

Article

Reduction Smelting of the Waelz Slag from Electric Arc Furnace Dust Processing: An Experimental Study

Pavel Grudinsky ^{1,*}, Dmitry Zinoveev ¹, Alex Kondratiev ², Leonid Delitsyn ³, Ruslan Kulumbegov ³, Anton Lysenkov ¹, Pavel Kozlov ⁴ and Valery Dyubanov ¹

¹ A.A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Science, 49 Leninsky Prosp., 119334 Moscow, Russia

² Thermochemistry of Materials Scientific Research Centre, National University of Science & Technology "MISIS", 4 Leninsky Prosp., 119049 Moscow, Russia

³ Joint Institute for High Temperatures of the Russian Academy of Sciences, 13 Izhorskaya st., 125412 Moscow, Russia

⁴ UMMC Technical University, 3 Uspensky Prosp., 624091 Verkhnyaya Pyshma, Sverdlovsk Region, Russia

* Correspondence: pgrudinsky@imet.ac.ru

Abstract: Waelz slag is an iron-containing waste generated during electric arc furnace (EAF) dust processing in a rotary kiln named the Waelz process. This study focuses on the reduction smelting of the Waelz slag to produce iron-based alloy. The thermodynamic simulation using FactSage 8.0 software was carried out to predict temperatures of the metal and slag obtained as well as their compositions. Based on the simulation results, reduction smelting experiments were performed on a laboratory scale using two approaches, with and without preliminary froth flotation of carbon, respectively. The experiments have confirmed the technological possibility of reduction smelting of the Waelz slag from EAF dust processing. The approach using preliminary flotation of carbon and reduction smelting at 1500 °C resulted in high-copper cast iron production, while the approach without flotation, where the Waelz slag was smelted at 1650 °C with the addition of SiO₂ flux, led to obtaining low-silicon ferrosilicon with high Cu content, as well as slag attractive for construction industry.

Keywords: Waelz slag; electric arc furnace dust; reduction smelting; recycling; pig iron; cast iron; ferrosilicon



Citation: Grudinsky, P.; Zinoveev, D.; Kondratiev, A.; Delitsyn, L.; Kulumbegov, R.; Lysenkov, A.; Kozlov, P.; Dyubanov, V. Reduction Smelting of the Waelz Slag from Electric Arc Furnace Dust Processing: An Experimental Study. *Crystals* **2023**, *13*, 318. <https://doi.org/10.3390/cryst13020318>

Academic Editor: Xiaochun Li

Received: 26 January 2023

Revised: 6 February 2023

Accepted: 10 February 2023

Published: 15 February 2023



Copyright: © 2023 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

Steelmaking dust produced in electric arc furnaces (EAF) is a valuable material for non-ferrous metals extraction due to high contents of zinc and lead [1]. Approximately 7.5 million tons of the EAF dust are generated in the world annually, about 45% of which is recycled [2]. So far, the most widely used way for EAF dust treatment is the Waelz process, which recycles about 85% of the dust [3]. The Waelz process is the pyrometallurgical processing of the dust-containing charge with a carbonaceous reducing agent in a rotary kiln at 1200–1300 °C [4]. Zinc, lead, and other volatile components during the roasting at reducing conditions are fumed into the so-called Waelz oxide. The enriched in zinc and lead the Waelz oxide is transported to zinc plants for further separation and extraction of the non-ferrous metals.

About 600–650 kg of the remaining non-evaporable by-product with a high Fe content called the Waelz slag is generated per ton of EAF dust [5]. Two types of the Waelz slag should be distinguished: lime-rich and silica-rich, with the basicity index higher than 1 and lower than 1, respectively [6]. The type of the generated slag depends on the composition of slag-forming addition used in the Waelz process. It also should be noted that contents of remaining non-ferrous metals such as Zn, Pb, Cu and other impurities such as As, Sb, Cr, P, S can vary widely [7,8]. Basicity and contents of different impurities mainly determine [6] ways of recycling the Waelz slag generated in different plants. Silica-rich slag

is generally more suitable for construction industry than lime-rich slag due to the standards compliance according to the results of leaching tests. Silicate components promote the glass phase formation that often leads to a significant decrease in harmful heavy metals contents in the filtrates of the corresponding leaching tests [9]. Various studies have shown the possibility of the Waelz slag application in making of concrete [10], bricks [11–14] and photocatalysts [15,16], as well as in road construction [17], where most of the slag samples were silica-rich. The recycling of the Waelz slag in metallurgy is limited mainly due to a high content of remaining zinc, which is harmful for ironmaking process [18]. Zinc content in the Waelz slag can vary over a range of 0.2–3.8% [6]. Few authors have studied the recycling of the Waelz slag in metallurgy, namely, in a top-blown rotary converter [19], in a vertical retort [20,21], and as a charge to an electric arc steelmaking furnace [22]. However, either the published results consist of calculation without experimental verification [19,22], or even the research projects were suspended due to their inefficiency [20,21]. Nevertheless, iron is the main element of the Waelz slag, so iron metallurgy is one of the possible ways for its utilization. Currently, recycling of Fe-containing wastes is attractive due to a significant depletion of high-grade iron ore reserves and mining of iron ore deposits of lower grade and complicated mineralogy [23].

In this paper, we test a promising method of high-temperature reduction smelting of the lime-rich Waelz slag to extract iron, zinc, and copper, as well as to obtain slag suitable for construction industry. This approach is proved to be feasible for iron recovery from other industrial by-products such as red mud [24–26], steelmaking slag [27–29], metallurgical dust along with ore fines [30,31], chromite ore tailings [32], copper slag [33–35]. Based on the thermodynamic simulation, we investigated experimentally reduction smelting of the Waelz slag and characterized the obtained metal and slag samples to assess their applicability.

2. Materials and Methods

2.1. Waelz Slag Characterization

The lime rich Waelz slag produced via EAF dust processing was taken from JSC “Chelyabinsk zinc plant” (Chelyabinsk, Russia). An X-ray fluorescence spectrometer PANalytical AXIOSmax Advanced (Almelo, the Netherlands) was used for elemental analysis of the Waelz slag sample. The contents of carbon and sulfur were measured by a LECO CS-400 gas analyzer (St. Joseph, MI, USA). Potassium dichromate titration methods were used to analyze the contents of ferrous [36] and metallic iron [37]. The content of ferric iron was calculated as a difference between total and sum of metallic and ferrous iron. Table 1 shows the chemical composition of the sample.

Table 1. The chemical composition of the Waelz slag sample, wt.%.

Fe _{total}	Fe _{met}	Fe ²⁺	Fe ³⁺	Zn	Cu	Pb	Ca	Mg	Al	Si	Mn	Na	K	Cr	As	Ni	Ti	C	P	S
26.4	12.5	12.4	1.50	0.94	0.84	0.25	9.93	4.15	1.91	5.98	2.15	0.63	0.31	0.33	0.32	0.074	0.15	18.7	0.17	1.84

The mineralogical composition of the sample was analyzed by an ARL X'TRA (Waltham, MA, USA) diffractometer with X-rays of Cu-K_α and Match 3.12 (Germany) software [38] using the Crystallography Open Database [39]. Figure 1 shows the X-ray diffraction (XRD) pattern of the Waelz slag sample, which indicates that the main iron-free phases of the sample are melilite, monticellite, periclase and forsterite.

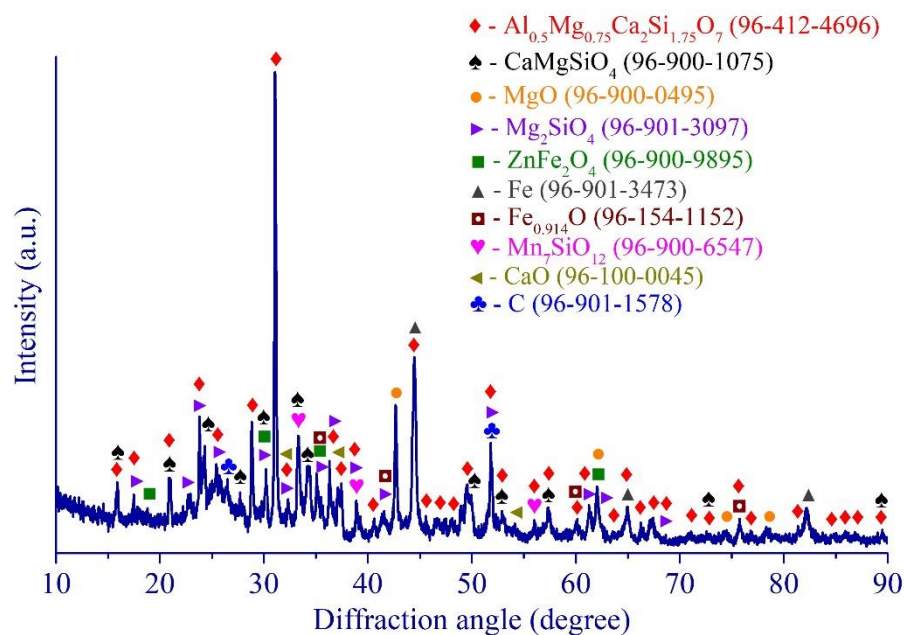


Figure 1. The XRD pattern of the Waelz slag sample.

2.2. Thermodynamic Calculation

Thermodynamic calculation was carried out using FactSage 8.0 software with FToxide, FactPS, and FTMisc database [40] at 1000–1800 °C for the slag, gas, and iron phases, respectively. The model system was based on a simplified composition of the Waelz slag sample (Table 1 excluding As, Sb, Ti, Ni) when all iron is supposed to be reduced from the Waelz slag.

