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The Influence of Varying Thermal Treatment Conditions on Reducing Zinc Content from a Steelmaking and Blast Furnace Sludge

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Abstract: The prospects of processing blast furnace and steelmaking sludge using the Waelz process in a laboratory rotary kiln, is shown. The influence of different processing temperatures, furnace atmosphere and the type of reducing agents on the level of zinc reduction from sludges was analyzed. In general, the blast furnace sludge contains a high portion of iron (approx. 48 wt.%) and can be reused as a charge after satisfactory zinc reduction. It was found that N- atmosphere and a high content of the graphite or coke oven reducing agent in combination with high temperature can reduce the content of Zn in the sludge to 0.08 wt.% at 1200 °C for a mixture of steelmaking and blast furnace sludge. A significant reduction in the Zn content to 0.66 wt.% occurs at 1100 °C. The content and type of reducing agent plays an important role; graphite has shown a better reducing ability compared to coke oven dust. When nitrogen is used, zinc is reduced even without an additional reducing agent, since the carbon contained in the sludge is made use of for the reduction. In an air atmosphere, without the use of a reducing agent, there was no reduction in the Zn content.

Keywords: blast furnace sludges; steelmaking sludges; carbothermal reduction; Waelz-kiln process; zinc; zinc oxide

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1. Introduction

The importance of obtaining certain economically valuable components of waste is one of the key issues of waste policy for the green economy. From a global perspective, 50% of the largest sources of waste are industrial activity, 40% energy and 10% waste from the municipal sector, electronics [1] and agriculture. Industrial waste could be of various types, from tailings, through metallic and non-metallic waste, to highly toxic or otherwise dangerous substances.

As different components of metallurgical waste, we can distinguish blast furnace and steel dusts and sludges, oil sludges and sewage sludges. According to the state in which they occur, they can be divided into solid (slag, scale, returnable steel waste, etc.), liquid (sludge, water, oil, lye, etc.) and gaseous (flue gas, exhalation). Sludge can be further divided according to usability into: directly returnable waste (materials that can be returned to the metallurgical cycle without treatment, e.g., steel waste); returnable after treatment (metal-bearing substrates that need to be physically and chemically treated before reprocessing); metallurgically irreversible (raw materials usable in other sectors, e.g., blast furnace slag); and irreversible (mostly mixed materials, not yet usable, e.g., remnants of textiles, rubber, linings, oils). Furthermore, waste is divided into metal, metal-bearing and non-metal. Metal-bearing waste occurs in gaseous and condensed form, and the methods of their capture and the possibilities of their further processing are related to this. This group of waste includes the following materials: sludge and wastewater from agglomerations and blast furnaces; scale; steel dust and sludge; and metal-bearing fractions from the processing of steel slag [2,3].

Blast furnace and steelmaking sludges are a by-product of the production of pig iron, i.e., steel in blast furnaces and oxygen converters. Blast furnace sludges and dust are captured in certain types of separators in the process of cleaning blast furnace gas in a dry or wet way [4–6]. Some elements that these sludges contain (Cr, Pb, Cd, Zn, Na, K) are described as harmful, both for the environment and because they can cause problems in the blast furnace, especially the accumulation of zinc in the lining of the blast furnace, saturation in the molten metal and the subsequent expansion of its volume that destroys the lining [7]. For example, during the production of steel from scrap iron in an electric arc furnace, 11–20 kg of sludge is produced from each tone of steel [8].

The dominant component of blast furnace sludge is reduced iron, and carbon and blast furnace slag components, such as calcium or magnesium oxide. Zinc occurs here in the form of an oxide. Table 1 shows an example of the chemical composition of blast furnace sludge [5]. Table 2 gives examples of the chemical composition of steelmaking sludges.

Table 1. Chemical composition of blast furnace sludge [wt.%] [5].

Fe	ZnO	C	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Pb	LOI
33.94	3.57	16.30	5.54	1.90	6.52	2.82	1.64	0.92	0.29	13.04

Table 2. Chemical composition of steelmaking sludge [wt.%].

Source	**Ca**	**Fe**	**Mg**	**Mn**	**Pb**	**Zn**	**Author**
Dofasco Hamilton	-	61.0	-	-	-	1.59	Kelebek [9]
Dofasco Hamilton	-	50.16	-	-	-	2.4	Goetz [10]
Tata Steel Port	-	-	-	-	-	4.8	Steer [11]
Tata Steel Port	3.0	50.0–80.0	0.20–5.0	0.40–2.20	0.20–1.80	1.7–6.5	Heinrich [12]
ArcelorMittal	4.18	50.65	1.49	-	0.07	4.37	Cantarino [13]
US Steel Košice	5.5	49.87	2.68	-	0.24	9.37	Vereš [14]

In general, the processes of recovering valuable metals from dust can be divided into dry and wet processing. Dry includes the Waelz method and the plasma method. Electrolytic wet processing involves the method of using an alkaline leach solution and an acid leach solution [6].

One of the very harmful elements, which must be removed from sludge before their reuse, is zinc. Zinc has a negative effect across equipment in the metallurgical industry, reducing the service life of blast furnace linings and steel aggregates, and at the same time its occurrence in steel is undesirable. In 2020, 12,000 kt of zinc were mined worldwide, of which approximately 30 % came from recycled or secondary zinc. Sources of recycled zinc include galvanized steel waste, zinc from car batteries and, more recently, zinc from blast furnace and steelmaking sludges [15].

