite and larnite are indicated by the reddish areas. As secondary S-bearing phase, oldhamite (CaS) was found to be either concentrated around metallic iron particles or, less frequently, randomly distributed within the slag matrix, as indicated by the orange areas. In this regard, the superior effectiveness of alkaline roasting followed by leaching was evident in the presence of small, isolated spots of oldhamite in the R3-WS pellet, as opposed to the clusters observed in the Un-WS and L3-WS pellets. The reduction in S content from the untreated to the pretreated WS also explains the substitution of jasmundite with larnite, as it shifted the phase equilibrium towards oldhamite and larnite itself [85]. In any case, the occurrence of oldhamite phase, along with jasmundite for the Un-WS pellet, was highly beneficial for the overall process, as they protected the recovered iron particles from sulfidation. The absence of zincite or Zn-based phases suggests that they were completely reduced to metallic zinc, which subsequently evaporated due to the temperature of the carbothermic reduction process. This was confirmed by the accretion of zinc oxide crystals evenly distributed across the

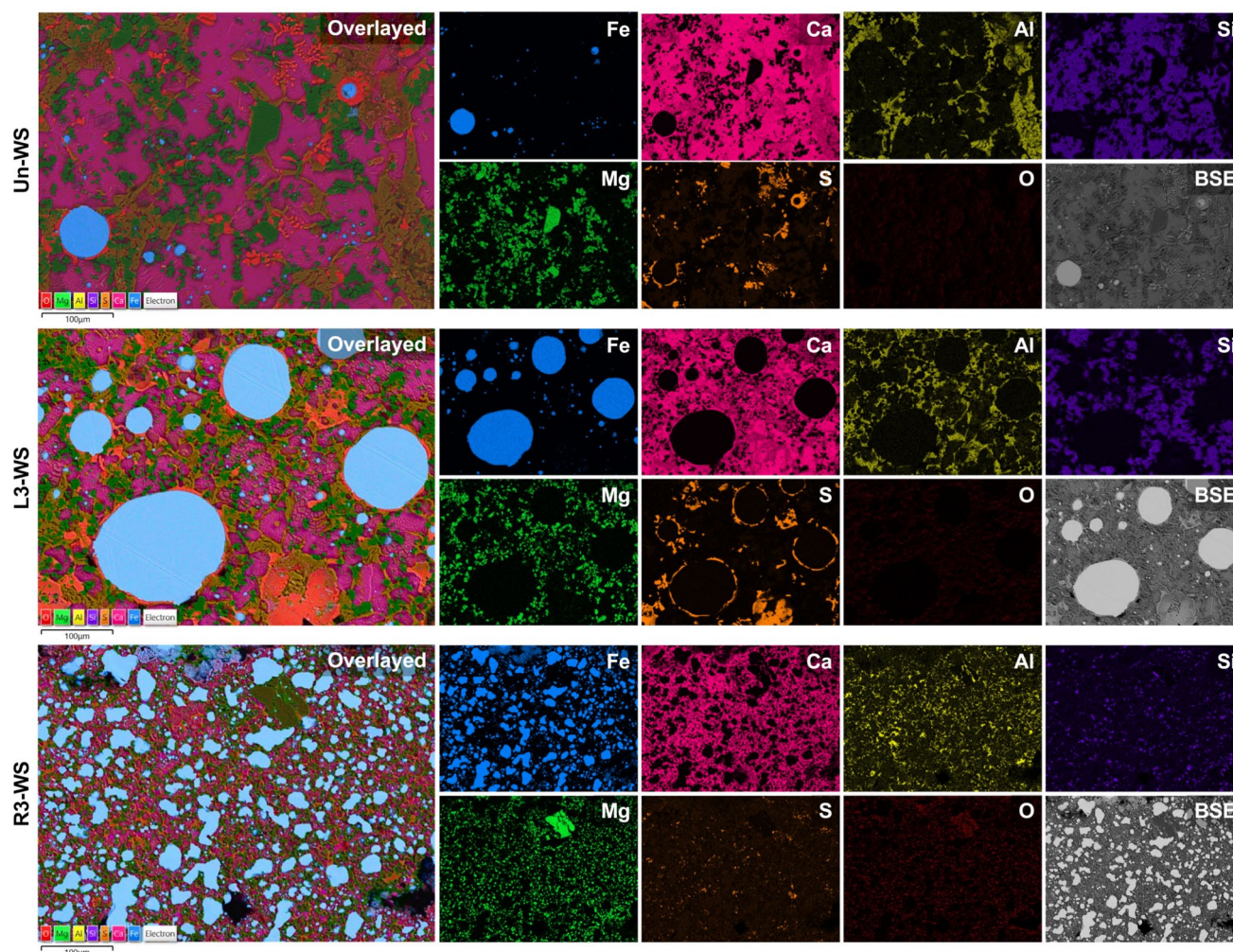


Fig. 11 SEM-BEX imaging of the Waelz slag-based pellets at 1500 °C

crucible used for the treatment and especially on its lid (Fig. S2 and Table S2). In light of this, it is possible to argue that while the Zn contained in the WS could be mostly recovered by the traditional hydrometallurgical approach, the residual Zn present in the pretreated WS could be recovered by condensing it from the vapors generated during the pyrometallurgical treatment, similarly to what was performed in the Waelz process itself. On the one hand, consistent with the results reported by Su et al. [81] from sodium carbonate-assisted reduction of iron oxides, no Na-bearing phases were observed in the slag phase of the R3-WS pellet, nor was any significant amount of Na found dissolved in the metallic iron or slag phase itself (max amount 0.10 wt%, Table S1). On the other hand, traces of Na were observed in the chemistry of the zinc oxide crystal deposited on the lid (max amount 10 wt%, Table S2). This indicates that Na and Zn volatilized together during the process and conclusively confirms the hypothesis regarding sodium ferrite decomposition. Therefore, it is important to emphasize that reducing large quantities of alkaline-roasted

WS in traditional metallurgical furnaces would require careful evaluation and further investigation, specifically regarding the exact chemical composition and quantity of vapors produced. Indeed, vapors containing high concentrations of Na and Zn are known to pose a technical risk to the stability of the acid refractory linings (e.g., SiO_2 - and Al_2O_3 -based) [21, 86]. Consequently, basic refractory linings (e.g., MgO- and MgO-CaO-based), which are commonly used in electric arc furnaces and Waelz kilns, are