2.3. Experiments

Figure 2 shows a schematic of the experimental furnace. Charge (5) was placed into a graphite crucible (4). The crucibles were put in a Tammann resistance furnace (1) with a graphite heater (2) on a graphite stand (3). The furnace is 360 mm in height, 300 mm in diameter; the inner heater diameter is 74 mm. The temperature was set by an automatic controller (8) with a tungsten-rhenium thermocouple (7) in an alumina sheath (6) submerged into the charge. In order to reduce the oxidation potential of the furnace atmosphere and to prevent burnout of the heater, the furnace was blown by argon at the flow rate of 0.5 L/min through the bottom hose (9).

Reduction smelting experiments were carried out as follows. The Waelz slag sample ground to -0.054 mm fraction, and reagent-grade SiO_2 were mixed to a selected ratio in a V-shell blender. The obtained mixtures were poured into graphite crucibles and placed in the Tammann furnace. The used crucibles were 90 mm in height, 20 and 14 mm in outer and inner diameter, respectively. The furnace was heated up to 1300 °C at a maximum attainable rate, then at a rate of 10–20 °C/min until the required temperature in the range of 1450–1750 °C was reached. The holding time at a certain temperature was 30 min in all the experiments. After the holding, the samples were cooled down with the furnace, then grinded and screened through a sieve of 0.054 mm.

Elemental composition of the obtained metal samples was analyzed by an atomic emission spectrometer Horiba Jobin-Yvon Ultima 2 (Longjumeau, France), and an inductively coupled mass spectrometer Perkin Elmer ELAN-6100 (Waltham, MA, USA). Carbon and sulfur contents were analyzed by a Leco CS-400 gas analyzer (St. Joseph, MI, USA). Elemental composition of the obtained slag samples was analyzed by an X-ray fluorescence spectrometer PANalytical AXIOSmax Advanced (Almelo, The Netherlands). The XRD spectra were obtained using a DRON-4 (Saint Petersburg, Russia) diffractometer with $\text{Cu-K}\alpha$ radiation.

The froth flotation experiments to remove an excess of carbon from the Waelz slag were carried out using a flotation machine FML-3 (Saint Petersburg, Russia). The methodology of the flotation experiments was quite similar to extraction of carbon from fly ash of thermal power plants as reported in [41]. The grinding fineness of the Waelz slag sample in the froth flotation experiments was -0.16 mm. Firstly, 250 g of the Waelz slag and 1.6 L of tap water were mixed and stirred for 10 min. Then the collecting agent was poured into the mixture, and it was stirred another 2 min. Afterwards, the frothing agent was added to the pulp, and the stirring continues for another 2 min. The emulsion containing 4 g of kerosene and thermal cracking gas oil in a ratio of 1:1, as well as 0.1 L of water was used as a collecting agent. The emulsion containing 0.4 g of Oxal T-66 flotation reagent and 0.1 L of water was used as a frothing agent. Finally, the flotation was carried out with air flow for 12 min.

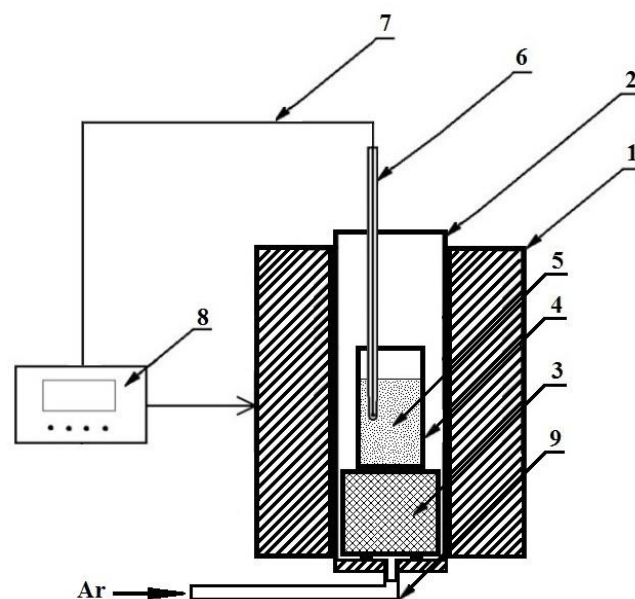


Figure 2. Schematic diagram of experimental apparatus: 1—furnace body; 2—graphite heater; 3—graphite stand; 4—crucible; 5—charge; 6—sheath for thermocouple; 7—thermocouple wire; 8—automatic temperature controller; 9—hose for protective gas inlet.

The slag sample obtained by reduction smelting under the best conditions was tested as an additive to Portland cement. Comparative compressive strength tests of the Portland cement samples of CEM I 42.5 grade were carried out without additives and with the addition of 5%, 10%, 15%, 20% of the slag after 7 and 28 days of curing. The slag for the tests was crushed in a cast iron mortar; then iron metallic particles were magnetically separated. Afterwards, the samples were grinded using a Fritsch Pulverisette 7 ball mill (Idar-Oberstein, Germany) and screened through the sieve of $+0.063$ mm to a residue of less than 5% wt. The tests were performed by a compression testing machine IP-1000-1 (ZIM TOCHMASHPRIBOR, Russia). The compression strength of the samples was determined using cubes dimensions $2\text{ cm} \times 2\text{ cm} \times 2\text{ cm}$ with the cement-to-sand (C/S) ratio of $1/3$ and the water-to-cement (W/C) ratio of 0.40 according to the Russian State Standards GOST 310.1–310.3-76, GOST 310.4-81.

3. Results

3.1. Thermodynamic Calculation

Thermodynamic simulation was carried out to determine the conditions of slag-metal separation during the Waelz slag smelting, as well as to predict the slag and metal compositions.

Figure 3 shows the temperature dependence of the equilibrium amounts of the metal, slag, and gas phases. As can be seen, the amount of liquid slag sharply increases above 1150 °C, achieves a plateau at 1340 °C, then decreases gradually. The amounts of the metal and gas phases grow up with the temperature rising. Evidently, the plateau reaching is associated with almost full slag melting, therefore, to separate slag and metal the temperatures above 1340 °C should be considered.

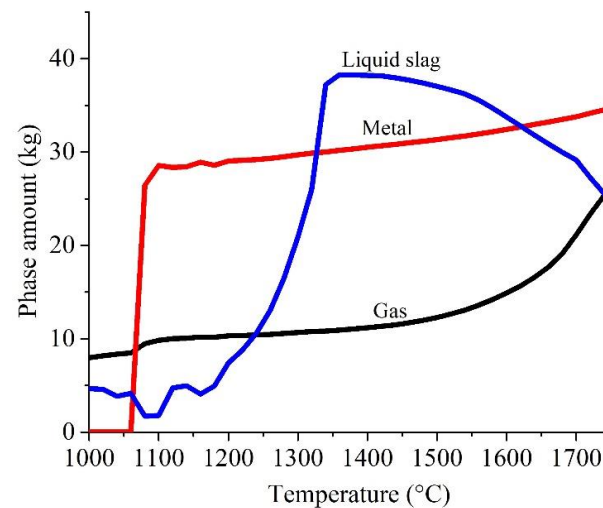


Figure 3. Effect of temperature on equilibrium amounts of liquid slag, metal, and gas obtained from the Waelz slag.

Figure 4 illustrates the calculated composition of the metal and slag phases in a temperature range of 1340–1750 °C. The carbon contents in the range of 3.91–4.51% indicate the possibility to obtain pig iron. Unfortunately, as shown in Figure 4a, the main part of copper and phosphorous, which are usually undesirable impurities [42], can pass from the Waelz slag sample into the obtained pig iron. In contrast to this, as follows from both the plots, the main part of sulfur, which is also undesirable impurity [42], can be transferred in the slag phase owing to high desulphurizing capacity of basic charge [43]. A temperature rise causes an increasing content of silicon and manganese in pig iron due to their reduction by carbon [44].

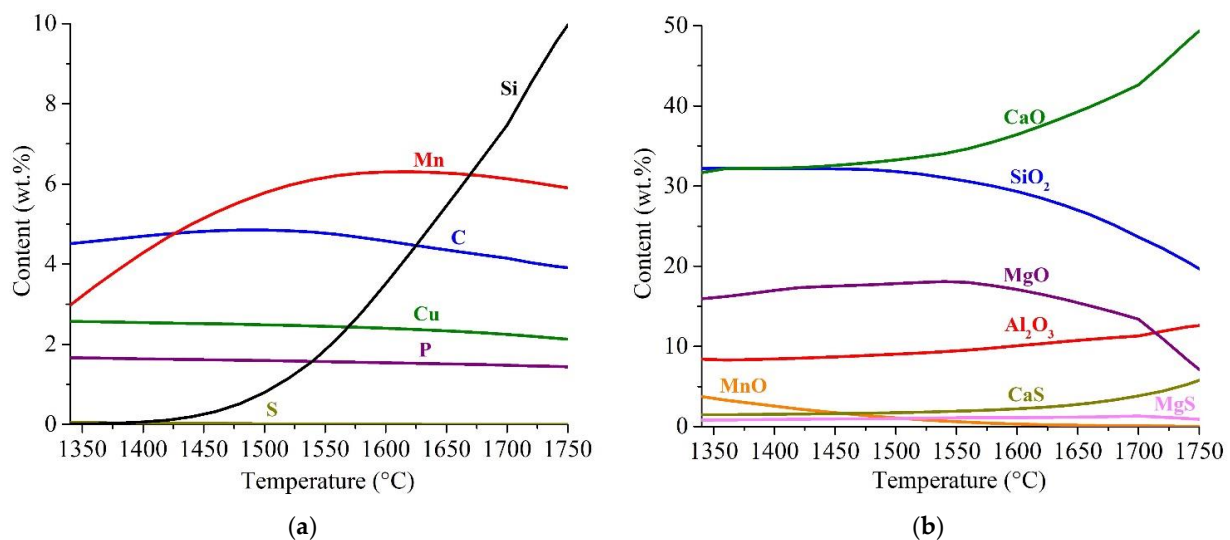


Figure 4. Effect of temperature on the equilibrium compositions of the iron-based alloy (a) and liquid slag (b) obtained from the Waelz slag.