According to a study by Wang et al. [16], approximately 80 % of the Waelz kilns rotary kiln is now used to recycle these sludges. Therefore, research into recycling the material in these furnaces has environmental and economic benefits. In January 2022, the market price of zinc was approximately 3600 USD/ton; in April 2022 the market price of zinc was 4331 USD/ton [17]. The Waelz process, see Figure 1, is a method of recovering zinc and other relatively low boiling-point metals from metallurgical waste (typically EAF flue dust) and other recycled materials using a rotary kiln or similar equipment [18,19]. The process is based on the carbothermal reduction of Zn and Fe oxides. This is shown by the following Equations (1)–(4), which are described in a number of publications and used by the author [20] below:

$$ZnO\ (s) + CO\ (g) \rightarrow Zn\ (g) + CO_2\ (g) \quad (1)$$

$$Fe_2O_3\ (s) + 3\ CO\ (g) \rightarrow Fe\ (s) + 3\ CO_3\ (g) \quad (2)$$

$$Zn\ (g) + \frac{1}{2} O_2\ (g) \rightarrow ZnO\ (s) \quad (3)$$

$$CO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow CO_2\ (g) \quad (4)$$

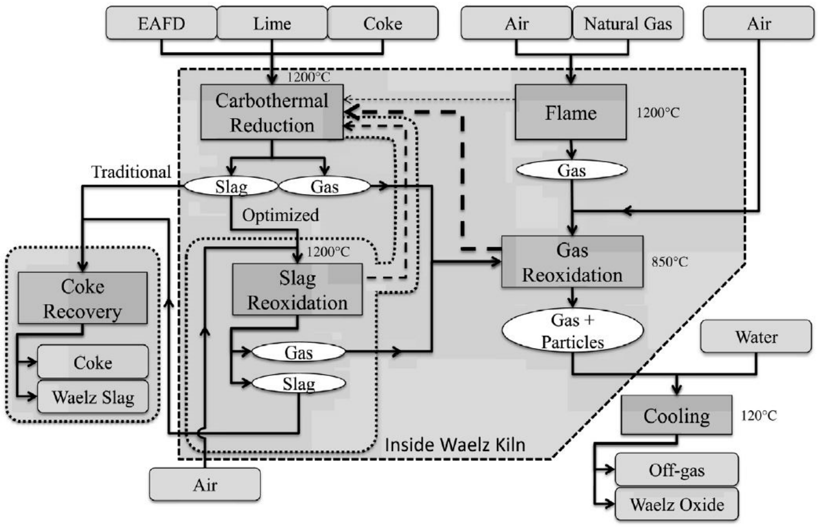

Figure 1. Schema of Waelz process [18].

These processes take place in a rotary kiln at temperatures of approximately 1200 °C. The sludge is mixed with carbon or a slag-forming agent and placed in a furnace. The carbon reduces the dust, forcing the volatile elements such as Zn, Pb and Cd along with halides to evaporate [8].

The process flow sheet of the Waelz kiln process shows both the traditional and the optimized operation. The gray-rounded rectangles represent the input and output streams, while internal-process streams are represented as white ellipses. For the optimized operation, the slag stream is first treated in the slag reoxidation reaction before passing through the coke recovery treatment, whereas for the traditional operation, the slag is only treated with coke recovery. The dashed arrows in this figure indicate the heat flow in the process [8].

The authors [20] performed an experiment in a horizontal tube furnace with a nitrogen atmosphere for testing the efficiency of the carbothermal reduction of ZnO with the addition of $CaCO_3$, Fe_2O_3 and iron scale at different temperatures. The purity of the substances used in the case of Fe_2O_3, ZnO and $CaCO_3$ was 99.9 wt.% and in the case of graphite 99.99 wt.%. The chemical composition of iron scale was 59.20 wt.% FeO and 39.03 wt.% Fe_2O_3. Other authors found that the optimal ratio of ZnO:Fe_2O_3 is 1:0.05 and that with increasing temperature the reduction of Zn from sludge increases. Better results were obtained using iron scales containing 59.20 wt.% FeO and 39.03 wt.% Fe_2O_3. The best results were obtained using a ratio of 1:0.10 for ZnO:Fe scale. The highest reduction rate was achieved using $CaCO_3$. The acceleration of the reaction after the addition of $CaCO_3$ is the decomposition of $CaCO_3$ into CaO and CO_2, which participates in the Boudouard reaction. The ideal ratio of ZnO to $CaCO_3$ is 1:0.10 [21].

Carbon and methane can serve as an effective reducing agent for zinc reduction. The reducing ability of methane can be used in the removal of zinc compounds from metallurgical waste. The main source of zinc is zinc oxide, the removal of which proceeds according to the Equation (5) [20,22]:

$$2\ ZnO + CH_4\ (g) \rightarrow 2\ Zn + CO_2\ (g) + 2\ H_2\ (g) \quad (5)$$

The author [20] performed an experiment in which dust from a foundry furnace with a high zinc content was heated at a rate of 10 °C.min^{-1} with 90 min. withstands a temperature of 900 °C and subsequent cooling at a rate of 10 °C.min^{-1} with a constant supply of CH_4 and an inert gas (Ar, N_2). A simple furnace of square cross-section filled from above with the possibility of a gas supply and exhaust was used for heating. The reaction itself described in Equation (5) proceeds at a temperature of 900 °C, and the reduced zinc, whose boiling point is 907 °C, evaporates immediately [20].

In our study, we would like to point out that from an ecological, raw material and economic aspect, it is very important to ensure that waste from production plants is subsequently converted into usable raw materials. Many components of the recycled metallurgical waste are used either in the company itself or in other industries and advanced technologies [22]. Due to the current low use of sludge as a secondary raw material, this work is focused on the influence of varying thermal treatment conditions on reducing zinc content from a steelmaking and blast furnace sludge.

