

Article

In-Line Co-Processing of Stainless Steel Pickling Sludge Using Argon Oxygen Decarburization Slag Bath: Behavior and Mechanism

Zheng Zhao ¹, Yanling Zhang ^{1,*} , Fang Yuan ² and Tuo Wu ²

¹ State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China; suc_zheng@163.com

² Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

* Correspondence: ustbzly1108@163.com

Abstract: Stainless steel pickling sludge (SSPS) is classified as hazardous solid waste, while Argon Oxygen Decarburization (AOD) slag is challenging to utilize due to the leaching toxicity of Cr. This study introduces a novel in-line co-processing technique for AOD slag and SSPS, parallel to the steelmaking process, aimed at metal recovery, sulfur fixation, and slag detoxification: pre-treatment-AOD slag bath approach. The transformations and migrations of sulfur and metal elements, such as Fe and Cr, in the co-processed mixture were analyzed using thermogravimetric–mass spectrometry (TG-MS) and scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS). The results indicated that sulfur in SSPS could be transformed from CaSO_4 to CaS under controlled low pre-reduction temperatures (below 800 °C), facilitating its stabilization in the slag and achieving a sulfur fixation rate of over 99%. Metal elements, including iron and chromium, first formed a small portion of spinel (FeCr_2O_4) during the pre-reduction phase, then Fe-Cr or Fe-Cr-C-based alloy particles were rapidly formed at high temperatures and in the presence of reducers in the slag bath (1550 °C), aggregating and growing spontaneously, ultimately achieving a metal recovery rate of over 95%. Furthermore, a reaction model for SSPS briquettes in the AOD slag bath was established to further reveal the mechanisms of sulfur, iron, and chromium stabilization and migration, thereby providing a basis for the harmless disposal of both materials. The product alloys are expected to be used as additives in stainless steel production, while the harmless slag could be safely utilized in the preparation of cementitious auxiliary materials.

Keywords: stainless steel pickling sludge; sulfur fixation; AOD slag bath; in-line co-processing; metal extraction



Citation: Zhao, Z.; Zhang, Y.; Yuan, F.; Wu, T. In-Line Co-Processing of Stainless Steel Pickling Sludge Using Argon Oxygen Decarburization Slag Bath: Behavior and Mechanism. *Sustainability* **2024**, *16*, 1895. <https://doi.org/10.3390/su16051895>

Academic Editor: Edoardo Bocci

Received: 24 December 2023

Revised: 20 February 2024

Accepted: 21 February 2024

Published: 26 February 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

China's burgeoning stainless steel industry has led to the substantial generation of stainless steel pickling sludge (SSPS), estimated at 750,000 tons annually, or 2.5 wt%~5.0 wt% of the nation's stainless steel output [1]. Predominantly, domestic manufacturers use H_2SO_4 or hybrid acids for surface treatment, producing high-sulfur sludge through lime neutralization, which contains S (5 wt%~9 wt%), Cr (3 wt%~5 wt%), and Fe (15 wt%~22 wt%) [2,3]. Classified as hazardous waste (HW17) by the "National Dangerous Waste Catalog (2016)" for its toxicity and corrosiveness [4], SSPS management is now tightly regulated under the "Control Law of Solid Waste Environmental Pollution" [5,6]. Therefore, managing SSPS within the plant and throughout the production line is of paramount importance and demands immediate focus.

However, in the disposal process of SSPS, the method most stainless steel companies adopt is landfilling or stacking. This undoubtedly increases the risk of heavy metal leaching and also leads to the wastage of land resources [1–3]. The best way to dispose of such hazardous solid waste as sludge is to make it harmless. The existing research on sound disposal mainly focuses on the separation and recovery of heavy metal Cr and physico-chemical solidification treatment. High-temperature carbothermal reduction process is

widely considered as a complete detoxification way to treat stainless steel pickling sludge. Li et al. [7] investigated the thermodynamics of sludge with carbon desulfurization to avoid S into the metal to recover valuable metals. Wang et al. [8] used sludge as raw material for carbothermal reduction to produce low-sulfur low-carbon Fe-Cr-Ni alloy, and the process also removed the S element first. Wu et al. [9] studied the effect of temperature, C/O ratio, and reduction time of low-temperature direct reduction–magnetic separation on the reduction of Cr in stainless steel sludge. Liu et al. [10] proposed a semi-molten method for sludge reduction recovery after studying the growth and migration trend of low-melting-point Fe-Cr-C droplets. The described reductive separation and recovery methodology is distinguished by two principal characteristics: firstly, the sulfur element is removed to avoid its incorporation into the metal. Secondly, a reduction technique is utilized to prepare a low-melting-point alloy, enabling metal recovery. However, this disposal strategy may result in the release of sulfur-rich gases, representing a grave environmental hazard. Furthermore, should the alloy be synthesized via direct reduction, it is likely to yield a metal product with an excessively high sulfur concentration for practical application. Zhao et al. [11] and Yang et al. [12] prepared glass ceramics with pickling sludge as a doping material and then solidified Cr. Pan et al. [13] and others used sludge and gypsum to prepare glass ceramics, first removing the sulfur in the mixture and then preparing glass ceramics. In the context of solidification and stabilization treatment, while a heightened level of safety performance is achieved, this approach results in the underutilization of Cr resources, coupled with the detrimental environmental impact due to the release of sulfur. Moreover, the intricacy of the treatment process results in suboptimal efficiency when tasked with managing sludge volumes of significant scale. Different from SSPS, the Cr concentration in argon oxygen decarburization (AOD) slag is relatively low, exempting it from classification as hazardous solid waste.

Presently, the utilization of AOD slag is notably limited [14–16]. Post-cooling, the slag exhibits high γ -C₂S content, leading to volume instability. Additionally, the slag contains Cr concentrations ranging from 0.1 to 3 wt%, presenting significant leaching risks of the heavy metal Cr(VI) [17,18]. These factors substantially limit the direct application of AOD slag in supplementary cementitious materials. Certain studies [19–21] have demonstrated the carbonation and solidification treatment of AOD slag, converting γ -C₂S into calcium carbonate, thereby reducing expansion, enhancing cementitious properties, and lowering leaching toxicity. This offers significant theoretical support for the application of AOD slag as a supplementary cementitious material. While carbonation is a feasible approach, an unresolved issue identified in these studies is the presence of heavy metal Cr. Direct immobilization of Cr in cementitious materials not only wastes metal resources but also poses potential environmental hazards. Furthermore, SSPS and AOD slag are two waste products simultaneously produced in stainless steel plants. Their joint disposal process may hold greater research and application potential, an aspect yet unreported.

This study introduces a novel process utilizing high-temperature molten AOD slag baths for treating carbon-containing pickling sludge briquettes (C-SSPS). The method aims to separate and recover valuable metals such as Cr and Fe from SSPS and AOD slag, while also stabilizing sulfur in the slag to reduce SO₂ emissions. The process further achieves detoxification of the mixed AOD slag and SSPS, enabling the use of Cr-free AOD slag in cementitious materials. Additionally, the study delves into the reduction mechanisms within the slag bath treatment, providing significant insights for industrial production.

2. Experimental

2.1. Technical Route

As shown in Graphical abstract:

Step 1: Preparation and Pre-reduction of Carbon-Containing SSPS (C-SSPS Briquettes)

- (a) Stainless steel pickling sludge (SSPS) is initially mixed with a reducing agent and extruded into briquettes with diameters ranging from 15–20 mm.