3.2. Reduction Smelting Experiments

3.2.1. The Smelting of the Waelz Slag without Additions

The reduction smelting experiments were carried out with the Waelz slag sample at 1350, 1450, 1550, 1650, 1750 °C. Contrary to the thermodynamic calculations, metal and slag have not fully been separated at all the temperatures. Figure 5 demonstrates the samples after the smelting at 1450 and 1550 °C. It is clear that melting process have partly occurred, but there were no separate phases of metal and slag.

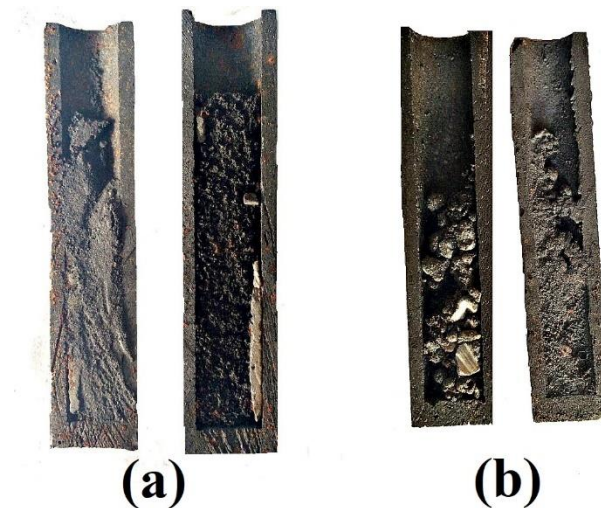


Figure 5. The samples after the reduction smelting of the Waelz slag sample at 1450 (a) and 1550 °C (b).

It is well-known that the separation of metal and slag depends not only on their melting point, but also on their viscosity. In our case, a discrepancy of the thermodynamic simulation and the experiments are probably due to the presence of a significant carbon content in the Waelz slag sample (Table 1); it remains in the smelted charge as a solid suspension that increases the viscosity of the slag [45] and impedes the separation of metal and slag.

3.2.2. The Smelting of the Waelz Slag with SiO₂ Additions

In order to separate metal and slag phases, the experiments with the addition of 12, 15, 18% pure SiO₂ to 100% Waelz slag were carried out to decrease the melting point of the slag phase. Figure 6 shows the liquidus projections calculated for the CaO–MgO–SiO₂–8% Al₂O₃ system using FactSage as well as the slag samples without and with SiO₂ addition (marked by a black square and triangles, respectively). It is clear that the SiO₂ addition to the Waelz slag sample shifts its composition to the pyroxene primary phase field, thereby decreasing the melting point of the system by 150–200 °C.

Table 2 lists the results of separation of metal and slag in the experiments with the SiO₂ addition. As follows from the data, the separation has occurred only in 5 samples at 1650 and 1750 °C.

Table 2. The effect of temperature and the SiO₂ addition on the separation of metal and slag after the reduction smelting of the Waelz slag sample.

% SiO ₂	Temperature, °C				
	1350	1450	1550	1650	1750
12	×	×	×	×	✓
15	×	×	×	✓	✓
18	×	×	×	✓	✓

×—no separation or insufficient separation; ✓—successful separation.

Figures 7 and 8 demonstrate the composition of the metal samples obtained at 1650 and 1750 °C, respectively. Table 3 includes the composition of the corresponding slag samples.

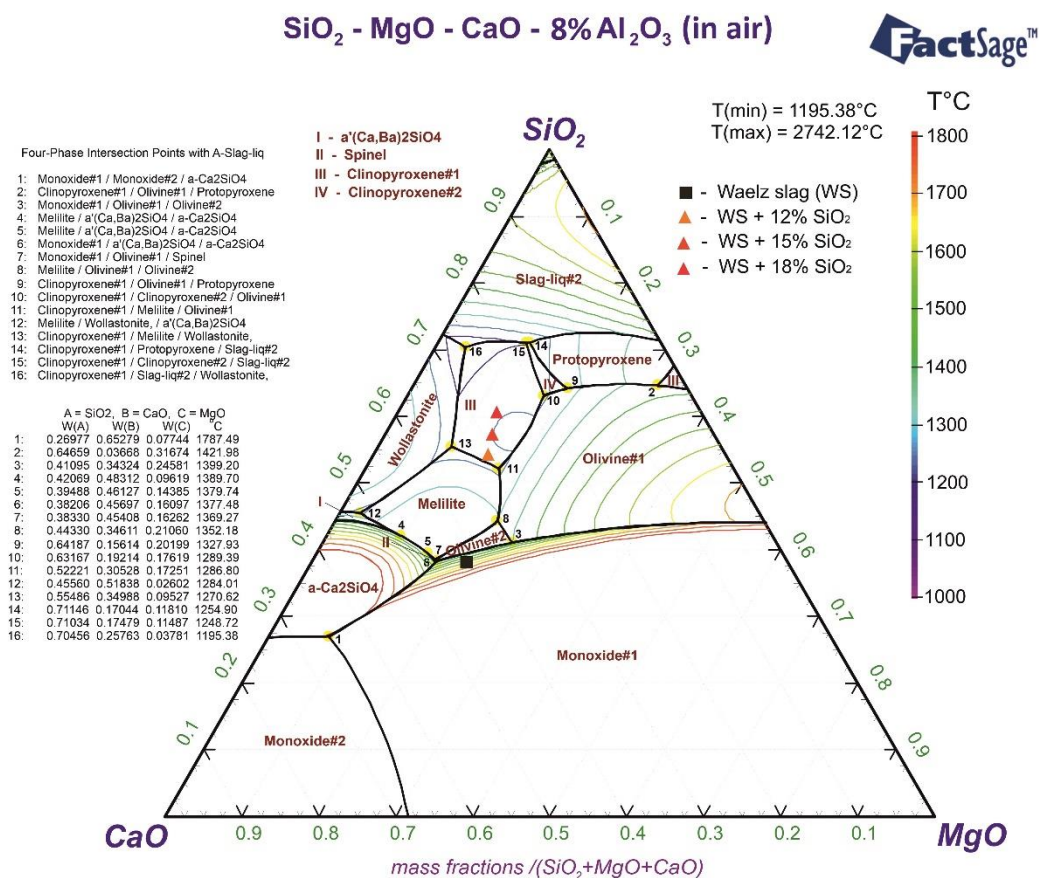


Figure 6. The liquidus projections for the CaO–MgO–SiO₂–8%Al₂O₃ system from 1000 to 1800 °C with the marked points of charge composition for the experiments.

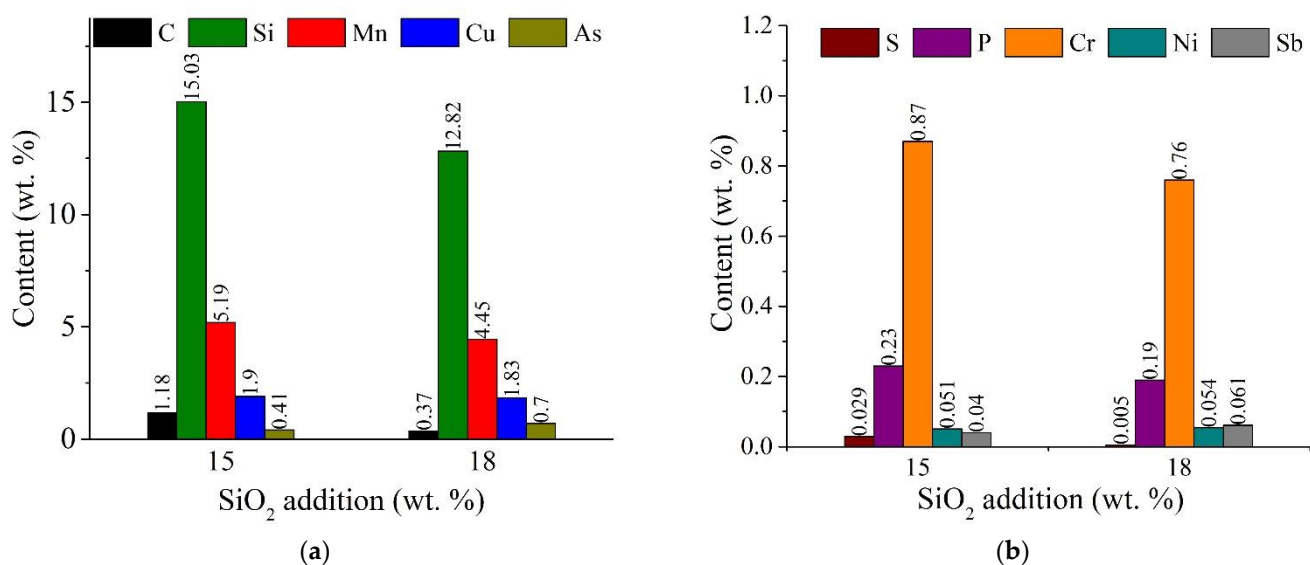


Figure 7. The effect of SiO₂ addition to 100% of the Waelz slag on the contents of C, Si, Mn, Cu, as (a) and S, P, Cr, Ni, Sb (b) in the iron-based alloy obtained by the reduction smelting at 1650 °C.