2. Materials and Methods

The experimental part is divided to experiment in kiln and characterization of the obtained products. A total of 41 experiments to reduce the content of Zn from metallurgical sludges were carried out in laboratory rotary kiln type 8016T-MMV (Czech Republic, CLASIC CZ, 2020), see Figure 2.

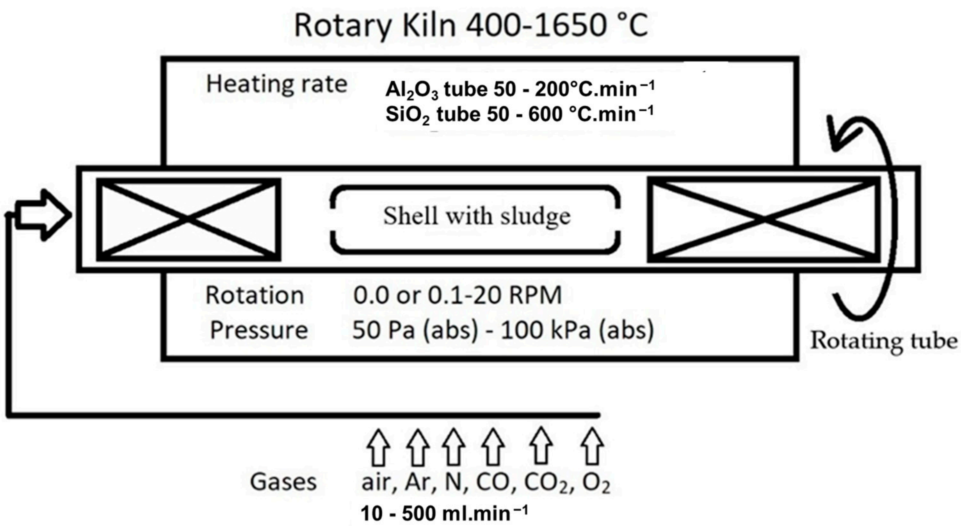

Figure 2. Experimental scheme of technological process in laboratory rotary kiln.

The chemical composition of the steelmaking sludge (SS) and mixtures of steelmaking and blast furnace sludge (SS + BFS) and coke oven dust (COD) used for experiments is shown in Table 3. X-ray fluorescence spectroscopy analysis {XRFS] was used to determine the elemental content. Samples for XRFS analysis were prepared on a FLUXANA VULCAN device (HD ELEKTRONIK, Kreßberg, Germany) that allows via the fusion technology to prepare samples to be analyzed with an X-ray fluorescence machine. It is also used to improve precision over pressed powder technology. Subsequently, pellets samples were measured using an ARL ADVANT'X device (THERMO SCIENTIFIC, Reinach, Switzerland). Elements carbon and sulfur were analyzed using a CS 230 device (LECO, St. Joseph, MI, USA). The Fe content in the samples was determined using a LAMBDA 20 instrument, UV/VIS spectrometer (Waltham, MA, USA).

Table 3. The chemical composition of the steelmaking sludge and mixtures of steelmaking and blast furnace sludge and coke oven dust [wt.%] obtained from XRFS analysis.

	C	S	Fe_{metal}	FeO	Fe_2O_3	Fe_{total}	Al_2O_3	CaO	SiO_2	Cr_2O_3
Steelmaking sludge	4.30	0.11	0.21	11.65	55.63	48.17	0.880	1.80	2.200	0.230
Steelmaking and blast furnace sludge	2.34	0.1	0.01	14.58	55.19	2.37	0.319	1.43	1.805	0.255
Coke oven dust	15.60	x	x	x	5.80	x	18.06	2.88	28.59	0.03
	MgO	MnO	P_2O_5	TiO_2	V_2O_5	BaO	CdO	CuO	PbO	Zn
Steelmaking sludge	1.650	1.120	0.230	0.030	0.010	<0.01	<0.01	0.100	0.430	11.17
Steelmaking and blast furnace sludge	1.091	0.975	0.265	0.004	0.017	0.008	0.000	0.137	0.408	7.77
Coke oven dust	3.02	0.07	0.36	0.48	0.03	0.10	0.00	0.00	0.00	0.03

x—means was not detected.

During the experiments, the gases air and nitrogen (purity 99.99 % N) were used, as well as Graphite fine powder extra pure with a Particle size <50 µm (min. 99.5 %).

The weights in one experimental batch were as follows:

- SS+N—50 g of steelmaking sludge (SS) processed in a nitrogen atmosphere (N),
- SS+air—50 g of steelmaking sludge (SS) processed in an air atmosphere,
- SS+N+graphite—50 g of steelmaking sludge (SS) with the addition of 50 g of graphite processed in a nitrogen atmosphere (N),
- SS+BFS+air—50 g of a mixture of steelmaking (SS) and blast furnace sludge (BFS) processed in an air atmosphere,
- SS+BFS+air+COD—50 g of a mixture of steelmaking (SS) and blast furnace sludge (BFS) with the addition of 50 g of coke oven dust (COD) processed in an air atmosphere,
- SS+BFS+air+graphite—50 g of a mixture of steelmaking (SS) and blast furnace sludge (BFS) with the addition of 25 g of graphite processed in an air atmosphere,
- SS+BFS+air+COD+2.0RPM—50 g mixture of steelmaking (SS) and blast furnace sludge (BFS) with 50 g of coke oven dust (COD) in an air atmosphere with 0.5, 2.0 and 4.0 revolutions per second (RPM).