- (b) The briquettes are calcined at temperatures up to 800 °C to achieve adequate strength, with each briquette exhibiting a compressive strength exceeding 1800 N. The density of the briquette is 1.45 g/cm³.

Step 2: In-line Processing of C-SSPS in Molten AOD Slag Bath for Metal Reduction Recovery and Slag Separation

- (a) The calcined briquettes are pre-loaded into a slag pot.
- (b) The slag discharged from the AOD furnace creates a high-temperature mixed slag flushing pool within the slag bag.
- (c) At elevated temperatures, the sludge briquettes cooperatively reduce valuable metals present in the chromium-containing slag.
- (d) The cooled slag is crushed, and metal particles are recovered via magnetic separation for use in the smelting of stainless steel products.
- (e) The chromium-free residue can be recycled/reused as part of building materials such as cement and concrete.

2.2. Materials

SSPS was taken from Taiyuan Stainless Steel Co., Ltd., Taiyuan, China. The moisture content of raw SSPS is close to 55 wt%. SSPS was first dried at 80 °C for 4 h to remove most of the free water and then ground to less than 150 µm. The chemical composition of SSPS is shown in Table 1. The mass fraction of sulfur is 13.98 wt%, and assuming that sulfur exists solely in the form of CaSO₄, the corresponding mass fraction of CaSO₄ would be 59.4 wt%.

Table 1. Chemical composition of pickling sludge (SSPS)/wt%.

Raw Material	F	Na	S	Cr	Ca	Fe	Ni	Si	Al	O
SSPS	0.22	0.74	13.98	2.88	18.6	21	0.1	1.05	0.29	40.4

The AOD slag was sourced from Jinhui Stainless Steel Co., Ltd., Henan, China, with its composition as shown in Table 2. The AOD slag was first dried at 80 °C to a constant weight, and then ground to a size less than 2 mm for future use.

Table 2. Chemical composition of AOD slag/wt%.

Raw Material	CaO	SiO ₂	Al ₂ O ₃	MgO	Cr ₂ O ₃	MnO	CaF ₂	Fe ₂ O ₃	S
AOD slag	50.6	31.1	1.2	5.9	0.5	3.7	5.4	0.21	0.19

2.3. Pre-Reduction and Slag Bath Reduction

SSPS with a moisture content of about 10 wt% was first mixed with the reducing agent graphite, and then the mixture was put into a steel mold with an inner diameter of 20 mm, and the briquette was prepared at a pressure of 30 MPa for 2 min. The prereduction was carried out in a horizontal tube furnace (Figure 1a), and the reduction temperature was controlled by a type B thermocouple. The sludge briquettes in the corundum crucible are pushed into the furnace tube, and high-purity Ar gas with a flow rate of 400 mL/min is introduced to exhaust the air. After holding at the target temperature of 800 °C for 1 h, the balls were cooled to room temperature.

During the slag bath reduction process, 150 g of AOD slag were put into a MgO crucible, fed into the furnace, and started to heat up (Figure 1b). Until the temperature reached the target temperature, the pre-reduced calcined material with 4.5 wt% mass of AOD slag was put into the MgO crucible. Throughout the entire process, high-purity Argon gas was used to evacuate the air, and the temperature of the slag bath was maintained at 1550 for 20 min. The furnace tube is in a sealed state, and the exhaust gas can be collected through the gas collection bag at the furnace mouth. After the reduction of the slag bath, the crucible was taken out for water quenching.

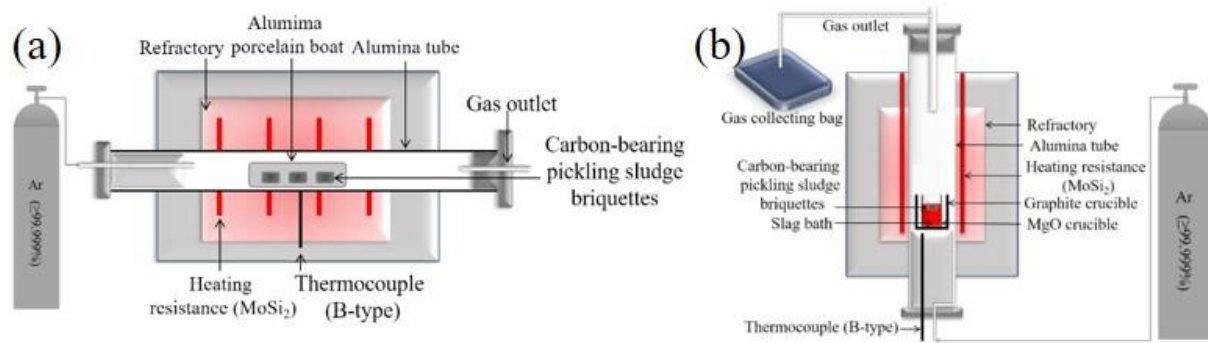


Figure 1. (a) Pre-reduction and (b) slag bath reduction experimental setup.

2.4. Characterization and Evaluation

2.4.1. Thermodynamic Analysis

The standard free energy of carbothermal reaction and mineral phase formation in the above two processes was calculated by using the Reaction module of thermodynamic software FactSage8.0 [22]. The FToxid, FactPS, and FTmisc databases were used. Regardless of possible kinetic effects, the general likelihood of a chemical reaction can be predicted based on the value of ΔG , with the most negative ΔG values indicating more favorable reactions.

2.4.2. Composition and Phase Analysis

The chemical composition of SSPS and AOD slag was analyzed by different methods, including X-ray fluorescence spectrometer (XRF, Shimadzu XRF-1800, Kyoto, Japan), high-frequency infrared carbon-sulfur analyzer (CS, HORIBA EMIA-920V2, Kyoto, Japan). XRD patterns were identified by a diffractometer (XRD, SmartLab Rigaku, Akishima, Japan) using a Cu target at a scanning speed of $10^\circ/\text{min}$. Micrographs of the samples were determined by a scanning electron microscope (SEM-EDS, Tescan MLA-250, Brno, Czech Republic) equipped with an X-ray spectrometer.

2.4.3. TG-MS Analysis

The reduction of SSPS and the release of gaseous products were performed in a thermogravimetric analyzer (TGA, Netzsch STA 449C, Selb, Germany) equipped with an in-line mass spectrometer (MS, Horiba GSD-320, Kyoto, Japan). The temperature regime of TG is a heating rate of $20^\circ\text{C}/\text{min}$, the temperature is raised to 850°C , and after 120 min of heat preservation, it is naturally cooled to room temperature. The components of the collected waste gas were analyzed by gas mass spectrometry, and the steady flow rate of the carrier N_2 gas was $40\text{ mL}/\text{min}$. It should be noted that the molar mass of N_2 is the same as that of CO , and the two overlap in the mass spectrum, but they can be distinguished according to the reaction conditions.