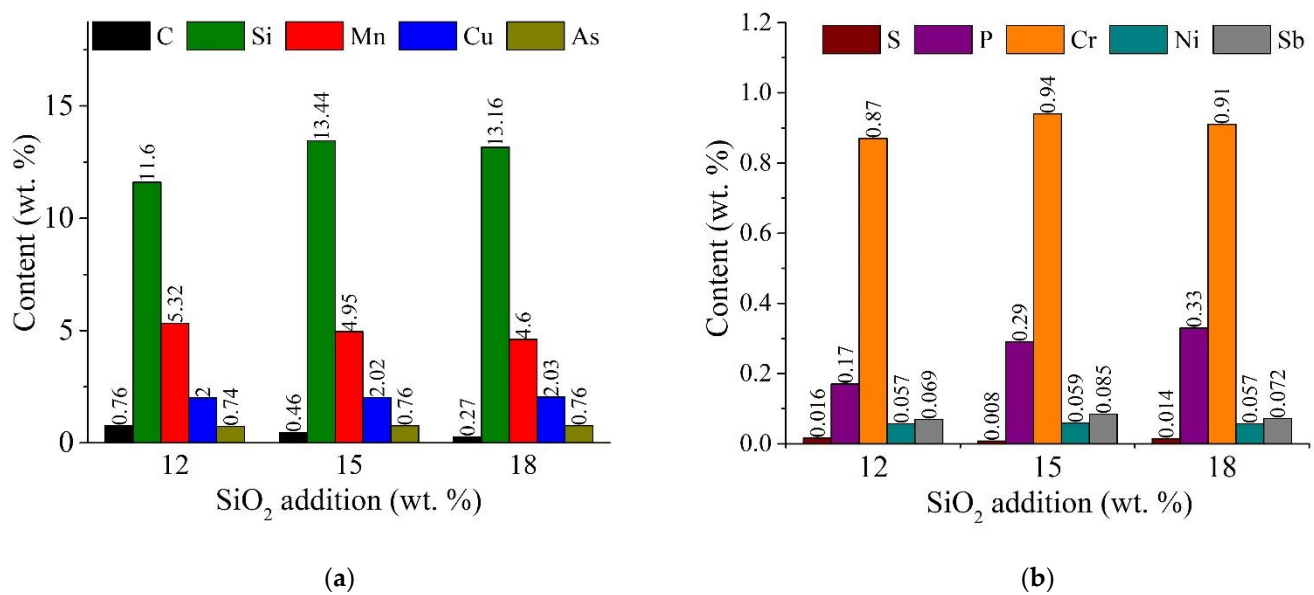


Figure 8. The effect of SiO₂ addition to 100% of the Waelz slag on the contents of C, Si, Mn, Cu, As (a) and S, P, Cr, Ni, Sb (b) in the iron-based alloy obtained by the reduction smelting at 1750 °C.

Table 3. The effect of temperature and SiO₂ addition on the chemical composition of slag obtained by reduction smelting of the Waelz slag sample.

Reduction Smelting Temperature, °C	Added % SiO ₂	Slag Composition, wt. %											
		CaO	SiO ₂	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	Mn	Cr	P	S	Fe
1650	15	34.2	33.8	15.3	7.44	0.24	0.16	0.27	0.66	0.07	0.019	3.75	2.20
	18	30.5	36.8	16.5	7.69	0.39	0.11	0.21	0.53	0.02	0.011	3.77	1.30
1750	12	34.3	32.2	17.1	8.58	0.31	0.09	0.18	0.72	0.03	0.017	4.74	0.61
	15	33.2	34.4	16.6	8.45	0.36	0.08	0.19	0.56	0.03	0.006	4.32	0.48
	18	32.5	36.5	15.8	7.63	0.51	0.15	0.25	0.71	0.02	0.005	4.03	0.49

As reflected by the bar charts, the dependences for certain elements in iron-based alloys are ambiguous. The carbothermic reduction led to the obtaining metal phase according to the corresponding general reactions:



Silicon content in all the metal samples is proved to be in the range of 11.6–15%, but there is no correlation between the temperature and silica amount. Such Si contents in the iron-based alloys are associated with the reduction in silica at the experimental temperatures that occurs according to the following reactions [46]:



A discrepancy of the calculated (Figure 4) and experimental (Figures 7a and 8a) data of carbon content is due to substantial decreasing carbon solubility in melts with an increase in Si content in Fe-Si system [47].

The main part of manganese is present in the alloy samples in the range from 4.45 to 5.32%. It is reported [48] that reduction in manganese at 1600 °C can occur not only by carbon dissolved in liquid iron and solid carbon, but also by liquid iron and dissolved silicon. The behavior of copper, sulfur and phosphorus in a good qualitative agreement with the simulation results (Figure 4). It should be noted that chromium along with copper passed into the alloy phase almost fully. The considerable contents of arsenic and antimony in the alloy also deserves attention.

As followed from the Table 3, residual Fe content in the slag samples is rather low; it decreases with reduction smelting temperature rise. All the slag samples are quite similar in chemical composition.

3.2.3. The Smelting of the Waelz Slag after Carbon Excess Removal by Froth Flotation

Another way to separate metal and slag is carbon excess removal by froth flotation from the Waelz slag sample before the reduction smelting. Table 4 shows the composition of the products of the Waelz slag froth flotation. The presented composition of the froth floated Waelz slag indicates a considerable decrease in carbon content compared with initial the Waelz slag sample from 18.7% to 5.1%, while the contents of the other elements remained at the same level or slightly increased. The obtained carbon flotation concentrate with 68% C content can be considered for recycling into the Waelz process as a partial substitution of coke breeze.

Table 4. The composition of the froth flotation products, wt.%.

Sample	Fe	Zn	Cu	Pb	Ca	Mg	Al	Si	Mn	Na	K	Cr	As	Ti	Ni	C	P	S
Froth-floated Waelz slag	26.3	0.63	0.84	0.28	10.3	6.49	2.61	7.00	2.26	0.68	0.19	0.27	0.12	0.16	0.09	5.1	0.25	1.59
Carbon flotation concentrate	5.14	0.39	0.38	0.12	3.48	1.83	1.80	2.89	0.83	0.59	0.64	0.08	0.06	0.14	0.01	68.0	0.16	1.00

Figure 9 illustrates the XRD pattern of the froth floated Waelz slag sample. As shown in Figures 1 and 9, the phase composition of the Waelz slag before and after the froth flotation differs insignificantly: the major phases remain the same, there is some other minor phases of $\text{Mg}(\text{OH})_2$ and FeOOH due to reactions with water during the treatment.

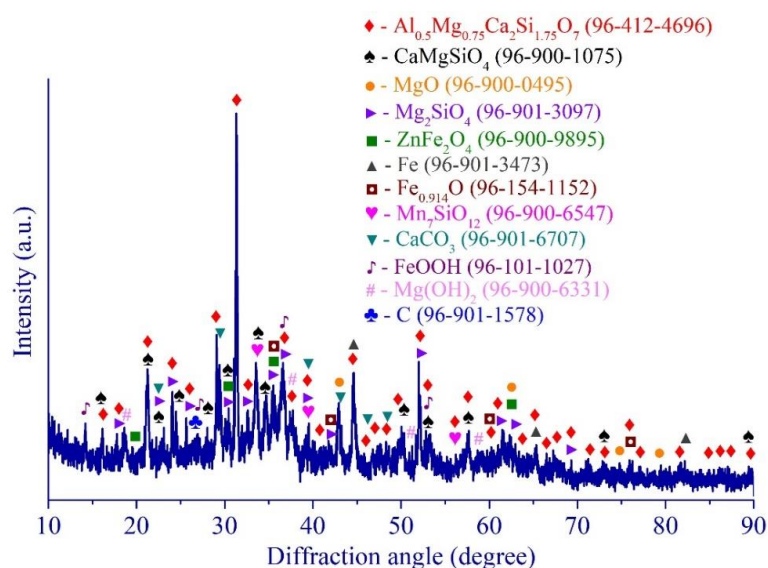


Figure 9. The XRD pattern of the froth floated Waelz slag sample.

The reduction smelting experiments were carried out with the froth-floated Waelz slag sample; it was found that full metal-slag separation occurs at 1500 °C and above. Figure 10 demonstrates the separated samples after smelting at 1500 and 1600 °C. These results are more consistent with the thermodynamic simulation (Figure 3) and the presented pseudo-ternary diagram (Figure 6) than the previous results of the reduction smelting of the Waelz slag without the treatment (Section 3.2.1), where there was no metal-slag separation even at 1750 °C. Accordingly, it is important to emphasize that carbon content in the Waelz slag is crucial for reduction smelting results.

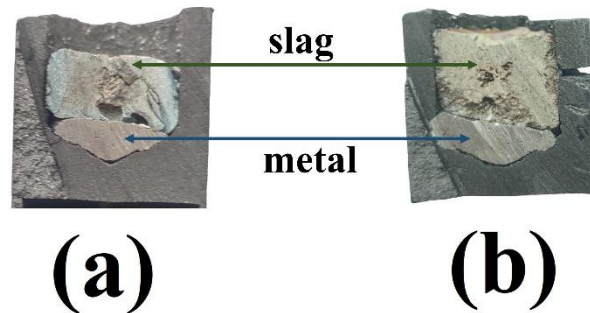


Figure 10. The samples after the reduction smelting of the froth-floated Waelz slag sample at 1500 (a) and 1600 °C (b).