The experimental batch was poured into a ceramic shell of Al_2O_3 material. The shell was then inserted into a rotating ceramic tube of OD 90 mm/ID 80 mm and a length of 1200 mm made of Al_2O_3, located in a rotary kiln. In the rotary kiln, nitrogen or air was blown into the furnace with a flow rate of 150 $mL.min^{-1}$. The device is equipped with a rotating mechanism driving a ceramic tube with a set speed of 1.0 RPM. In the rotary kiln, the experiments were prepared in the temperature range 700–1200 °C with a heating rate and a cooling rate of 200 $°C.h^{-1}$, with a temperature control accuracy of 1 °C. The heat treating was performed for 2h at certain process temperature.

3. Results and Discussion

Thermally treated sludges were evaluated mainly in terms of changes in the Zn con tent, however, during processing a change in the content of Fe_2O_3, FeO, metallic Fe and C was observed.

In experimental batches that contained the reducing agent graphite or COD, or were processed in an inert nitrogen atmosphere, the Fe_2O_3 content was observed to be reduced, see Figure 3. Figure 3 shows that the reduction of the Fe_2O_3 content already occurs at temperatures above 900 °C and the most significant is the reduction of the Fe_2O_3 content at the temperature of 1100 °C. The most important observation for the experiment is that in the experimental batches that were thermally processed in an oxidizing air atmosphere and did not use a graphite or COD reducing agent, the Fe_2O_3 content has increased.

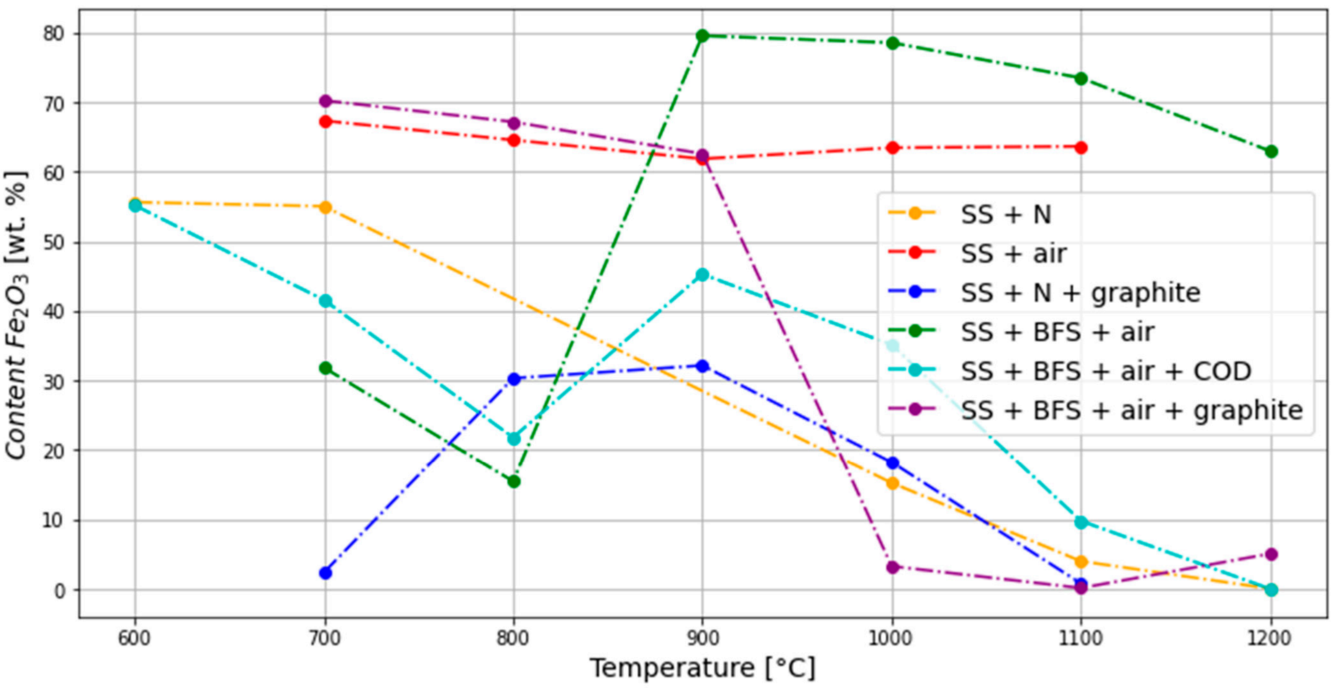

Figure 3. Effect of temperature, atmosphere and reducing element on Fe_2O_3 content in sludge.

The fluctuation of the values is visible in the case of SS+BFS+air+COD, however, reaching the key temperature above 900 °C, the content of observed oxide is getting comparable trend as other combination of agents it is gradually dropping.

The decrease in the Fe_2O_3 content occurred in individual batches with a simultaneous increase in the FeO content (Figure 4), and primarily with a simultaneous increase in the Fe metallic content (Figure 5).