2.4.4. Slag Bath Reduction Analysis

Within the AOD slag and SPSS mixture, the calculations for the sulfur fixation rate, the recovery rate of Fe-Cr-based alloys, and the sulfur distribution ratios across slag, metal, and gas phases were as follows [8]:

$$F = \frac{M_3 * a_3 + M_4 * a_4}{M_1 * a_1 + M_2 * a_2} \times 100\text{pct} \quad (1)$$

$$R = \frac{M_4 * b_3}{M_1 * b_1 + M_2 * b_2} \times 100\text{pct} \quad (2)$$

$$S_M = \frac{M_4 * a_4}{M_1 * a_1 + M_2 * a_2} \times 100\text{pct} \quad (3)$$

$$S_S = \frac{M_3 * a_3}{M_1 * a_1 + M_2 * a_2} \times 100\text{pct} \quad (4)$$

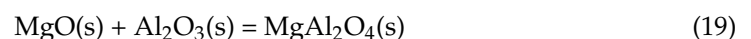
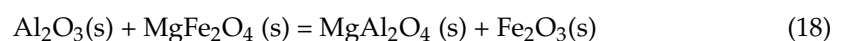
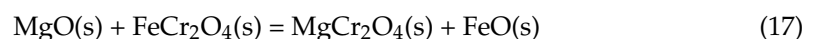
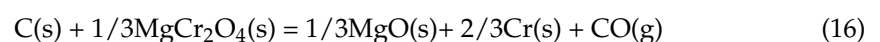
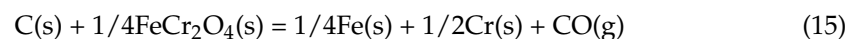
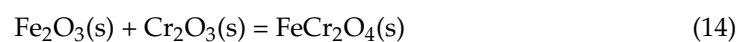
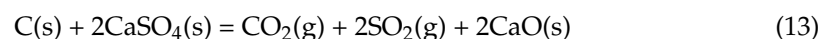
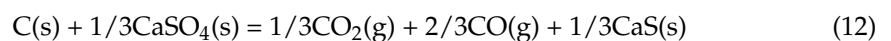
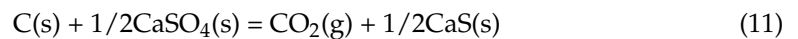
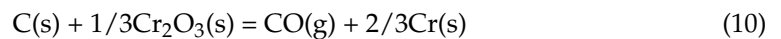
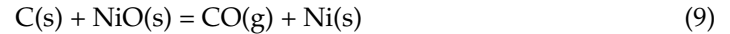
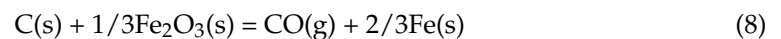
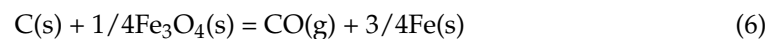
$$S_G = 100pct - S_S - S_M \quad (5)$$

In Equations (1)–(5), F represents the sulfur fixation rate, while R stands for the metal recovery rate. S_M , S_S , and S_G , respectively, denote the distribution ratio of sulfur in metal, slag, and gaseous phases. M_1 is the mass of the briquettes before calcination, M_2 is the mass of the slag before the reaction, M_3 is the mass of the slag after the reaction, and M_4 is the mass of the alloy after the reaction. a_1 is the mass fraction of sulfur in the briquettes before calcination, a_2 is the mass fraction of sulfur in the slag before the reaction, a_3 is the mass fraction of sulfur in the slag after the reaction, and a_4 is the mass fraction of sulfur in the alloy. b_1 represents the sum of the mass fractions of metals in the briquettes before the reaction, b_2 represents the sum of the mass fractions of metals in the slag before the reaction, and b_3 represents the sum of the mass fractions of metals in the alloy.

3. Results and Discussion

A. Thermodynamic model of pre-reduction and slag-bath smelting

The slag-bath co-processing process proposed and studied in this paper involves two processes: (1) low-temperature pre-reduction of C-SSPS and (2) subsequent high-temperature slag-bath smelting of the briquettes. The selective reduction of SSPS is based on the reaction of metal oxides and sulfates [23–27]. These reactions describe the thermodynamic properties of the carbothermal reduction and mineral phase formation of single species contained in sludge.



It should be noted that the carbothermal reduction products of $CaSO_4$ are complex in the low-temperature range, the desulfurization product is CaO , and the sulfur fixation product is CaS . The ΔG curve of the main phase carbothermal reaction during SSPS calcination is shown in Figure 2a, while Figure 2b shows the ΔG curve of phase formation during slag bath reduction. As shown in Figure 2a, the carbothermal reduction of nickel oxide is the most favorable among the metal oxides, followed by iron oxides, with the reduction temperatures of different iron oxides being relatively close to one another. In comparison to the aforementioned categories, Cr oxides exhibit the least favorable carbothermal reduction, with their ΔG remaining positive even at a temperature of 1000 °C [9,25]. There are two ways to form solid-phase CaS from $CaSO_4$, as shown in Equations (11) and (12). Low carbon content is more favorable than high carbon content to form CaS , which releases part of CO .

In contrast, the formation of solid-phase CaO and SO₂ by CaSO₄ is not thermodynamically favorable, and the minimum temperature for the reaction to occur needs to be higher than 800 °C, which has been confirmed in many studies [4,9,23]. It can be seen from Figure 2b that at the considered slag bath reaction temperature, FeCr₂O₄ and MgCr₂O₄ are conducive to carbothermal reduction to form alloys, and the reaction of FeCr₂O₄ combined with MgO to form MgCr₂O₄ mineral phase also exists. In Equations (16) and (17), involving Al₂O₃, the ΔG for the conversion of MgFe₂O₄ to MgAl₂O₄ exhibits a more negative value compared to the ΔG for the direct formation of MgAl₂O₄ from MgO, indicating a thermodynamically more favorable pathway.