Figure 11 and Table 5 show the composition of metal and slag samples from the reduction smelting of the froth-floated Waelz slag, respectively. According to carbon content, the metal samples correspond to pig iron. The contents of C, Si, Cu are proved to be close to the simulation results (Figure 4a). The content of Mn is lower than expected, but the trend with the temperature is similar. Moreover, the manganese content is less than in the samples from the smelting with SiO₂ (Figures 7a and 8a) that is likely due to less content of dissolved silicon acting in manganese reduction [48]. Phosphorus content is proved to be significantly lower than the calculated value, which is favorable. The contents of S, Cr, As, Sb, Ni differ insignificantly from the samples from the smelting with SiO₂.

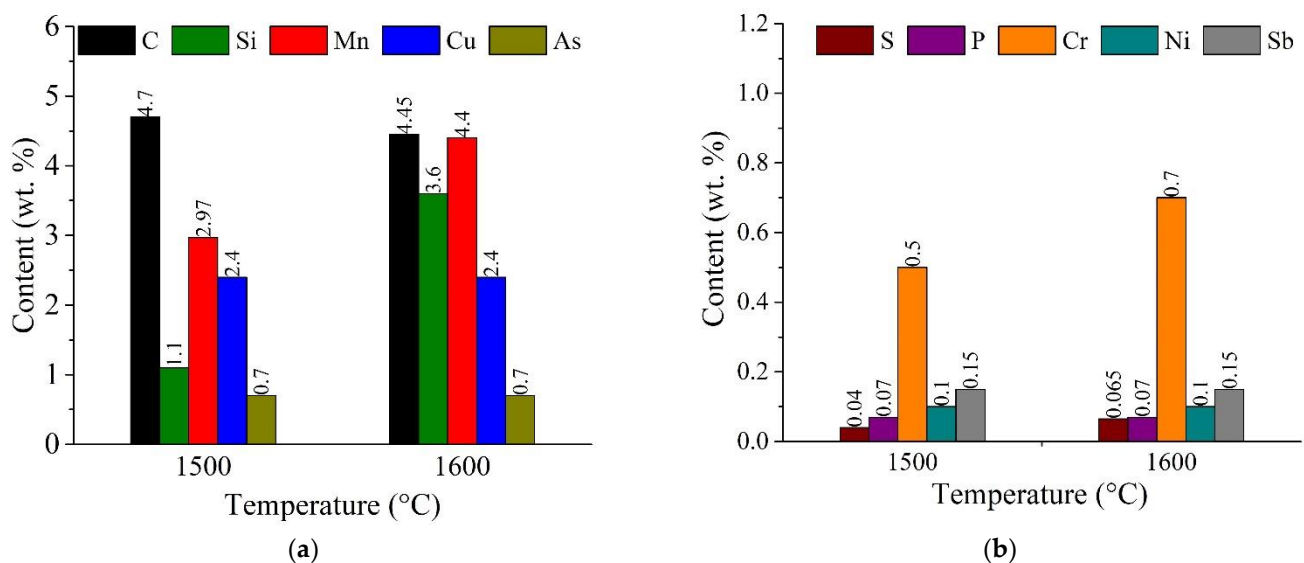


Figure 11. The effect of temperature on the contents of C, Si, Mn, Cu, As (a) and S, P, Cr, Ni, Sb (b) in the iron-based alloy obtained by the reduction smelting of the froth-floated Waelz slag sample.

Table 5. The effect of temperature on the chemical composition of slag obtained by reduction smelting of the froth floated Waelz slag sample.

Reduction Smelting Temperature, °C	Slag Composition, wt. %											
	CaO	SiO ₂	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	Mn	Cr	P	S	Fe
1–13 1500	30.85	29.87	16.02	7.43	0.11	0.12	0.78	1.35	0.05	0.01	0.60	2.30
1600	31.23	28.60	16.25	7.50	0.11	0.12	0.62	2.40	0.06	0.01	0.10	1.70

3.2.4. Optimal Reduction Smelting Conditions and Physical Testing of the Obtained Slag

Despite possible advantages of the approach with the froth flotation such as decreased temperatures of the reduction smelting and possibility of the recycling of carbon concentrate, it seems to be economically unviable due to high costs and considerable energy losses of cooling, grinding, flotation and pelletizing stages. Therefore, the reduction smelting of the Waelz slag with SiO₂-containing flux was considered as the primary approach. The minimal smelting temperature and the SiO₂ addition to obtain metal and slag were 1650 °C and 15%, respectively (Table 2). However, due to a high loss of Fe with slag at those conditions (Table 3), we have chosen the reduction smelting at 1650 °C with 18% SiO₂ as optimal. To elucidate the properties of the smelting slag, we repeated the treatment of the Waelz slag sample of increased portion at the optimal conditions. Figure 12 presents a photograph of the metal and slag sample in and out of the crucible after the reduction smelting of 300 g of the Waelz slag sample with the addition of 54 g SiO₂, which evidences the successful separation.

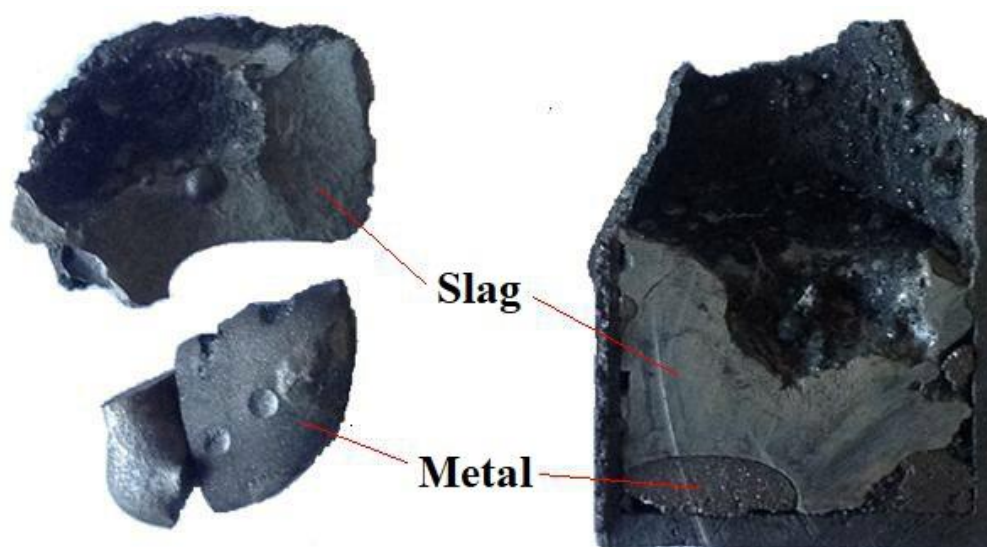
**Figure 12.** The samples after the reduction smelting of the Waelz slag sample at 1650 °C with the addition of 18% SiO₂.

Table 6 shows the chemical composition of the obtained alloy and compares it with the selected Russian State Standards. As can be seen, there is no full compliance of the alloy composition with the requirements. The closest chemical composition to the obtained metal sample is proved to be ferrosilicon FeSi10, but a discrepancy by manganese, chromium and phosphorus content was observed. It also should be noted the presence of high content of copper, arsenic and antimony, which are not rated, but may affect the applicability of the alloy. An adjustment of the charge can be used to obtain a standards-compliant alloy for phosphorus and chromium contents, which slightly exceeds the requirements in our case. The manganese content in the alloy significantly exceeds the requirements, hence it is impossible to reduce substantially its content in the metal sample by charge dilution. It also seems to be impossible to control the charge of the Waelz process by the content of

manganese due to its high content in the EAF dust [1]. It is well-known that low-silicon ferrosilicon is commonly used as a charge in the melting of foundry cast iron [49]. Taking into account the composition of the obtained alloy, we deem expedient to use it as a charge for the smelting of alloyed cast iron grades with a high content of copper and manganese (see the composition of cast iron ChG8D3, Table 6).

Table 6. A comparison of composition of the metal sample after the reduction smelting of the Waelz slag sample at 1650 °C with the addition of 18% SiO₂ with some state standards, wt.%.

Alloy	C	Si	Mn	S	P	Cu	Cr	As	Sb
Obtained	0.48	12.67	4.27	0.01	0.19	1.86	0.83	0.22	0.07
Cast iron L1 (GOST 4832-95)	3.2–3.6	3.1–3.6	0.9–1.5	≤0.04	≤0.7	-	≤0.1	-	-
Cast iron L2 (GOST 4832-95)	2.8–3.2	2.8–3.2	0.9–1.5	≤0.04	≤0.7	-	≤0.1	-	-
Pig iron P1 (GOST 805-95)	-	0.5–0.9	>1.5	≤0.06	≤0.3	≤0.3	-	-	-
Pig iron P2 (GOST 805-95)	-	<0.5	>1.5	≤0.06	≤0.3	≤0.3	-	-	-
Pig iron PL1 (GOST 805-95)	4.0–4.5	0.9–1.5	≤1.5	≤0.06	≤0.3	≤0.3	≤0.04	-	-
Pig iron PL2 (GOST 805-95)	4.0–4.5	0.5–0.9	≤1.5	≤0.06	≤0.3	≤0.3	≤0.04	-	-
Cast iron ChS13 (GOST 7769-82)	0.6–1.4	12–14	≤0.8	≤0.07	≤0.1	-	-	-	-
Cast iron ChS15 (GOST 7769-82)	0.3–0.8	14.1–16	≤0.8	≤0.07	≤0.1	-	-	-	-
FeSi10 (GOST 1415-93)	≤2	8–13	≤3	≤0.06	≤0.15	-	≤0.8	-	-
Cast iron ChG8D3 (GOST 7769-82)	3–3.8	2–2.5	7–9	≤0.1	≤0.3	2.5–3.5	-	-	-

Table 7 and Figure 13 demonstrate the chemical composition and the XRD pattern of the obtained slag, respectively.