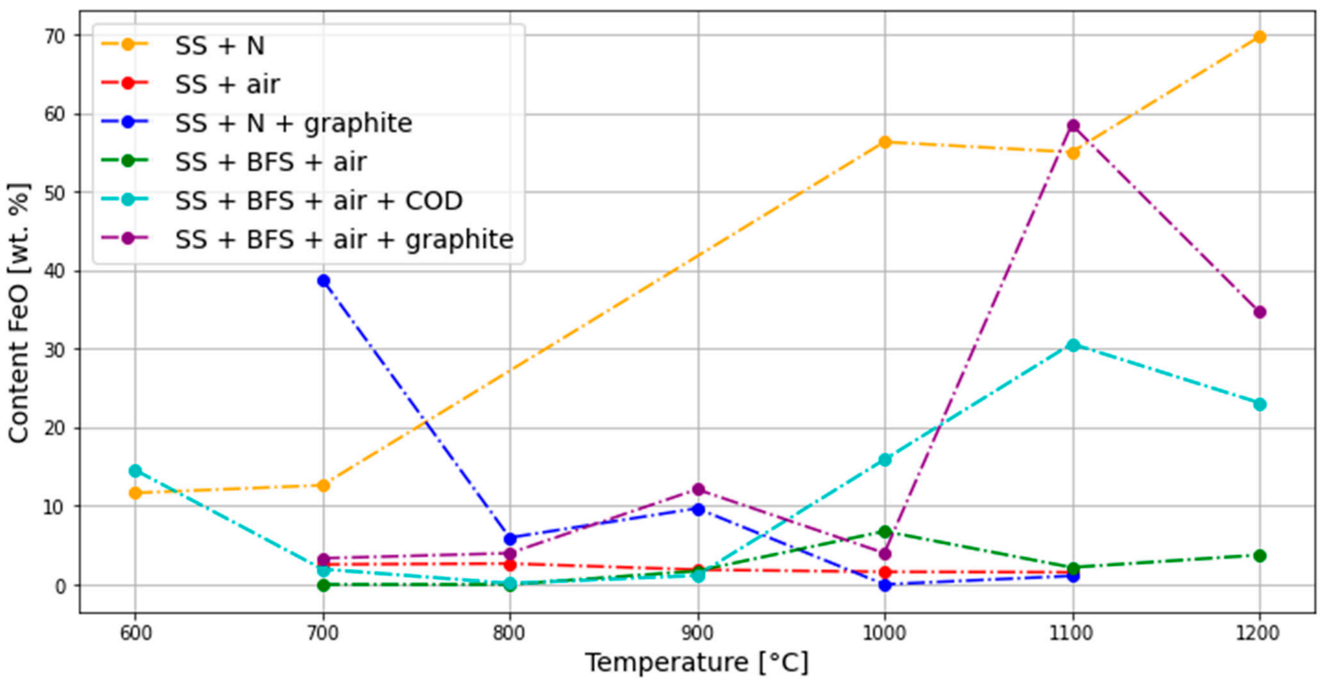

Figure 4. Effect of temperature, atmosphere and reducing element on FeO content in sludge.

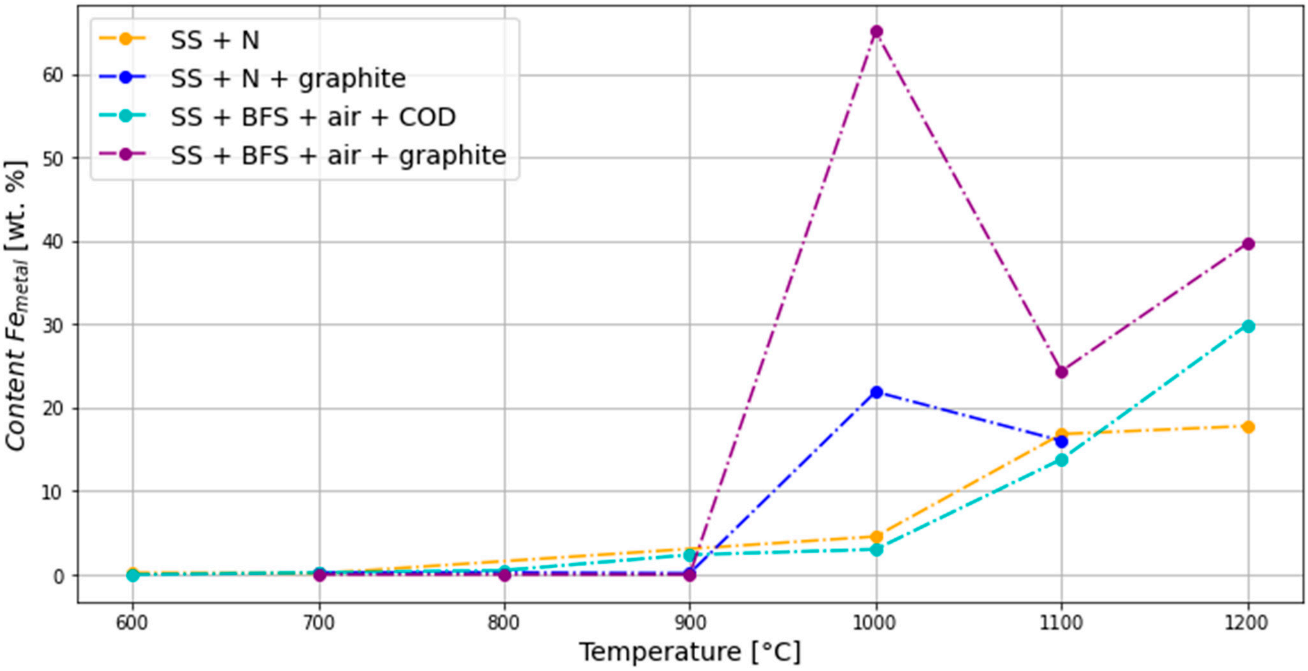

Figure 5. Effect of temperature, atmosphere and reducing element on metallic Fe content in sludge.

The thermal treatment of sludge has a secondary effect, i.e., a reduction in iron content. The highest reduction in iron in the SS+BFS+air+graphite charge, at a temperature of 1000 °C was achieved, when the metallic Fe content increased to 65 wt.%. Generally, the content of reduced Fe is increasing for all tested mixtures.

