

REDUCTION OF ZINC CONTENT IN METALLURGICAL SLUDGES GENERATED BY BASIC OXYGEN FURNACES

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Abstract

This paper summarizes research focused on the evaluation of metallurgical sludge generated during steel production in an oxygen converter, with the aim of preserving its high iron content for further use in the steel industry. The technology employs pyrometallurgical processing using secondary waste as a reducing agent. Under optimal conditions—at temperatures ranging from 1100 to 1200 °C in an oxygen atmosphere—a significant reduction in pollutant content and an increase in the proportion of metallic iron were achieved. The resulting material is suitable as a secondary raw material, and usable zinc products are simultaneously produced. The research confirmed the technological feasibility of the proposed process and its contribution to the circular economy and the reduction of environmental impact.

Keywords: Pyrometallurgy, zinc, recycling, rotary kiln

1. INTRODUCTION

The issue of reducing zinc content in sludge and dust from metallurgical processes is primarily addressed through a combination of pyrometallurgical and hydrometallurgical methods, with the key objective being to maintain a high iron content while selectively removing zinc. This is because the presence of zinc bound in various forms significantly limits the recyclability of these materials [1][2][3]. In general, zinc can be removed from sludge using pyrometallurgical methods in a Waelz rotary kiln, where the material is heated with a reducing agent to temperatures of around 1000-1100 °C. Under these conditions, zinc oxides are reduced to metallic zinc, which subsequently evaporates and transitions into the gaseous phase. In the gaseous phase, the zinc is reoxidized and captured as zinc oxide. The process utilizes high temperatures to volatilize metals, allowing them to be separated from the solid residue. The residual material contains only a small amount of zinc [1]. The key is to ensure suitable reduction conditions and high temperatures that allow zinc to transition into the gaseous phase while the iron remains in the product. The choice of a specific technology depends primarily on operating and local conditions [2]. Hydrometallurgical processes, particularly ammonia leaching, have proven to be highly effective due to their high selectivity for zinc and minimal iron losses. The study [4] found that zinc can be effectively removed from oxygen converter sludge using ammonia-based solutions, with ammonium chloride proving to be the most effective reagent (NH₄Cl).

Another significant approach is the combination of thermal and hydrometallurgical treatment. According to [3], effective removal of zinc requires first thermally decomposing the stable phase of franklinite. Subsequently, the zinc can be selectively leached using an alkaline NaOH solution, while the iron remains almost entirely in the solid residue. This process is highly selective and allows for the removal of up to approximately 95 % of the zinc.

Modern approaches also include advanced leaching methods, such as the use of mixtures of ammonia and ammonium salts or innovative solvents, which are highly effective while having a lower environmental impact. Physical treatment of the material, such as sorting by particle size, also plays a significant role [5][6][7]. Another possible strategy involves combining multiple methods-pyrometallurgical, hydrometallurgical, and physical-which not only reduces the zinc content to the desired level but also maximizes the utilization of the iron component and minimizes waste [8][9][10].

The novelty of this work lies in the design and experimental validation of a pyrometallurgical process that utilizes a combination of two waste materials (converter sludge and coke oven dust) to simultaneously achieve the deep decomposition of zinc and the nearly complete metallization of iron, while enabling the parallel recovery of usable ZnO and an iron-rich product. The aim of this study is to design and experimentally verify a method for treating fine converter slag that would reduce the zinc content to below 0.1 %, thereby enabling its further use as a secondary source of iron.

2. EXPERIMENTAL

The feedstock used in this study was fine converter sludge (hereinafter referred to as FFSludge) originating from the Ostrava industrial agglomeration. This sludge consists of fines generated during the wet scrubbing of gases from an oxygen converter. After separation of the so-called coarse sludge, these fine particles are carried by the water medium and subsequently settle in sedimentation tanks. After sedimentation, the FFSludge is stored in a sludge pond, where it undergoes gradual dewatering. Due to contact with atmospheric oxygen, exothermic oxidation reactions occur simultaneously, which can significantly affect the material's physicochemical properties, particularly its mineralogical composition and reactivity. The chemical composition of the sludge used is listed in **Table 1**. Carbon and sulfur were determined by combustion elemental analysis; the concentrations of Al₂O₃, SiO₂, CaO, MgO, and ZnO were measured using X-ray fluorescence (XRF) using fused bead samples; and the individual forms of iron were determined spectrophotometrically from solutions, with 1,10-phenanthroline used as the chelating agent.