Table 7. The chemical composition of slag obtained by reduction smelting of the Waelz slag sample with the addition of 18% SiO₂ at 1650 °C.

CaO	SiO ₂	MgO	Al ₂ O ₃	BaO	Na ₂ O	K ₂ O	TiO ₂	Mn	Cr	P	S	Fe
28.5	40.8	14.9	7.54	0.47	0.53	0.2	0.24	0.84	0.14	0.02	1.66	1.74

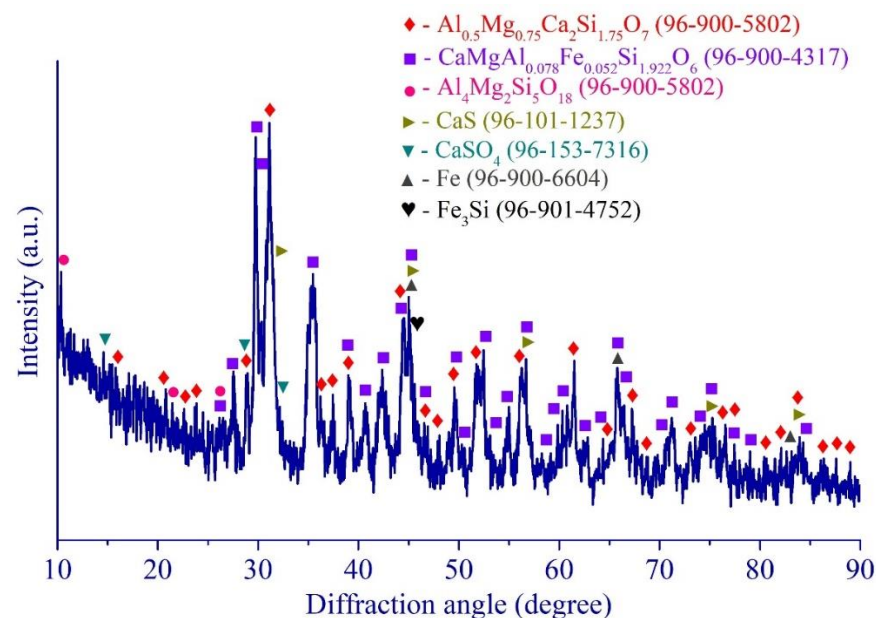


Figure 13. The XRD pattern of the slag sample obtained by the reduction smelting of the Waelz slag with the addition of 15% SiO₂ at 1650 °C.

The slag mainly consists of calcium, silicon, and magnesium oxides, while the total content of alkali metal oxides (K₂O + Na₂O) is 1.13%. The main slag minerals are melilite Ca₂Mg_{1-x}Al_xSi₂O₇ and diopside CaMgSi₂O₆. The slag also contains 1.74% iron, distributed

between pure metallic iron and iron silicide (Fe_3Si). Sulfur is present both in the form of calcium sulfide CaS and calcium sulfate CaSO_4 .

Figure 14 illustrates the effect of the slag sample addition to Portland cement on its compressive strength.

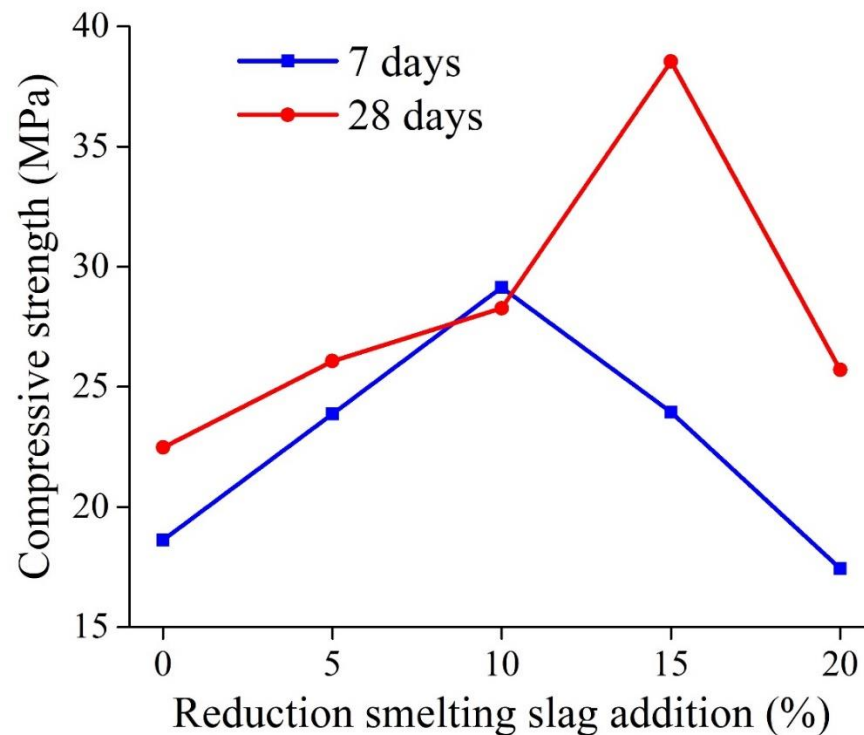


Figure 14. Effect of the Waelz slag addition to 100% of Portland cement on compressive strength of cement-sand mixture after 7 and 28 days of curing.

As it appears from the plot, after 28 days of curing, the addition of the reduction smelting slag up to 15% increases the Portland cement strength and then decreases at 20% of the addition. The compression strength grew up after 7 days of curing by 56% at 10% of the addition, while after 28 days at 15% it rose by 71%. Such results are due to the slag mineralogical composition. Melilite, the main phase of the slag, is considered to have almost no hydration reactivity [50], but there is no an adverse effect on Portland cement properties when it is added up to a certain percentage [51]. Diopside has also poor hydration reactivity under normal conditions [52]. However, the addition of hydroxides, chlorides or sulfates of magnesium and calcium can significantly increase diopside hydration reactivity [53]. This fact likely led to a substantial increase in compressive strength (Figure 14) due to the presence of CaSO_4 in the sample (Figure 13). Thus, the results have pointed out that the application of the slag as a mineral additive to Portland cement can improve its physical and mechanical properties.

4. Discussion

The study has confirmed the technological possibility of reduction smelting of the Waelz slag from EAF dust processing to produce an iron-based alloy. Two approaches were applied: the reduction smelting with SiO_2 -containing flux and the reduction smelting after the froth flotation. Figure 15 clearly demonstrates the flowsheet of two approaches investigated in this study. Table 8 qualitatively compares the main characteristics of the studied approaches.

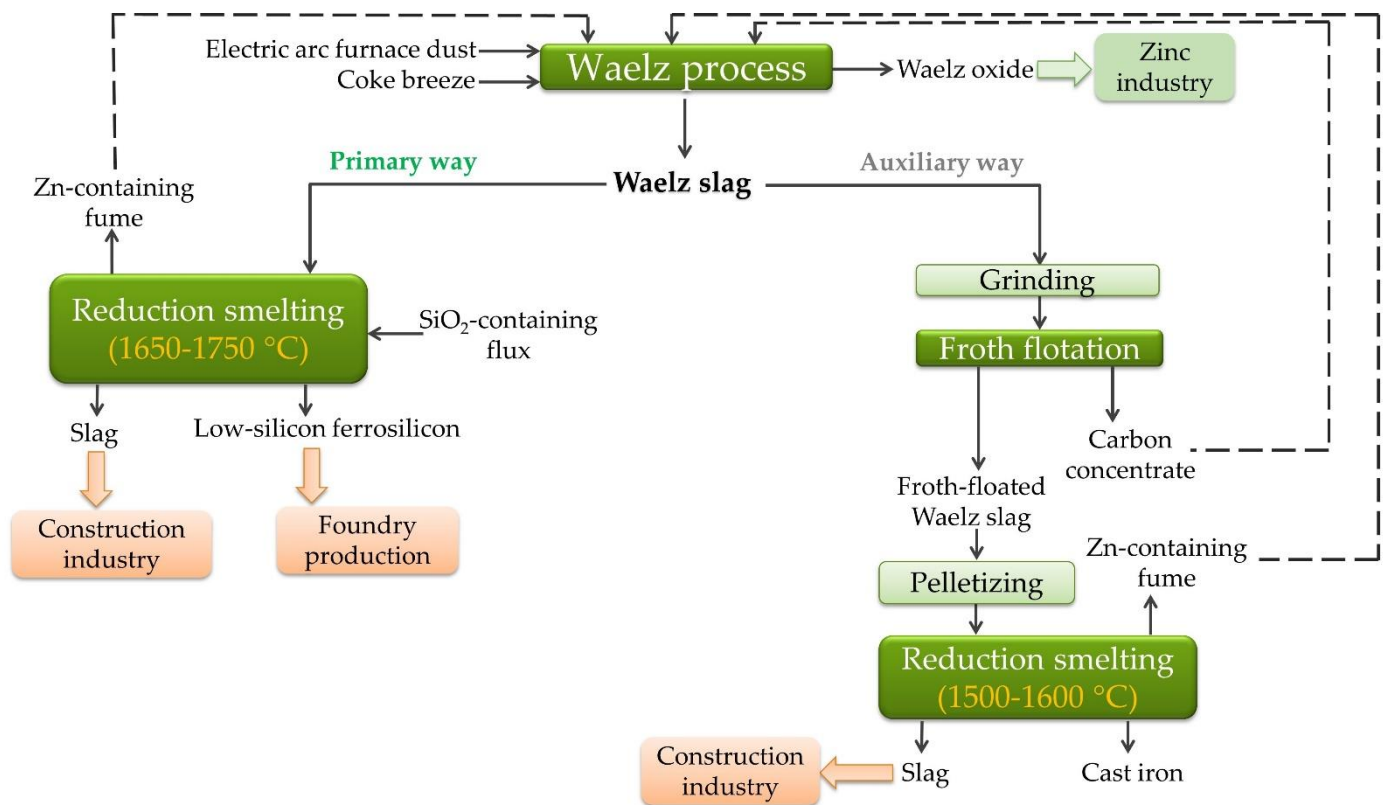


Figure 15. The flowsheet of two approaches based on the reduction smelting of the Waelz slag studied in this work.