The C contained in the sludge was also used to reduce oxygen from the sludge, the content of which decreased after heat treatment (Figure 6). The carbon content of the batch dropped to zero, using the batch without additional reducing agent and under the simultaneous action of an air atmosphere. On the contrary, in the batch with a graphite reducing agent and under the influence of air, there was 3.6 wt.% C remained in the sludge after heat treatment. It can be stated that the carbon contained in the sludge itself also contributes to the reduction process in the rotary kiln. However, if an external carbon source is added, this external source is consumed first and only then the carbon contained in the sludge.

The reduction of the zinc content was thermally achieved in the same experiments in which the metallic Fe was increased. Increasing the Fe-metal content and decreasing the Zn content are interdependent. These were batches in which graphite, COD and internal atmosphere were added. The reduction of Zn content starts in the same way for all these batches, when the batch is heated above 900 °C (Figure 7). They refer to the following batches: SS+N+graphite, SS+N, SS+BFS+air +COD and SS+BFS+air +graphite. The lowest content of 0.06 wt.% Zn was achieved in the dose of SS+BFS+air+COD at a temperature of 1200 °C. In contrast, the batch that did not contain a reducing agent and was last in an air atmosphere showed almost no reduction in Zn content, see the SS+air and SS+BFS+air batches in Figure 7. Figure 7 shows that the content of the reducing agent and only then the atmosphere in the rotary kiln plays a vital role in reducing the Zn content in the sludge. The performed and presented experiments showed that the basic temperature for reducing the Zn content is 900 °C. Above 900 °C, the Zn content decreases. However, if there is no reduction at 1000 °C, the Zn content will not decrease even at higher temperatures. The results are summarized in more detail in Tables 4 and 5, which also show that the lowest Zn content is reached at 1200 °C for SS+BFS+air+COD.

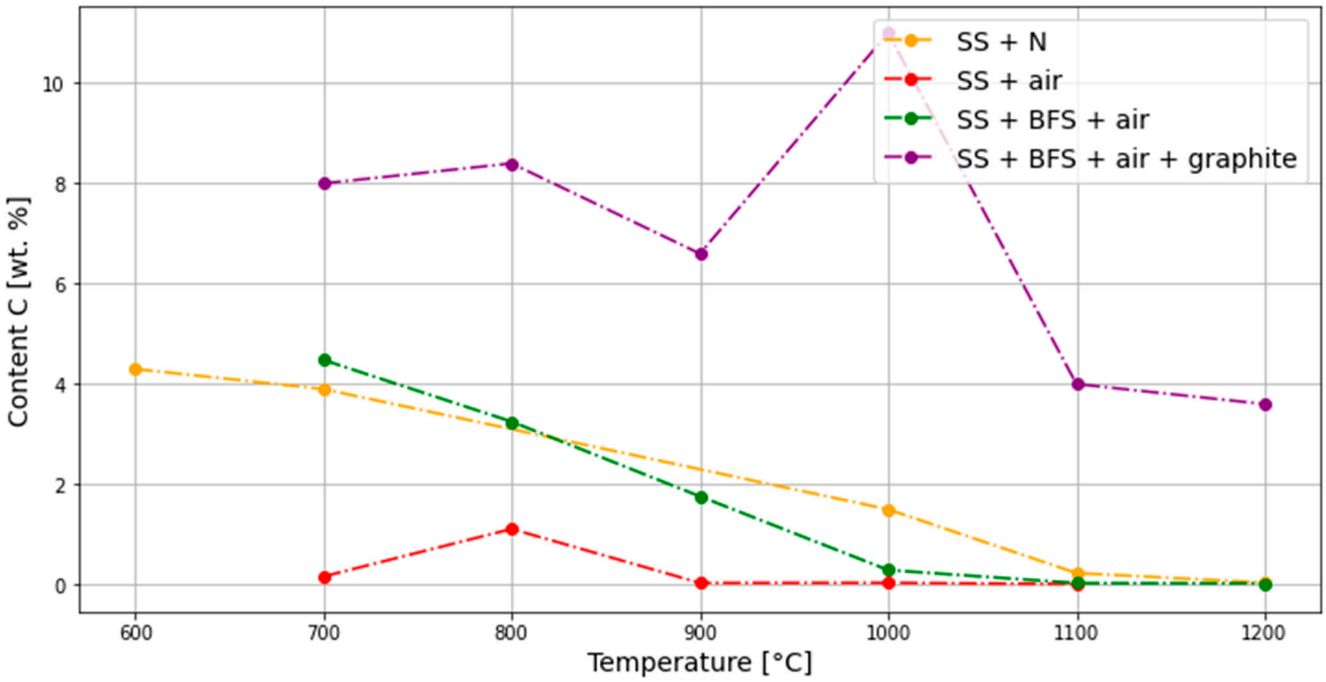

Figure 6. Effect of temperature, atmosphere and reducing element on C content in sludge.