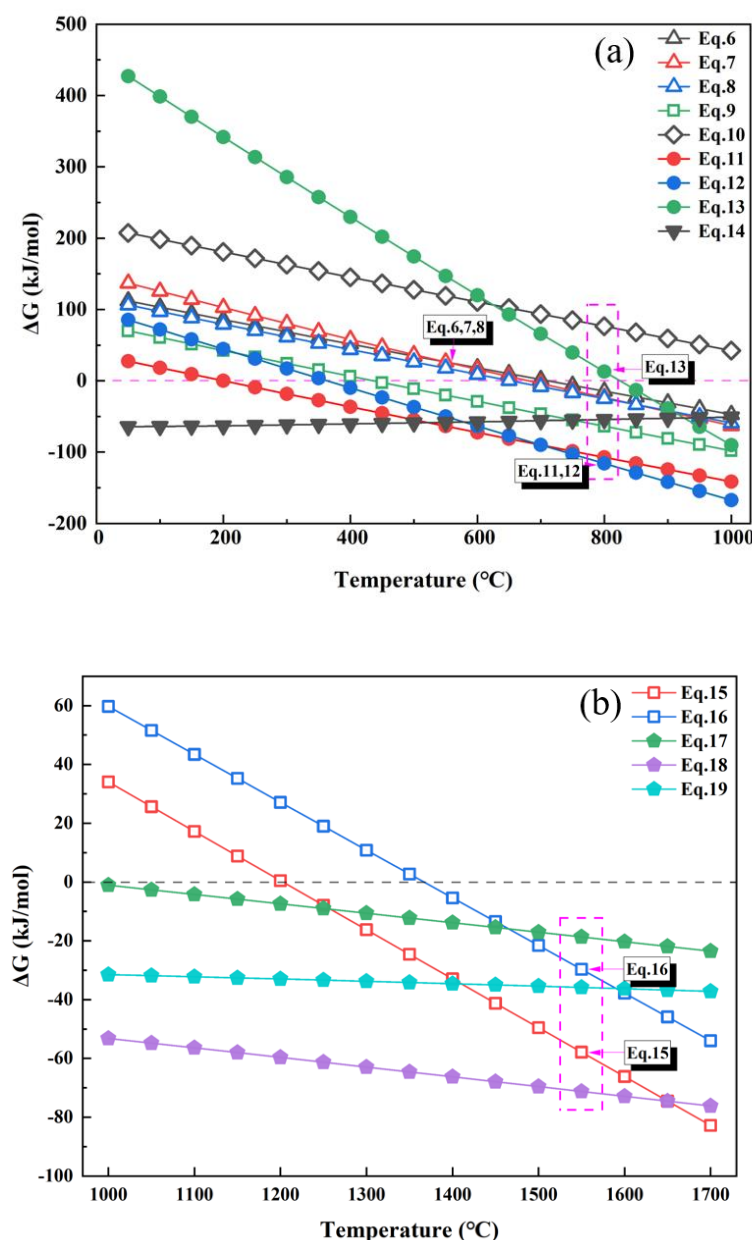


Figure 2. The standard free energy changes for reactions occurring in the (a) pre-treatment stage and (b) slag bath stage.

Based on the basic thermodynamic model, during the calcination process, the iron-nickel alloy can be formed, and the sulfur-fixed product CaS can be formed without causing SO₂ to escape, which is the expected result. At the same time, some FeCr₂O₄ mineral phases are inevitably formed. The calcined products enter the slag bath smelting stage. After the

briquettes contact the slag pool, the MgO or Al_2O_3 in the slag participates in the reactions of Equations (15) and (16). However, after considering the kinetic process, the product formed by the combination of FeCr_2O_4 and MgO can be in the form of $\text{Mg}(\text{Fe,Cr})_2\text{O}_4$ complex, that is, MgFe_2O_4 and MgCr_2O_4 participate in related reactions together. Therefore, MgCr_2O_4 containing Cr in the slag is finally reduced to metal and MgO, while MgFe_2O_4 will be converted to MgAl_2O_4 , that is, MgAl_2O_4 still exists in the slag at the end of the reduction.

B. Pre-reduction stage of C-SSPS

1. Thermal analysis and gas release

Figure 3 illustrates the change law for the weight loss rate and gas products of C-SSPS particles as analyzed by the TG-MS online analysis system. The findings from TG and DTG analyses indicated a total weight loss rate of 41.9 wt% for the particles, characterized by five stages with peaks of varying intensities. Integrating temperature and MS analysis, the initial phase demonstrated that around 100 °C, the adsorbed water began to release from the particles. The rate of water release increased with the rise in temperature, reaching a peak at 605 °C, suggesting that bound water was the dominant form. The disposal of moisture is also very important in pyrometallurgical processes and may cause fumes or an increase in hydrogen content in the raw material. The findings of Zhao et al. [2] indicated that the temperature for the water of crystallization in SSPS needed to exceed 550 °C to ensure its rapid and complete elimination.

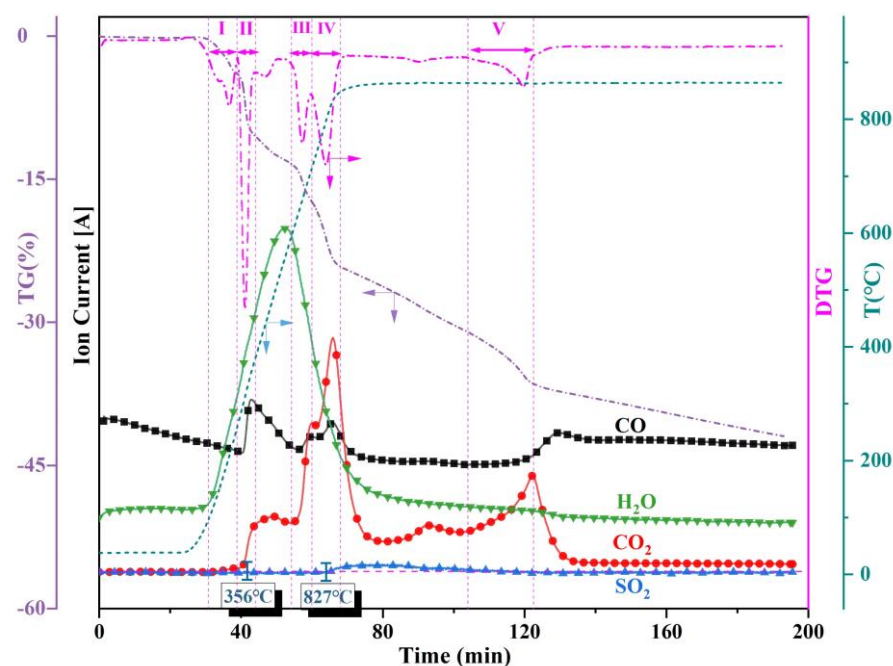


Figure 3. TG–MS of exhaust gas release in the pre-reduction.

When the drying temperature reached around 200 °C in the second stage, CO_2 gas began to be emitted. Equation (11) illustrates the corresponding reaction. The reaction continued to speed up as a result of the rising temperature and minor rise in the resultant gas. As indicated in Equation (12), a significant weight loss peak of DTG resulted from the simultaneous production of a large amount of CO and CO_2 at temperatures above 358 °C. This was brought on by the excess C in the particles, which in some areas had led to a C/S molar ratio of 3. At this temperature, only the conversion of calcium sulfate resulted in the production of carbon monoxide; the metal oxides in SSPS had not yet reached the reaction temperature. In the third and fourth stages, the formation rate of CO_2 significantly exceeded that of CO, indicating that Equation (11) predominated over Equation (12). The gas phase of SO_2 was not discovered until the fourth stage's temperature reached 827 °C. It is possible that a small amount of calcium sulfate had not fully reacted due to the rapid

consumption of the reducing agent graphite, resulting in the C/S molar ratio being less than 0.5 as given in Equation (13). The progressive drop in SO_2 level during the continuous isothermal process showed that the reaction requirements of Equation (13) were difficult to achieve. In contrast to the strategy of Wang et al. [8] and Zhao et al. [23], the SO_2 escape situation is strictly considered in this study to avoid increasing the cost of flue gas desulfurization.

The amount of CO_2 produced grew dramatically in the last stage, or about 50 min after isothermal, along with the creation of CO gas, although no SO_2 gas was formed. In conclusion, the results of the online TG-MS analysis demonstrated that the gas phase sulfur development could be fully prevented by limiting the calcination temperature below 800 °C.

2. Mineral phase formation of the product

The TG-MS data intuitively suggest that the pre-reduction process can control sulfide release, but more research is needed to understand the formation of sulfur-bearing minerals. As shown in Figure 4 and Table 3, combined with XRD patterns and SEM-EDS analysis, it was confirmed that following the pre-reduction of C-SSPS at 800 °C, the predominant mineral phases within the sludge consisted of unreacted graphite and the sulfur-fixed product, CaS. The primary microstructures observed included flake graphite, large particles of FeCr_2O_4 - CaSO_4 -CaS-FeS composite phase, small-sized CaSO_4 particles, and transformed CaS phase. Notably, CaS was predominantly distributed around the carbon particles. This indicated that the substantial quantity of CaSO_4 initially present in the SSPS converted to CaS due to the influence of temperature and carbon, whereas the Fe and Cr oxides also resulted in the formation of FeCr_2O_4 . This was in agreement with the results of the thermodynamic and correlation studies described above [9,10,23].