Table 8. A comparison of two approaches for the Waelz slag processing considered in this study.

Attribute	Primary Approach	Auxiliary Approach
Essence	Reduction smelting of the Waelz slag sample with SiO_2 -containing flux	Reduction smelting of the froth floated Waelz slag sample with decreased carbon content
Smelting temperature	1650 °C	1500 °C
Obtained alloy	Low-silicon ferrosilicon	Cast iron
Slag	Attractive for construction industry	Attractive for construction industry
Zn-containing fume	Recyclable in the Waelz process	Recyclable in the Waelz process
Cooling	Dispensable	Yes
Grinding	No	Yes
Froth flotation	No	Yes
Pelletizing	Dispensable	Yes
Carbon concentrate	No	Yes

As mentioned above and clearly shown from the presented data, the approach with the froth flotation is less attractive economically due to higher cost stages.

The primary approach vaguely resembles the PRIMUS® process [54], where instead of the Waelz kiln, a multiple-hearth furnace is used, which produces direct reduced iron (DRI). Then DRI reduction smelting was applied to obtain impure pig iron, which is used as a charge along with metal scrap for another EAF to produce raw steel. To comply with the targeted steel quality, the charge consisting of only 25% of the impure pig iron and 75% of metal scrap was used in the process. A similar way to comply with the standards for metal can be also considered in our case.

The separation of metal and slag during the reduction smelting of the Waelz slag from EAF dust processing has proved to be complicated due to high carbon content. It is noteworthy that carbon of coke breeze added in the Waelz kiln is used as a reductant

and fuel, as well as inhibits processes of melting and sticking [4]. It is unfavorable in the case of carbon excess for the subsequent reduction smelting due to an increase in the slag viscosity and hence the impossibility of the separation of metal and slag. However, in order to improve the separation, fluxing additives or carbon excess elimination can be applied. Another way to improve characteristics of the reduction smelting is condition modification of the Waelz process to obtain more favorable composition of the Waelz slag. The enhancement of the Waelz process, especially in order to obtain a low carbon content in the Waelz slag, should be considered as the one of the main ways to optimize the conditions and improve the quality of the products of the subsequent reduction smelting.

5. Conclusions

Based on the thermodynamic calculation and laboratory experiments, the study of the reduction smelting of the lime rich Waelz slag has pointed out as follows:

- The reduction smelting at 1650 °C for 30 min of the Waelz slag sample containing 18.7% carbon with the addition of 18% SiO₂ led to obtaining low-silicon ferrosilicon with high Cu content, as well as slag attractive for construction industry;
- The reduction smelting at 1500 °C for 30 min of the froth-floated Waelz slag sample containing 5.1% carbon resulted in the production of high-copper cast iron, slag; carbon concentrate of 68% C suitable for recycling in the Waelz process is also generated during froth flotation.

Author Contributions: Conceptualization, P.G., D.Z. and P.K.; methodology, P.G., D.Z., A.K., L.D. and R.K.; software, A.K., D.Z. and P.G.; validation, P.G. and D.Z.; formal analysis, P.G. and A.K.; investigation, D.Z., L.D., R.K., A.L. and P.G.; resources, V.D.; data curation, D.Z. and P.G.; writing—original draft preparation, P.G.; writing—review and editing, D.Z.; visualization, P.G.; supervision, P.G. and D.Z.; project administration, V.D.; funding acquisition, V.D. and P.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research of primary approach was funded by UMMC Technical University, contract number 339-2018-NIR. The research of auxiliary approach was carried out within Russian state assignment, number 075-01176-23-00.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: The authors would like to appreciate the Chemical Analytical Laboratory of the JSC “Design & Survey and Research & Development Institute of Industrial Technology” for chemical analysis. The authors are also grateful to Alexander Ilyushechkin (CSIRO, Australia) for his assistance in thermodynamic calculations.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Stefanova, A.; Aromaa, J. Dust formation in iron and steel industry. In *Alkaline Leaching of Iron and Steelmaking Dust*; Aalto University: Helsinki, Finland, 2012; pp. 6–22.
2. Global Steel Dust Ltd. Available online: <http://www.globalsteeldust.com/about> (accessed on 16 December 2022).
3. Yakornov, S.A.; Panshin, A.M.; Kozlov, P.A.; Ivakin, D.A. Current state of electrical arc furnace dusts processing in Russia and abroad. *Tsvetnye Met.* **2017**, *4*, 23–29. [CrossRef]
4. Kozlov, P.A. *The Waelz Process*; Ore and Metals PH: Moscow, Russia, 2003.
5. Popovici, V. By-Products from EAF Dust Recycling and Their Valorisation. Available online: <https://cdn.shawcor.com/shawcor/files/f5/f5469bfd-e3a2-4c95-9201-550c7c30e2fc.pdf> (accessed on 16 December 2022).
6. Barna, R.; Bae, H.R.; Méhu, J.; Van der Sloot, H.; Moszkowicz, P.; Desnoyers, C. Assessment of chemical sensitivity of Waelz Slag. *Waste Manag.* **2000**, *20*, 115–124. [CrossRef]
7. Bae, H.R.; Barna, R.; Méhu, J.; Van der Sloot, H.; Moszkowicz, P.; Desnoyers, C. Assessment of Chemical Sensitivity of Waelz Slag. *Stud. Environ. Sci.* **1997**, *71*, 647–660. [CrossRef]
8. Onuk, P.; Melcher, F. Mineralogical and Chemical Quantification of Waelz Slag. *Int. J. Miner. Process. Extr. Metall.* **2022**, *7*, 50–60. [CrossRef]
9. Mombelli, D.; Mapelli, C.; Barella, S.; Gruttadauria, A.; Di Landro, U. Laboratory investigation of Waelz slag stabilization. *Process Saf. Environ. Prot.* **2015**, *94*, 227–238. [CrossRef]