Table 1 Chemical composition of the incoming FFSludge

C (wt%)	S (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	Fe _{metal} (wt%)	FeO (wt%)	Fe ₂ O ₃ (wt%)	CaO (wt%)	MgO (wt%)	ZnO (wt%)
3.40	0.13	0.21	1.61	27.51	35.12	0.01	14.58	1.63	3.98

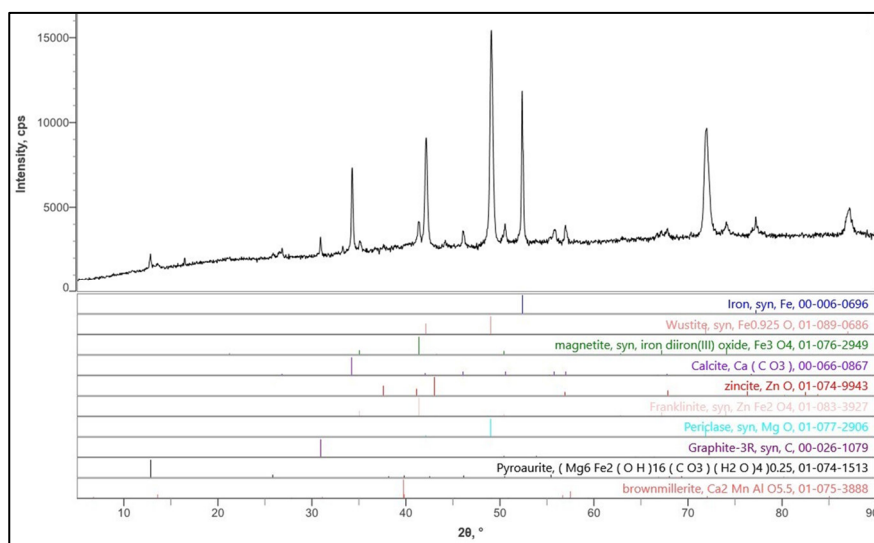


Figure 1 XRD analysis of the incoming FFSludge

The values presented in **Table 1** indicate that the material under study is characterized by a high iron content, both in metallic form and in the form of oxides. Also significant is the relatively high zinc content, which may play an important role in subsequent processing, particularly in terms of its volatility at high temperatures. X-ray diffraction analysis (**Figure 1**) confirmed that wüstite (FeO) is the dominant form of iron oxide.

Another type of metallurgical waste—coke oven dust—was used as a reducing agent for the pyrometallurgical treatment of sludge. Its chemical composition is shown in **Table 2**.

Table 2 Chemical composition of coke oven dust

C (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	Fe _{metal} (wt%)	FeO (wt%)	Fe ₂ O ₃ (wt%)	CaO (wt%)	S (wt%)	ZnO (wt%)
86	3.47	6.35	0.14	0.55	0.4	0.55	0.48	0.01

Table 2 shows that this material is characterized primarily by a very high carbon content, which makes it ideal for use as an effective reducing agent in pyrometallurgical processes. Minor components, such as silicon and

aluminum oxides, may then influence slag formation. The X-ray diffraction pattern of the sample, presented in **Figure 2**, revealed that, in addition to graphitic carbon, the sample also contains a significant amount of an amorphous, likely carbonaceous phase.