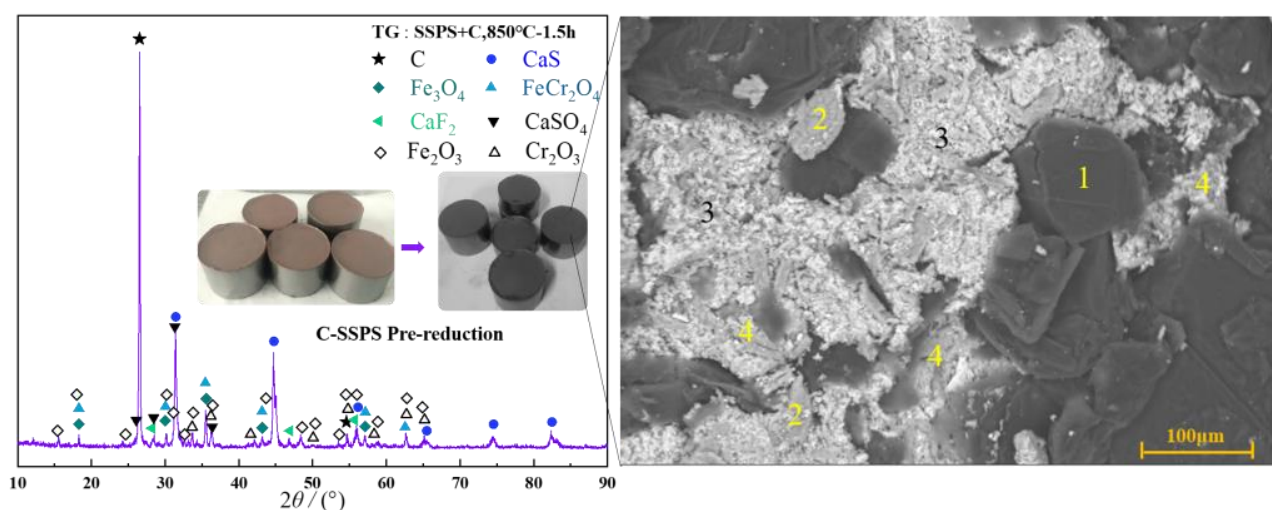


Figure 4. Phase and microstructure of pre-reduction products.

Table 3. Phase compositions of corresponding numbers.

No.	Phase
1	C
2	CaSO_4
3	FeCr_2O_4 - CaSO_4 -CaS-FeS
4	CaS

C. Slag bath reduction stage

1. Sulfide release and reduction rate

Mass spectrometry was used to study the release pattern of sulfide during slag bath smelting. Using the air sample as a reference, the ion current intensity value was used to monitor the waste gas collected in the C-SSPS slag bath reduction experiment. The SO_2 concentration in the exhaust gas between 0 and 10 min matched the air sample values (Figure 5), indicating no additional SO_2 production. Most of the existing forms of sulfur had been converted, with no occurrence of further desulfurization reactions. Trace amounts of SO_2 were detectable within the 10 to 20 min interval. The reaction progressed as the briquettes dissolved into the slag pool, dispersing minimal unreacted sulfate that subsequently decomposed and escaped. At the slag bath stage, unreacted CaSO_4 in the briquettes attained its decomposition temperature [4], yet a delay in SO_2 release was observed, suggesting that the briquettes and initial pre-reduction facilitated sulfur fixation product integration into the slag. Comparative analysis of waste gas and air samples revealed CO production during the initial stages of the slag bath treatment, primarily attributed to the high-temperature reduction of metal oxides like Fe and Cr [8,9]. The SO_2 concentration in the air is estimated to be 0.05 mg/m^3 , that is, in the pretreatment process and the initial stage of slag bath reduction, even if the gas does not undergo desulfurization treatment, the sulfur element concentration will not exceed the industrial limit of 0.25 mg/m^3 [3].

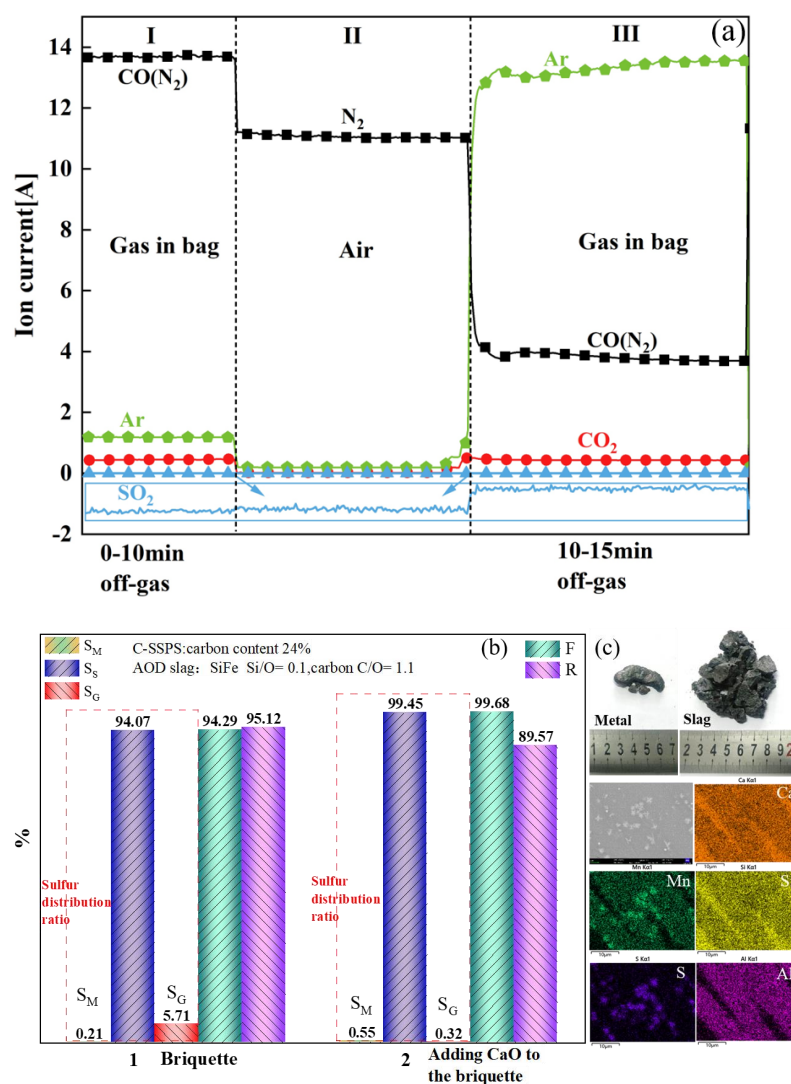


Figure 5. (a) Off-gas release, (b) reduction rate in slag-bath smelting, (c) product and SEM-EDS of final slag.