preferred. Furthermore, as previously mentioned, these vapors can be captured and condensed in secondary chambers, similarly to what is already done in electric arc furnaces and the Waelz process itself [87]. This would allow for the recovery of Na and Zn via additional extractive processes of the condensed dust [88]. For completeness, the presence of mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and periclase (MgO) was also observed in each reduced pellet and is represented by the green-yellow and dark green areas, respectively.

As a final comparison to highlight the effects of the WS pretreatment on its reduction behavior, the degree of

metallization and the areal fraction of metallic iron were evaluated. Figure 12 shows a summary of the results.

No significant differences were observed in the metallization degree achieved by the pellets after heating at 1500 °C. Specifically, the metallization degree of the untreated, caustic-leached, and alkaline-roasted WS-based pellets increased only slightly, from 93.30% to 95.35% and 97.13%, respectively. As Mombelli et al. [89] also reported, this behavior was primarily attributed to optimal C_r , which maximized the reduction reaction, rather than to the WS pretreatments. At the same time, both caustic leaching and alkaline roasting treatments enriched the metallic iron fraction of the reduced pellets. The caustic-leached WS-based pellets exhibited a twofold increase in areal fraction relative to the Un-WS sample (19.78–23.34% vs. 9.52%). Meanwhile, the metallic iron areal fraction of the alkaline-roasted WS-based pellets increased even further (25.92–28.80%) due to the higher extraction ability of the treatment, thereby highlighting the beneficial role of applying multiple caustic leaching cycles, either directly or after alkaline roasting, in improving the reduction process overall efficiency, particularly with regard to the amount of iron that can be recovered and concentrated in the reduced pellets.

Conclusions

This study investigated the carbothermic reduction of Waelz slag (one-step treatment) and the enhancement in the properties of reduction products through pretreatments, namely caustic leaching (two-step treatment) and alkaline roasting followed by caustic leaching (three-step treatment). The

chemistry and mineralogy of the WS were monitored during the pretreatment cycles and the resulting solid residue compacted into pellets. Biochar was consequently added to the WS whenever needed to ensure the target $C/(ZnO+Fe_2O_3)$ ratio of 0.262 g g⁻¹ in the pellet mixture. The untreated and pretreated WS-based pellets were then subjected to carbothermic reduction at 1500 °C in an inert atmosphere. Key parameters of the reduction products including the degree of reduction and metallization, the metallic iron areal fraction, and the mineralogical composition of the slag phase were compared to highlight the effect of the pretreatments on the overall reduction process.