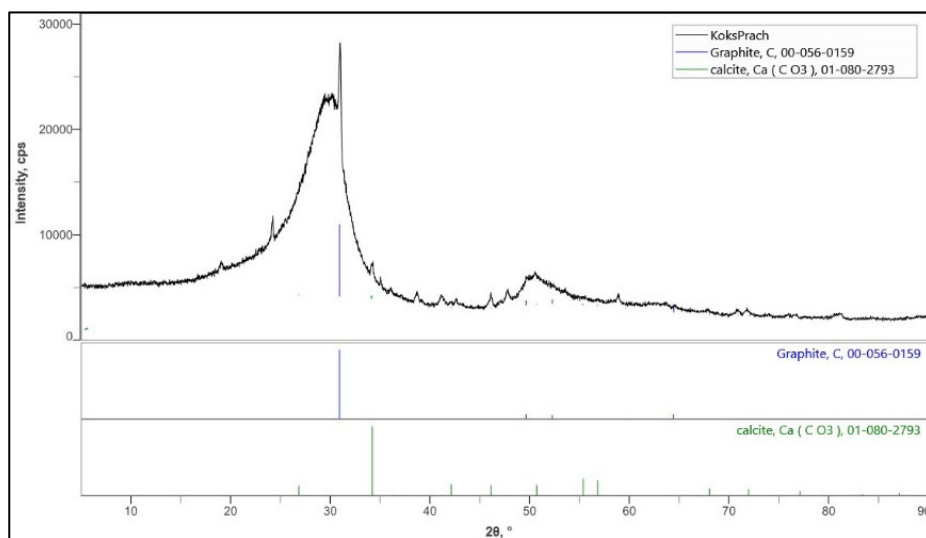


Figure 2 XRD analysis of coke oven dust

The particle size of both materials used was adjusted prior to experimental processing by grinding and subsequent sieving to a size of less than 0.1 mm, thereby achieving homogeneity of the charge and increasing the reactivity of the system.

The experimental smelting runs were carried out in a rotary kiln with indirect charge heating (hereinafter referred to as the rotary kiln), operated by MATERIÁLOVÝ A METALURGICKÝ VÝZKUM s.r.o. (MMV). The weight of each experimental charge was 100 g, consisting of a mixture of 50 wt% FFSludge and 50 wt% coke oven dust.

The prepared charge was placed in a refractory cartridge made of Al₂O₃. The cartridge was then placed in the working chamber of the rotary kiln. The charge was heated at a controlled rate of 10 °C·min⁻¹ to a target temperature in the range of 1100–1200 °C in an oxidizing air atmosphere with a constant flow rate of 100 cm³·min⁻¹.

Once the desired temperature was reached, the charge was held isothermally at that temperature for 60 minutes while maintaining the same air flow rate. The rotary kiln charge was then cooled to laboratory (room) temperature. After removing the cooled cartridge, the charge was extracted and subjected to chemical analysis to determine changes in composition following heat treatment.

The rotary kiln apparatus also includes a system for cooling the exhaust gases. In this cooler, entrained dust was captured and, simultaneously, the gaseous phases—particularly the gaseous metal components—condensed. The material captured in the cooler was subsequently subjected to chemical analysis.

3. RESULTS AND ITS DISCUSSION

Experimental smelting runs in a rotary kiln were conducted at two target temperatures, 1100 °C and 1200 °C, to assess the effect of temperature on the course of reduction-volatilization processes and the resulting chemical composition of the products. The results of chemical analyses following pyrometallurgical processing are presented in **Table 3**.

Table 3 Chemical composition of the charge mixture after pyrometallurgical processing

Temperature (°C)	C (wt%)	S (wt%)	Fe _{metal} (wt%)	FeO (wt%)	Fe ₂ O ₃ (wt%)	Fe _{total} (wt%)	ZnO (wt%)
1100	47.88	0.40	32.75	1.99	0.01	34.30	0.18
1200	49.00	0.43	40.20	<0.01	0.01	40.20	0.02

The results clearly show that as the temperature increases, both reduction and volatilization processes intensify significantly. At 1100 °C, the zinc content decreased from the initial 3.98 % to 0.18 % ZnO, while at 1200 °C it dropped further to 0.02 %. This effect can be attributed to the increased partial pressure of zinc vapors and the more intense volatilization of metallic Zn, or its oxides, at higher temperatures.

At the same time, a significant increase in the content of metallic iron is evident, reaching 40.20 % at 1200 °C, which corresponds to the practically complete conversion of iron into the metallic phase. The minimal concentrations of FeO (<0.01 %) and Fe₂O₃ (0.01 %) suggest that the reduction proceeds nearly to equilibrium, likely via the reaction sequence $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ in the presence of solid carbon and CO as a reducing agent. This interpretation is supported by the results of X-ray diffraction (XRD) analysis of a sample processed at 1200 °C. The diffraction pattern (**Figure 3**) shows no characteristic lines of wüstite (FeO), indicating its complete reduction. The dominant presence of metallic iron in the diffraction pattern thus confirms the advanced degree of metallization of the system.

Overall, it can be concluded that increasing the temperature from 1100 °C to 1200 °C not only leads to more efficient disintegration of the zinc-bearing component through volatilization but also significantly promotes the reduction of iron oxides to metallic iron, thereby improving the metallurgical properties of the resulting calcination product.