The high-temperature AOD slag bath reduction resulted in high metal recovery rates and sulfur retention in the residue. As shown in Figure 5, the recovery rate of the Fe-Cr-based alloy in the system exceeded 95%, with Fe and Cr contents in the metal phase being 59 wt% and 25 wt%, respectively. The metal phase also contained necessary carbon diffusion elements, partially reduced Mn, and trace amounts of Ni. The sulfur content of the impurity elements in the metal was 0.034%. The Cr content in the slag was only 0.15 wt%, while the sulfur content was 0.692 wt%, with over 94.29% of the sulfur remaining as sulfides in the slag phase. For elemental sulfur, only 5.71% was distributed in the gas phase, and 0.21% was in the recovered metal. To achieve better results, further optimization of the experimental plan is necessary. By adding 27 wt% CaO to adjust the chemical composition of SSPS, the sulfur retention rate in the solid phase exceeded 99.7%. According to Equation (11), when a certain amount of CaO is added, the reaction shifts to the left, resulting in less SO_2 generation and an increase in Ca^{2+} combining with S^{2-} . Studies [8,25] have shown that adjusting the alkalinity of slag can not only improve the desulfurization effect, but also promote the recovery of Cr.

2. Phase transformation at the interface between briquettes and slag

There are two significant processes in the gradual dissolution of the briquettes into the slag: the internal changes within the briquettes and the interface reaction with the slag. As illustrated in Figure 6a and Table 4, after 5 min in the slag bath, numerous fine C-Fe-Cr-Ni metal particles began to form within the C-SSPS, alongside a considerable amount of flake graphite and irregularly shaped CaS particles. After 10 min in the slag bath, larger metal particles had formed, settling to the bottom layer due to gravity. However, the initially smaller metal particles (region 12) continued to aggregate and grow (region 13), ultimately existing as Fe-Cr-based metal particles. It can be seen that Fe-Cr metal formation occurs through two distinct pathways: direct reduction to form Fe-Cr and reductive carburization to form Fe-Cr-C. The formation of Fe-Cr primarily results from the carbothermal reduction of spinel. The pathway to Fe-Cr-C alloy formation begins with the reductive carburization of Fe-containing oxides, leading to the production of Fe-C alloys with lower melting points. This process sets the stage for the complex formation of Fe-Cr-C. Specifically, during the reduction of Cr-containing oxides, Cr_7C_3 intermediates are formed, which impede the rate of Cr reduction. However, these Cr_7C_3 intermediates dissolve when interacting with pre-formed high-iron alloys, eventually forming Fe-Cr-C alloys [28,29]. Concurrently, with the incorporation of the low-melting-point phase $\text{CaF}_2\text{-Ca}_2\text{SiO}_4$ in the briquettes, the sulfur-fixing product CaS became interconnected.

Table 4. The phase composition of the corresponding number.

No.	Phase
7, 11	C
6, 9	CaS
5, 12	C-Fe-Cr
8	$\text{CaF}_2\text{-Ca}_2\text{SiO}_4$
10, 13	Fe-Cr
I	$\text{FeCr}_2\text{O}_4\text{-CaS-(Fe-Cr-C)}$
II	$\text{Ca}_3\text{SiO}_5\text{-Mg(Fe,Cr)}_2\text{O}_4$
III, VI	$\text{Ca}_2\text{MgSi}_2\text{O}_7$
IV	(Fe-Cr-C)-CaS
V	$\text{Mg(Al,Cr)}_2\text{O}_4\text{-Ca}_2\text{MgSi}_2\text{O}_7$
VII	$\text{Ca}_2\text{MgSi}_2\text{O}_7\text{-Ca}_2\text{Al}_2\text{SiO}_7\text{-CaS-FeS-MnS-MgCr}_2\text{O}_4$

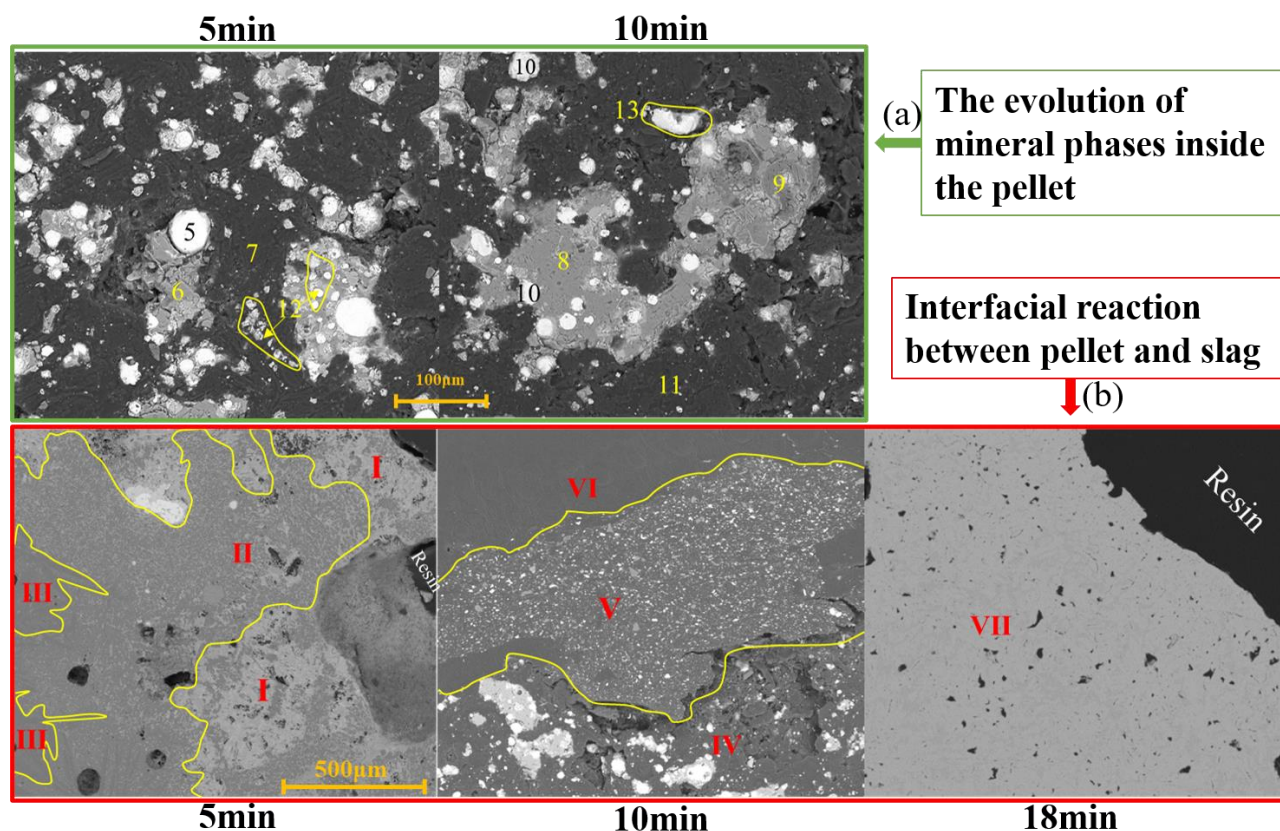


Figure 6. SEM images of micro-area at the interface between briquette and slag; (a) evolution of mineral phases within the briquette, (b) interfacial reaction between briquette and slag.