10. Abbà, A.; Sorlini, S.; Collivignarelli, M.C. Research experiences on the reuse of industrial waste for concrete production. *MATEC Web Conf.* **2017**, *121*, 1–8. [\[CrossRef\]](#)
11. Quijorna, N.; Miguel, G.S.; Andrés, A. Incorporation of waelz slag into commercial ceramic bricks: A practical example of industrial ecology. *Ind. Eng. Chem. Res.* **2011**, *50*, 5806–5814. [\[CrossRef\]](#)
12. Quijorna, N.; Coz, A.; Andres, A.; Cheeseman, C. Recycling of Waelz slag and waste foundry sand in red clay bricks. *Resour. Conserv. Recycl.* **2012**, *65*, 1–10. [\[CrossRef\]](#)
13. Muñoz, I.; Cifrian, E.; Andrés, A.; Miguel, G.S.; Ruiz, D.; Viguri, J.R. Analysis of environmental benefits associated with the incorporation of Waelz slag into fired bricks using LCA. *Constr. Build. Mater.* **2018**, *168*, 178–186. [\[CrossRef\]](#)
14. Cifrian, E.; Coronado, M.; Quijorna, N.; Alonso-Santurde, R.; Andrés, A. Waelz slag-based construction ceramics: Effect of the trial scale on technological and environmental properties. *J. Mater. Cycles Waste Manag.* **2019**, *21*, 1437–1448. [\[CrossRef\]](#)
15. Li, N.; He, Y.L.; Yi, Z.Z.; Gao, L.; Zhai, F.R.; Chattopadhyay, K. Multiple-metal-doped Fe₃O₄@Fe₂O₃ nanoparticles with enhanced photocatalytic performance for methyl orange degradation under UV/solar light irradiation. *Ceram. Int.* **2020**, *46*, 19038–19045. [\[CrossRef\]](#)
16. Jiang, Y.; Sun, L.D.; Li, N.; Gao, L.; Chattopadhyay, K. Metal-doped ZnFe₂O₄ nanoparticles derived from Fe-bearing slag with enhanced visible-light photoactivity. *Ceram. Int.* **2020**, *46*, 28828–28834. [\[CrossRef\]](#)
17. Vegas, I.; Ibañez, J.A.; San José, J.T.; Urzelai, A. Construction demolition wastes, Waelz slag and MSWI bottom ash: A comparative technical analysis as material for road construction. *Waste Manag.* **2008**, *28*, 565–574. [\[CrossRef\]](#)
18. Besta, P.; Janovská, K.; Samolejová, A.; Beránková, A.; Vozňáková, I.; Hendrych, M. The cycle and effect of zinc in the blast-furnace process. *Metalurgija* **2013**, *52*, 197–200.
19. Rösler, G.; Pichler, C.; Antrekowitsch, J.; Wegscheider, S. “2sDR”: Process Development of a Sustainable Way to Recycle Steel Mill Dusts in the 21st Century. *JOM* **2014**, *66*, 1721–1729. [\[CrossRef\]](#)
20. Pichler, C.; Antrekowitsch, J. Recycling of Zinc- and Lead-Bearing Residues with Pyrolysis Gas. *JOM* **2015**, *67*, 2038–2046. [\[CrossRef\]](#)
21. Pichler, C.; Antrekowitsch, J. Pyrolysis Gas as a Renewable Reducing Agent for the Recycling of Zinc- and Lead-Bearing Residues: A Status Report. *JOM* **2017**, *69*, 999–1006. [\[CrossRef\]](#)
22. Fröhling, M.; Schwaderer, F.; Bartusch, H.; Schultmann, F. A Material Flow-based Approach to Enhance Resource Efficiency in Production and Recycling Networks. *J. Ind. Ecol.* **2013**, *17*, 5–19. [\[CrossRef\]](#)
23. Holmes, R.J.; Lu, Y.; Lu, L. Chapter 1—Introduction: Overview of the global iron ore industry. In *Iron Ore Mineralogy, Processing and Environmental Sustainability*; Lu, L., Ed.; Woodhead Publishing: Sawston, UK, 2022; pp. 1–56. ISBN 978-0-12-820226-5.
24. Hu, J.; Li, Y.; Wu, K.; Liu, F.; Zhu, Q.; Li, Y. The exploration on synthesis of calcium aluminate and Fe-Si alloys using red mud and aluminum dross. *Adv. Mater. Res.* **2010**, *97–101*, 1104–1108. [\[CrossRef\]](#)
25. Balomninos, E.; Kastiris, D.; Parias, D.; Paspaliaris, I.; Boufounos, D. The Enxal Bauxite Residue Treatment Process: Industrial Scale Pilot Plant Results. In *Light Metals 2014*; Grandfield, J., Ed.; Springer: Cham, Switzerland, 2014; pp. 143–147.
26. Zinoveev, D.V.; Diubanov, V.G.; Shutova, A.V.; Ziniaeva, M.V. Recycling of red muds with the extraction of metals and special additions to cement. *Russ. Metall.* **2015**, *2015*, 19–21. [\[CrossRef\]](#)
27. Dildin, A.N.; Trofimov, E.A.; Chumanov, I.V. Process improvement for liquid-phase metal reduction from steelmaking dump slags. *Indian J. Sci. Technol.* **2016**, *9*, 1–10. [\[CrossRef\]](#)
28. Ma, J.; Zhang, Y.; Hu, T.; Sun, S. Utilization of converter steel slag by remelting and reducing treatment. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *382*, 022088. [\[CrossRef\]](#)
29. Sheshukov, O.Y.; Egiazar'yan, D.K.; Lobanov, D.A. Wasteless processing of ladle furnace and electric arc furnace slag. *Izv. Ferr. Metall.* **2021**, *64*, 192–199. [\[CrossRef\]](#)
30. Tzevelekou, T.V.; Geck, H.G.; Van Hüllen, P.; Höfer, F.; Papamantellos, D.C. Direct smelting of metallurgical dusts and ore fines in a 125t DC-HEP furnace. *Steel Res. Int.* **2004**, *75*, 382–391. [\[CrossRef\]](#)
31. Tzevelekou, T.; Lampropoulou, P.; Giannakopoulou, P.P.; Rogkala, A.; Koutsovitis, P.; Koukouzas, N.; Petrounias, P. Valorization of slags produced by smelting of metallurgical dusts and lateritic ore fines in manufacturing of slag cements. *Appl. Sci.* **2020**, *10*, 4670. [\[CrossRef\]](#)
32. Kumar, P.; Patra, S.K.; Tripathy, S.K.; Sahu, N. Efficient utilization of nickel rich Chromite Ore Processing Tailings by carbothermic smelting. *J. Clean. Prod.* **2021**, *315*, 128046. [\[CrossRef\]](#)
33. Wang, J.P.; Erdenebold, U. A study on reduction of copper smelting slag by carbon for recycling into metal values and cement raw material. *Sustainability* **2020**, *12*, 1421. [\[CrossRef\]](#)
34. Erdenebold, U.; Wang, J.P. Chemical and mineralogical analysis of reformed slag during iron recovery from copper slag in the reduction smelting. *Arch. Metall. Mater.* **2021**, *66*, 809–818. [\[CrossRef\]](#)
35. Zhu, M.L.; Xiao, N.; Tang, L.C.; Zhong, S.P.; Lü, X.L.; Chi, X.P. Preparation of new cementitious material by reduction and activation of copper slag and its application in mine filling. *Chinese J. Nonferrous Met.* **2020**, *30*, 2736–2745. [\[CrossRef\]](#)
36. Zheng, L.; Tao, J. Determination of iron(II) in direct reduced iron by iron trichloride decomposition-potassium dichromate titration. *Metall. Anal.* **2010**, *2*, 78–80.
37. Tao, J.; Zheng, L. Determination of metallic iron in direct reduced iron by potassium dichromate titration after decomposition of sample by ferric chloride. *Metall. Anal.* **2009**, *29*, 65–68.

38. Putz, H.; Brandenburg, K. Match!—Phase Identification from Powder Diffraction, version 3.12, Crystal Impact, Bonn. Available online: <https://www.crystalimpact.de/match> (accessed on 18 April 2022).
39. Vaitkus, A.; Merkys, A.; Grazulis, S. Validation of the Crystallography Open Database using the Crystallographic Information Framework. *J. Appl. Crystallogr.* **2021**, *54*, 661–672. [CrossRef] [PubMed]
40. Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Gheribi, A.E.; Hack, K.; Jung, I.H.; Kang, Y.B.; Melançon, J.; et al. Reprint of: FactSage thermochemical software and databases, 2010–2016. *Calphad* **2016**, *55*, 1–19. [CrossRef]
41. Delitsyn, L.M.; Ryabov, Y.V.; Kulumbegov, R.V. Method of extracting unburned carbon from TPP fly ash. European Patent RU2692334C1, 27 April 2018. issued: 24 June 2019.
42. Ghosh, A.; Chatterjee, A. *Ironmaking and Steelmaking: Theory and Practice*; PHI Learning Private Limited: New Delhi, India, 2008.
43. Schrama, F.N.H.; Beunder, E.M.; Panda, S.K.; Visser, H.J.; Moosavi-Khoonsari, E.; Sietsma, J.; Boom, R.; Yang, Y. Optimal hot metal desulphurisation slag considering iron loss and sulphur removal capacity part I: Fundamentals. *Ironmak. Steelmak.* **2021**, *48*, 1–13. [CrossRef]
44. Azof, F.I.; Kolbeinsen, L.; Safarian, J. Characteristics of Calcium-Aluminate Slags and Pig Iron Produced from Smelting-Reduction of Low-Grade Bauxites. *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **2018**, *49*, 2400–2420. [CrossRef]
45. Saito, N.; Hara, D.; Teruya, S.; Nakashima, K. Viscosity of slag suspensions with a polar liquid matrix. *ISIJ Int.* **2020**, *60*, 2807–2818. [CrossRef]
46. Filsinger, D.H.; Bourrie, D.B. Silica to Silicon: Key Carbothermic Reactions and Kinetics. *J. Am. Ceram. Soc.* **1990**, *73*, 1726–1732. [CrossRef]
47. Rubio, P.J.Y.; Sahajwalla, V. Carbon Dissolution Occurring during Graphite–Ferrosilicon Interactions at 1550 °C. *ISIJ Int.* **2009**, *49*, 1868–1873. [CrossRef]
48. Safarian, J.; Kolbeinsen, L.; Tangstad, M.; Tranell, G. Kinetics and mechanism of the simultaneous carbothermic reduction of FeO and MnO from high-carbon ferromanganese slag. *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **2009**, *40*, 929–939. [CrossRef]
49. Melting cast irons. In *Foseco Ferrous Foundryman's Handbook*; Brown, J.R., Ed.; Butterworth-Heinemann: Oxford, UK, 2000; pp. 40–61, ISBN 9780750642842.
50. Kurokawa, D.; Honma, K.; Hirao, H.; Fukuda, K. Quality design of belite-melilite clinker. *Cem. Concr. Res.* **2013**, *54*, 126–132. [CrossRef]
51. Gualtieri, A.F.; Boccaletti, M. Recycling of the product of thermal inertization of cement-asbestos for the production of concrete. *Constr. Build. Mater.* **2011**, *25*, 3561–3569. [CrossRef]
52. Grzeszczyk, S.; Szuba, J. Hydration Reactivity of Crystalline and Vitrified Diopside under Hydrothermal Conditions. *J. Am. Ceram. Soc.* **1990**, *73*, 2006–2008. [CrossRef]
53. Erdman, S.V.; Postnikova, A.N. Waterproof compound magnesia cement. *Fundam. Res.* **2013**, *8*, 773–778.
54. Roth, J.L.; Frieden, R.; Hansmann, T.; Monai, J.; Solvi, M. PRIMUS[®], a new process for recycling by-products and producing virgin iron. *La Rev. Métallurgie-CIT* **2001**, *98*, 987–996. [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.