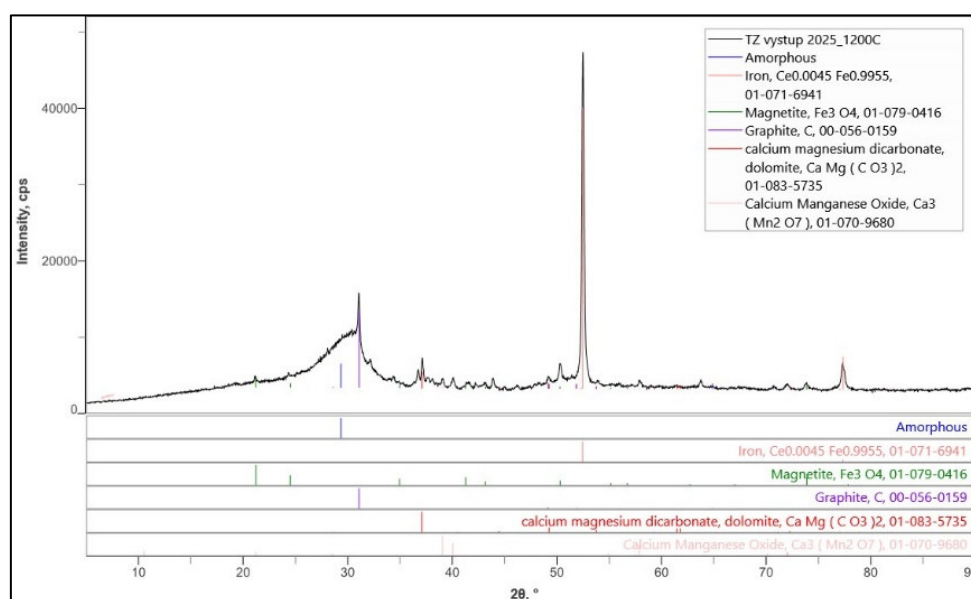


Figure 3 XRD pattern of the charge mixture after pyrometallurgical processing

The increasing efficiency of the pyrometallurgical process as a function of temperature is further confirmed by an analysis of the material collected in the cooler; its chemical composition for the individual temperature regimes is shown in **Table 4**.

Table 4 Chemical composition of the material captured by the cooler

Temperature [°C]	C (wt%)	S (wt%)	Fe ₂ O ₃ (wt%)	Al ₂ O ₃ (wt%)	CaO (wt%)	SiO ₂ (wt%)	Zn (wt%)
1100	19.48	0.37	1.63	3.21	0.31	7.26	52.79
1200	5.08	0.79	-	<0.10	0.76	0.99	69.72

The results show that at temperatures above 1000 °C, zinc compounds undergo intense carbothermic reduction to form metallic zinc, which subsequently transitions into the gaseous phase. This process is governed not only by the thermodynamic stability of the Zn–O–C system, but also by the kinetics of solid-state diffusion processes. The vaporized zinc is subsequently transported by the gas flow to the cooling section of the apparatus, where, due to a decrease in temperature and an increase in the partial pressure of oxygen, its secondary oxidation to ZnO occurs.

The higher ZnO content in the material collected at 1200 °C indicates a higher degree of zinc reduction and volatilization. This phenomenon can be interpreted as a consequence of more efficient utilization of the reducing agent, where at higher temperatures there is a more pronounced decrease in residual carbon (from ~19.5 % to ~5 %), which indicates its more intensive consumption in reduction reactions. At the same time, the higher temperature promotes a shift in the equilibrium toward the formation of gaseous Zn and CO, thereby increasing the total yield of zinc in the gas phase.

The phase composition of the material captured in the cooler, corresponding to the charge processed at 1200 °C, is documented by X-ray diffraction analysis (**Figure 4**).