Figure 6b illustrates the interface reaction between the briquettes and slag. Five minutes into the slag bath treatment, the interface between C-SSPS and the slag pool could be distinctly categorized into three zones. In zone I, close to the briquettes, the main phases were FeCr_2O_4 , CaS , and Fe-Cr-Ni-C metal particles from the briquettes. Zone II, the middle diffusion layer, predominantly featured fine $\text{Mg}(\text{Fe,Cr})_2\text{O}_4$ particles and the Ca_3SiO_5 phase in the slag. Zone III, the slag layer distant from the briquettes, mainly contained the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ phase, consistent with the original slag pool. This suggested that CaS and FeCr_2O_4 in the briquette gradually migrated into the slag. The metal particles, having aggregated and grown, began to diffuse and settle into the slag. The AOD slag contained some MgO . In the MgO diffusion zone, the strong binding ability between MgO and Cr_2O_3 resulted in the formation of the MgCr_2O_4 spinel phase, with the presence of the composite $\text{Mg}(\text{Fe,Cr})_2\text{O}_4$ phase not ruled out.

After 10 min in the slag bath, the near-briquette region IV had comprised Fe-Cr -based metal particles and the bulk CaS phase. The intermediate product layer V was characterized by $\text{Mg}(\text{Al,Cr})_2\text{O}_4$. In comparison to the situation at the 5-minute mark, the metal particles had grown larger. With the diminishing concentration gradient of MgO at the interface between the briquette and the molten slag, Al^{3+} ions had more readily reacted with MgO , displacing Fe^{3+} ions to form MgAl_2O_4 . This reaction also led to the formation of the $\text{Mg}(\text{Al,Cr})_2\text{O}_4$ phase. These observations were in agreement with the thermodynamic calculations as shown in Equations (16)–(19). After 18 min in the slag bath, the briquettes had completely dissolved in the AOD liquid slag, the slag phase was uniformly distributed, and the metal phase had aggregated and grown. During the dissolution, the products of sulfur fixation remained in the stabilized forms of CaS and MnS .

D. Slag Bath Reduction Mechanism and Model Establishment

Figure 7 presents a detailed model of the reaction mechanism, divided into two parts: the reduction behavior inside the briquette and the briquette's dissolution behavior in

the slag. The sulfur fixation mechanism in the briquette and the evolution rules of metal particle formation, aggregation, and growth were revealed.

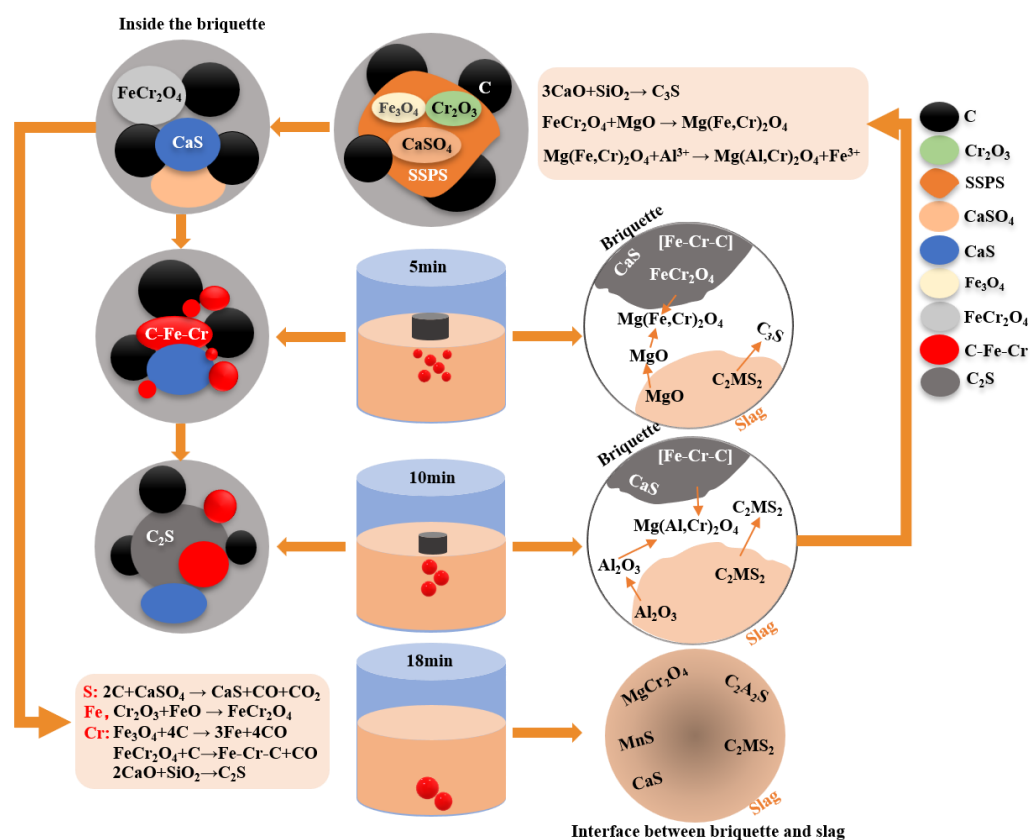


Figure 7. Slag-bath reduction model.

4. Conclusions

The use of stainless steel for smelting high-temperature AOD slag for in-line collaborative treatment of SSPS is an energy-saving and environmentally friendly method. The incorporation of pre-treatment and high-temperature slag bath smelting is both scientifically sound and essential. The following conclusions have been drawn:

According to the thermodynamic model, CaSO_4 are more likely to form CaS during the pre-reduction stage. In the slag reaction stage, metals exist in the form of Fe-Cr-Ni-C alloy in the system, and the final slag mainly consists of the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-CaS}$ system, with CaS remaining stable in the liquid slag phase. Furthermore, a model for the mineral phase evolution mechanism during the co-disposal process of SSPS and AOD slag has been established, which is thermodynamically consistent.

The process yielded a metal recovery rate of approximately 96%, mainly as an Fe-Cr alloy, which was ideal for stainless steel production. It also achieved an impurity sulfur content in the alloy of less than 0.034%. Additionally, exhaust gas emissions were free from sulfides, with up to 99% of sulfur effectively immobilized in a solid state within the slag. The total residual Cr content remained exceptionally low, under 0.4%, predominantly in the stable form of MgCr_2O_4 . Consequently, the treated slag proved to be suitable for the production of cementitious materials, concrete, and other construction materials.

An inline co-processing method parallel to the steelmaking process is proposed. The approach enables steel companies to lower energy and hazardous solid waste disposal costs. Additionally, it enhances metal recovery rates and creates revenue opportunities through the use of steel slag in cementitious materials.