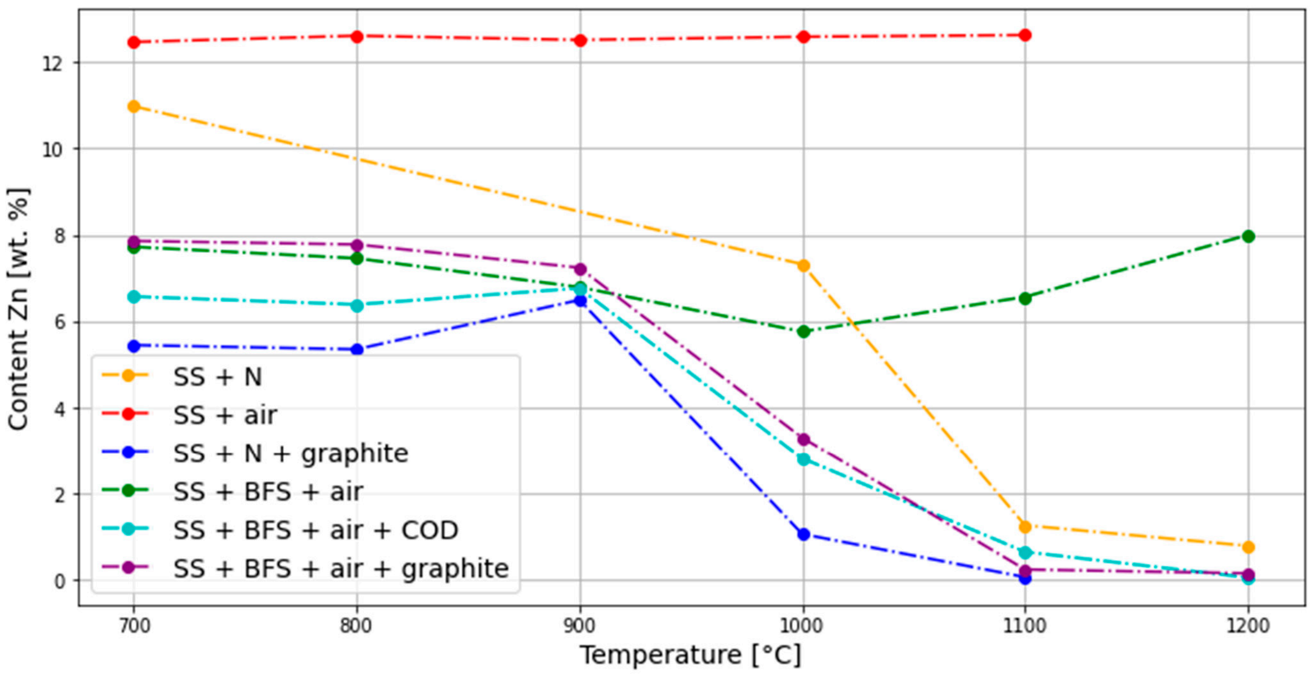

Figure 7. Effect of temperature, atmosphere and reducing element on Zn content in sludge.

For the best-found process for Zn reduction in steel and blast furnace sludge, designated SS+BFS+air+COD, an evaluation was made to determine whether the rate of Zn reduction was affected by rotary kiln speed. The above chemical analyzes shown in Table 6 and Figure 8 show that rates in the range of 0.5–4 s^{-1} have no effect on Zn reduction.

Table 4. The chemical composition of the experiments carried out for steelmaking sludge [wt.%] XRFS analysis.

Composition of Experimental Sludge	Temperature °C	C	Fe_{metal}	FeO	Fe_2O_3	Zn
SS+N steelmaking sludge (SS) in a nitrogen atmosphere (N)	700	3.9	0.1	12.6	55.0	10.98
	1000	1.5	4.6	56.3	15.2	7.32
	1100	0.2	16.8	55.0	4.0	1.27
	1200	0.0	17.8	69.7	0.0	0.80
SS+N+graphite steelmaking sludge (SS) with graphite in a nitrogen atmosphere (N)	700	x	0.2	38.9	2.3	5.45
	800	x	0.3	6.0	30.3	5.35
	900	x	0.2	9.7	32.2	6.49
	1000	x	21.9	0.0	18.2	1.07
	1100	x	16.0	1.1	0.8	0.07
SS+air steelmaking sludge (SS) in an air atmosphere	700	0.2	0.2	2.6	67.3	12.46
	800	1.1	0.0	2.7	64.6	12.61
	900	0.0	0.0	1.9	61.9	12.51
	1000	0.0	0.0	1.6	63.5	12.58
	1100	0.0	0.0	1.6	63.7	12.62

x—the element C was not detected.

Table 5. The chemical composition of the experiments carried out for mixture of steelmaking and blast furnace sludge [wt.%] XRFS analysis.

Experimental Batch Components	Temperature °C	C	Fe_{metal}	FeO	Fe_2O_3	Zn
SS+BFS+air+COD mixture of steelmaking (SS) and blast furnace sludge (BFS) with coke oven dust (COD) in an air atmosphere	700	x	0.2	2.0	41.6	6.57
	800	x	0.5	0.1	21.8	6.39
	900	x	2.4	1.1	45.3	6.77
	1000	x	3.0	15.9	35.1	2.82
	1100	x	13.8	30.6	9.8	0.66
	1200	35.0	29.9	23.1	0.0	0.06
SS+BFS+air+graphite a mixture of steelmaking (SS) and blast furnace sludge (BFS) with graphite in an air atmosphere	700	8.0	0.0	3.3	70.3	7.86
	800	8.4	0.0	4.0	67.2	7.78
	900	6.6	0.0	12.1	62.6	7.24
	1000	11.0	65.1	4.0	3.3	3.30
	1100	4.0	24.4	58.5	0.1	0.25
	1200	3.6	39.7	34.7	5.1	0.16
SS+BFS+air mixture of steelmaking (SS) and blast furnace sludge (BFS) in an air atmosphere	700	4.5	0.0	0.0	31.9	7.72
	800	3.3	0.0	0.0	15.5	7.46
	900	1.8	0.0	1.7	79.6	6.79
	1000	0.3	0.0	6.8	78.6	5.76
	1100	0.0	0.0	2.2	73.5	6.56
	1200	0.0	0.0	3.8	63.0	7.99

x—the element C was not detected.

Table 6. Chemical composition of the experiments performed for the mixture of steelmaking and blast furnace sludge, at different speeds [wt.%] XRFS analysis.