The key contributions of this investigation can be summarized as follows:

- Both pretreatments effectively removed the major undesired elements contained in WS (e.g., Zn, Pb, S), while limiting the Fe losses to values lower than 5 wt%. Alkaline roasting followed by caustic leaching was markedly more effective than caustic leaching alone at dissolving the Zn-, Pb-, and S-bearing phases, extracting 85 wt% of the Zn, 100 wt% of the Pb, and 100 wt% of the S already after one leaching cycle. Conversely, even after three cycles, caustic leaching alone could not extract more than 60 wt% of the Zn and Pb or more than 75 wt% of the S due to the low solubility of zinc ferrite and galena in aqueous NaOH solutions at low temperatures.
- While each reduced pellet achieved a metallization degree greater than 90%, the pretreated WS-based pellets yielded substantially higher amounts of metallic

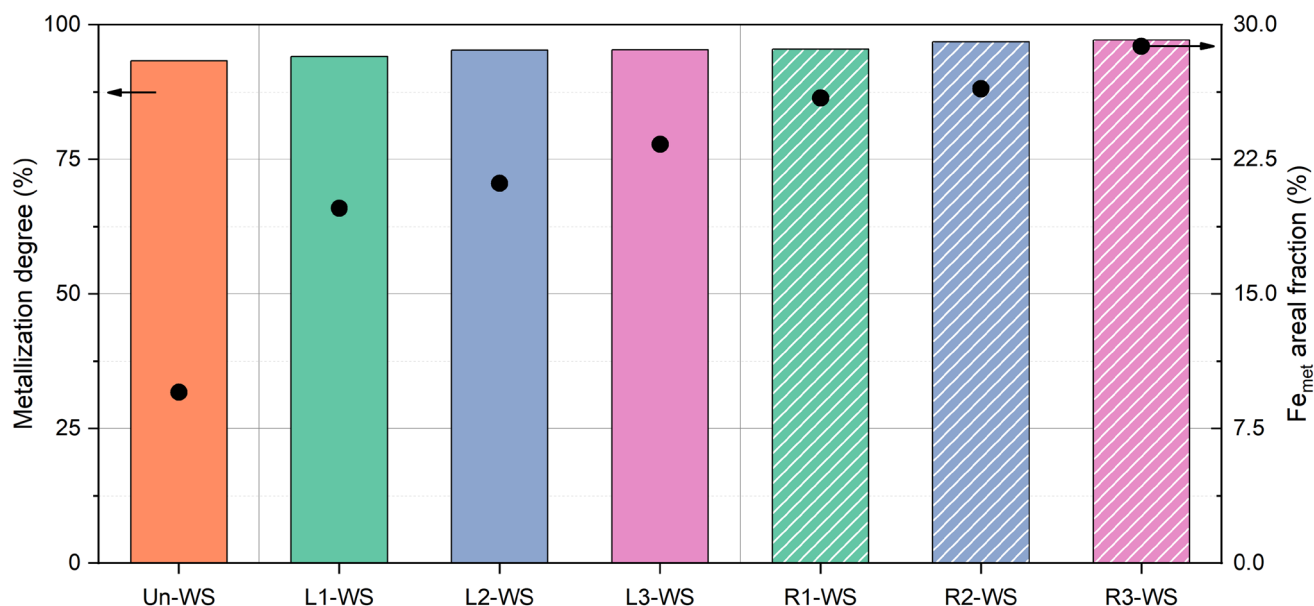


Fig. 12 Metallization degree (bars) and areal fraction of metallic iron (dots) of the Waelz slag-based pellets at 1500 °C

iron than those based on the untreated WS due to the removal of slag-forming elements (e.g., Al and Si) that occurred during the treatments themselves. The maximum areal fraction values of metallic iron were 23.34% and 28.80% for the caustic-leached and alkaline-roasted WS-based pellets, respectively.

- Despite the decrease in Al and Si content at the end of both treatments, the slag generated during the carbothermic reduction process was composed of calcium aluminates and calcium silicates. Due to their high viscosity and abundance, these compounds hindered proper slag–metal separation and full sintering of the metallic iron particles. Therefore, secondary separation treatments are still necessary (e.g., mechanical, gravity or magnetic) for extracting metallic iron particles.
- The significant presence of Ca in the WS after caustic leaching (> 25 wt%) enabled the formation of calcium sulfides, which protected the recovered iron from sulfidation. This problem was less significant in alkaline-roasted WS-based pellets, as most of the S was already removed during the treatment itself.

In conclusion, although there is still room for ad hoc gradient optimization of the pretreatment parameters, the best-performing route achieved in this study for the secondary iron recovery from WS is the one comprising its pretreatment via alkaline roasting, followed by one caustic leaching cycle and subsequent carbothermic reduction of the solid residue. This would reduce the amount of NaOH solution required without affecting the metallurgical quality of the pretreated WS reduction products. Nevertheless, assessments of the process cost and impact, as well as of the extraction yields and purity of the elements dissolved in the caustic solution and its regeneration, are still necessary to provide a comprehensive overview of the waste-to-resource route proposed.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s40831-026-01658-x>.

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Data Availability All data generated or analyzed during this study are included in this published article and its electronic supplementary material.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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