Author Contributions: Z.Z.: Conceptualization, Methodology, Investigation, Data curation, Writing—original draft. Y.Z.: Writing—review and editing. Supervision, and Funding acquisition. F.Y.: Investigation, Data curation. T.W.: Visualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China (2019YFC1905701), the National Natural Science Foundation of China (U1960201).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Tang, Z.; Ding, X.; Yan, X.; Dong, Y.; Liu, C. Recovery of Iron, Chromium, and Nickel from Pickling Sludge Using Smelting Reduction. *Metals* **2018**, *8*, 936. [CrossRef]
2. Junxue, Z.; Zhongyu, Z.; Ruimeng, S.; Xiaoming, L.; Yaru, C. Issues relevant to recycling of stainless-steel pickling sludge. *JOM* **2018**, *70*, 2825–2836. [CrossRef]
3. Yang, C.; Pan, J.; Zhu, D.; Guo, Z.Q.; Li, X.M. Pyrometallurgical recycling of stainless-steel pickling sludge: A review. *J. Iron Steel Res. Int.* **2019**, *26*, 547–557. [CrossRef]
4. Li, X.; Lv, M.; Yin, W.D.; Zhao, J.X.; Cui, Y.R. Desulfurization thermodynamics experiment of stainless-steel pickling sludge. *J. Iron Steel Res. Int.* **2019**, *26*, 519–528. [CrossRef]
5. Ministry of Ecology and Environment of the People's Republic of China. National Hazardous Waste Directory (New Version), Reference No. 000014672/2016-00564. Available online: http://www.mee.gov.cn/gkml/hbb/bl/201606/t20160621_354852.htm (accessed on 21 June 2016).
6. Regel-Rosocka, M. A review on methods of regeneration of spent pickling solutions from steel processing. *J. Hazard. Mater.* **2010**, *177*, 57–69. [CrossRef]
7. Li, G.; Wang, J.; Rao, M.; Luo, J.; Zhang, X.; You, J.; Jiang, T. Coprocessing of Stainless-Steel Pickling Sludge with Laterite Ore via Rotary Kiln-Electric Furnace Route: Enhanced Desulfurization and Metal Recovery. *Process Saf. Environ. Prot.* **2020**, *142*, 92–98. [CrossRef]
8. Wang, H.; Zhang, G.; Chou, K. Preparation of Low-Carbon and Low-Sulfur Fe-Cr-Ni-Si Alloy by Using CaSO₄-Containing Stainless-steel Pickling Sludge. *Metall. Mater. Trans. B* **2020**, *51*, 2057–2067. [CrossRef]
9. Wu, M.; Li, Y.L.; Guo, Q.; Shao, D.W.; He, M.M.; Qi, T. Harmless treatment and resource utilization of stainless-steel pickling sludge via direct reduction and magnetic separation. *J. Clean. Prod.* **2019**, *240*, 118187. [CrossRef]
10. Liu, S.; Li, Q.; Wang, Z.; Yang, F.; Lu, X. Metals droplet assembling mechanism during carbon reduction of stainless-steel pickling sludge. *J. Clean. Prod.* **2020**, *247*, 119580. [CrossRef]
11. Zhao, S.; Liu, B.; Ding, Y.; Zhang, J.; Wen, Q.; Ekberg, C.; Zhang, S. Study on glass-ceramics made from MSWI fly ash, pickling sludge and waste glass by one-step process. *J. Clean. Prod.* **2020**, *271*, 122674. [CrossRef]
12. Yang, J.; Zhang, S.G.; Pan, D.A.; Liu, B.; Wu, C.L.; Volinsky, A.A. Treatment method of hazardous pickling sludge by reusing as glass-ceramics nucleation agent. *Rare Met.* **2016**, *35*, 269–274. [CrossRef]
13. Pan, D.A.; Li, L.J.; Yang, J.; Bu, J.B.; Guo, B.; Liu, B.; Zhang, S.G.; Volinsky, A.A. Production of Glass-Ceramics from Heavy Metal Gypsum and Pickling Sludge. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 3047–3052. [CrossRef]
14. Shen, H.; Forssberg, E.; Nordström, U. Physicochemical and mineralogical properties of stainless-steel slags oriented to metal recovery. *Resour. Conserv. Recycl.* **2004**, *40*, 245–271. [CrossRef]
15. Tossavainen, M.; Engstrom, F.; Yang, Q.; Menad, N.; Larsson, M.L.; Bjorkman, B. Characteristics of steel slag under different cooling conditions. *Waste Manag.* **2007**, *27*, 1335–1344. [CrossRef] [PubMed]
16. Kriskova, L.; Pontikes, Y.; Cizer, Ö.; Mertens, G.; Veulemans, W.; Geysen, D.; Blanpain, B. Effect of mechanical activation on the hydraulic properties of stainless steel slags. *Cem. Concr. Res.* **2012**, *42*, 778–788. [CrossRef]
17. Liu, B.; Li, J.; Wang, Z.; Zeng, Y.; Ren, Q. Long-term leaching characterization and geochemical modeling of chromium released from AOD slag. *Environ. Sci. Pollut. Res.* **2020**, *27*, 921–929. [CrossRef]
18. Kriskova, L.; Pontikes, Y.; Zhang, F.; Cizer, Ö.; Jones, P.T.; Van Balen, K.; Blanpain, B. Influence of mechanical and chemical activation on the hydraulic properties of gamma dicalcium silicate. *Cem. Concr. Res.* **2014**, *55*, 59–68. [CrossRef]
19. Park, B.; Choi, Y.C. Investigation of carbon-capture property of foam concrete using stainless-steel AOD slag. *J. Clean. Prod.* **2021**, *288*, 125621. [CrossRef]
20. Moon, E.J.; Choi, Y.C. Development of carbon-capture binder using stainless-steel argon oxygen decarburization slag activated by carbonation. *J. Clean. Prod.* **2018**, *180*, 642–654. [CrossRef]

21. Wang, Y.J.; Zeng, Y.N.; Li, J.G.; Zhang, Y.Z.; Zhang, Y.J.; Zhao, Q.Z. Carbonation of argon oxygen decarburization stainless-steel slag and its effect on chromium leachability. *J. Clean. Prod.* **2020**, *256*, 120377. [[CrossRef](#)]
22. Bale, C.; Belisle, E.; Chartrand, P.; Decterov, S.; Eriksson, G.; Gheribi, A.; Hack, K.; Jung, I.H.; Kang, Y.B.; Melançon, J.; et al. FactSage thermochemical software and databases, 2010–2016. *Calphad* **2016**, *54*, 35–53. [[CrossRef](#)]
23. Zhao, J.; Su, H.; Zuo, H.; Wang, J.; Xue, Q. The Mechanism of Preparation Calcium Ferrite from Desulfurization Gypsum Produced in Sintering. *J. Clean. Prod.* **2020**, *267*, 122002. [[CrossRef](#)]
24. Shi, C.; Zhang, Y.; Zhou, S.; Jiang, J.; Huang, X.; Hua, J. Status of research on the resource utilization of stainless steel pickling sludge in China: A review. *Environ. Sci. Pollut. Res.* **2023**, *30*, 90223–90242. [[CrossRef](#)] [[PubMed](#)]
25. Li, Y.; Yang, Y.; Huang, Y.; Zhang, Z.; He, F.; Yang, H. A Sustainable Process for the Resource Utilization and Stabilization Disposal of Stainless Steel Pickling Sludge. *JOM* **2022**, *74*, 3910–3920. [[CrossRef](#)]
26. Pickles, C.A. Thermodynamic analysis of the selective carbothermic reduction of electric arc furnace dust. *J. Hazard. Mater.* **2008**, *150*, 265–278. [[CrossRef](#)]
27. Al-Harabsheh, M. Thermodynamic analysis on the thermal treatment of electric arc furnace dust-PVC blends. *Arab. J. Sci. Eng.* **2018**, *43*, 5757–5769. [[CrossRef](#)]
28. Wu, T.; Zhang, Y.; Zhao, Z.; Yuan, F. Effects of Fe_2O_3 on Reduction Process of Cr-Containing Solid Waste Self-Reduction Briquette and Relevant Mechanism. *Metals* **2019**, *9*, 51. [[CrossRef](#)]
29. Mori, T.; Yang, J.; Kuwabara, M. Mechanism of Carbothermic Reduction of Chromium Oxide. *ISIJ Int.* **2007**, *47*, 1387–1393. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.