Experimental Batch Components	Temperature °C	Zn
SS+BFS+air+COD+0.5 RPM mixture of steelmaking (SS) and blast furnace sludge (BFS) with coke oven dust (COD) in an air atmosphere at 0.5 revolutions per second (0.5 RPM)	900	5.29
	1000	4.99
	1100	2.06
SS+BFS+air+COD+2.0 RPM mixture of steelmaking (SS) and blast furnace sludge (BFS) with coke oven dust (COD) in an air atmosphere at 2.0 revolutions per second (2.0 RPM)	900	5.16
	1000	4.31
	1100	2.29
SS+BFS+air+COD+4.0 RPM mixture of steelmaking (SS) and blast furnace sludge (BFS) with coke oven dust (COD) in an air atmosphere at 4.0 revolutions per second (4.0 RPM)	900	5.54
	1000	4.76
	1100	2.31

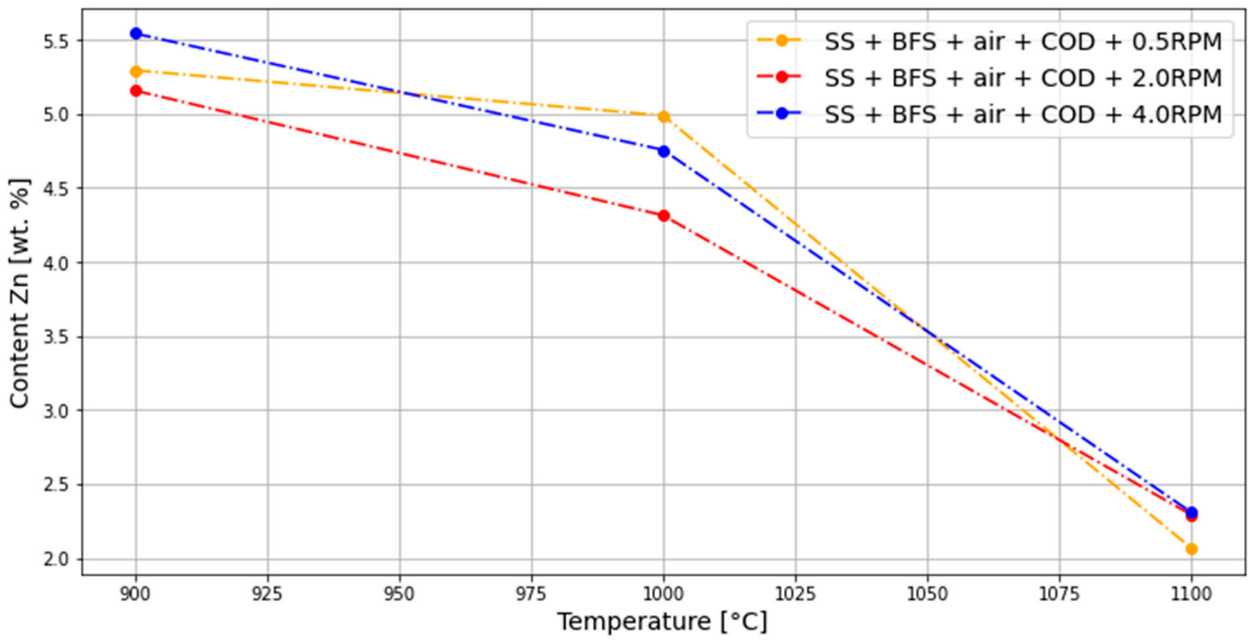

Figure 8. Effect of temperature, atmosphere and reducing element on Zn content in sludge in a mixture of steelmaking and blast furnace sludge in an atmosphere of air with coke oven dust, depending on the speed of rotation.

The content and type of reducing agent, the atmosphere in the rotary kiln and, finally, the temperature play an important role in reducing the Zn content.

4. Conclusions

The influence of varying thermal treatment conditions on reducing zinc content from a steelmaking and blast furnace sludge is presented as a main study aim.

It was found that the level of zinc reduction depends strongly on used atmosphere and the reducing element used. A neutral atmosphere and high content of the graphite or coke oven dust reducing agent in combination with high temperature can reduce the content of Zn in the sludge to 0.08 wt.% at 1200 °C for mixture of steelmaking and blast furnace sludge (SS+BFS+air+COD). A significant reduction in the Zn content to 0.66 wt.% already occurs at temperatures of 1100 °C. For this best-found process (SS+BFS+air+COD) to reduce the Zn content of steelmaking and blast furnace sludge, it was verified that a change in speed in the range of 0.5–4 s^{-1} has no effect on reducing the Zn content.

Obtained results showed that the baseline temperature for reducing the Zn content is 900 °C. Above 900 °C, the Zn content decreases. The content and type of reducing agent play an important role in reducing the Zn content; graphite has shown a better reducing ability compared to coke oven dust. When nitrogen is used, zinc is reduced even without the use of an additional reducing agent, since the carbon contained in the sludge is made use of for the reduction. In an air atmosphere, without the use of a reducing agent, there was no reduction in the Zn content.

The decrease in the Fe_2O_3 content occurred in individual batches with a simultaneous increase in the FeO. The thermal treatment of sludge has a secondary effect, i.e., a reduction in iron. The highest reduction in iron in the SS+BFS+air+graphite charge, at a temperature of 1000 °C was achieved, when the metallic Fe content increased to 65 wt.%. Generally, the key temperature in the process was found to be 1000 °C, there is mostly important braking point.

The results are original and usable for subsequent industrial research and experimental development in the field of metallurgical waste management. From the viewpoint of laboratory conditions, further work should be focused on reducing the Zn content by leaching and subsequent heat treatment in a rotary kiln.

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