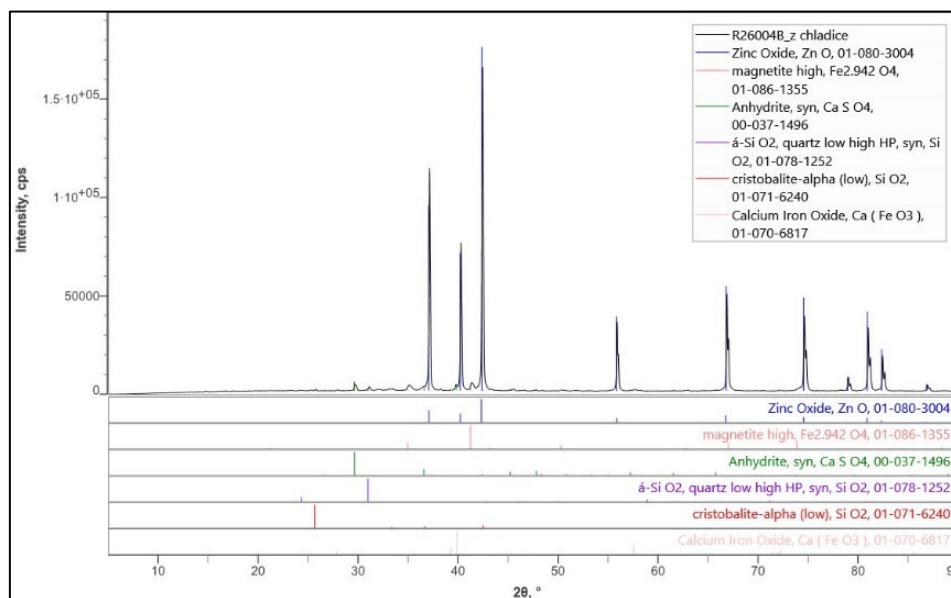


Figure 4 XRD pattern of the material captured by the cooler

The diffraction pattern clearly demonstrates the dominance of the ZnO phase, which is fully consistent with the chemical analysis and the proposed reaction mechanism. The character of the diffraction lines—their high intensity and narrow width—indicates a high degree of crystallinity in the resulting zinc oxide, suggesting that the oxidation took place under conditions conducive to the growth of well-developed crystals.

The minor presence of SiO_2 and complex oxide phases based on Fe and Ca can be attributed to the mechanical loss of fine particles from the charge or the condensation of less volatile components. The presence of magnetite (Fe_3O_4) indicates local reduction-oxidation conditions in the system, while the occurrence of anhydrite (CaSO_4) points to partial sulfur fixation in the oxidizing environment of the cooler. However, these secondary phases do not constitute a significant proportion and do not have a major influence on the dominant character of the product, which is highly crystalline ZnO.

4. CONCLUSION

Pyrometallurgical treatment of fine converter sludge carried out at temperatures of 1100 °C and 1200 °C clearly demonstrated the significant influence of temperature on the course of reduction-volatilization processes in the system. As the temperature increases, there is a significant shift in reaction equilibria in favor of reduction processes, which manifests itself in both the nearly complete metallization of iron and the intense volatilization of zinc. At a temperature of 1200 °C, virtually complete reduction of iron oxides to metallic iron was achieved, as evidenced by the high content of Fe metal (40.20 %) alongside negligible concentrations of FeO and Fe_2O_3 . This state corresponds to an almost equilibrium reduction process in the Fe–O–C system, likely carried out via the sequential mechanism $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ with CO as the dominant reducing agent. The resulting high degree of metallization represents a significant improvement in the metallurgical properties of the solid residue, which can be used as a secondary raw material for the production of iron or steel, e.g., in electric arc furnaces.

At the same time, it was demonstrated that an increase in temperature significantly promotes the volatilization of zinc. The ZnO content in the charge after processing dropped to as low as 0.02 %, indicating an almost complete transfer of zinc into the gaseous phase. This phenomenon is consistent with the increase in the partial pressure of zinc vapor and with the thermodynamic stability of the Zn–O–C system at higher temperatures. Analysis of the material captured in the cooler confirmed that the volatilized zinc is subsequently effectively captured in the form of ZnO. A higher ZnO content (up to ~70 %) at 1200 °C, together with a lower residual carbon content, indicates more intense carbothermal reactions and more efficient transport of zinc in the gas phase. X-ray diffraction analysis also demonstrated that the resulting zinc oxide has a high degree of crystallization, indicating stable conditions during its formation in the condensation-oxidation phase of the process. The obtained material with a high ZnO content could be particularly suitable for metallurgical processing as a secondary raw material for the production of metallic zinc (hydrometallurgical processes), as well as for the rubber industry as a vulcanization activator, where the presence of minor impurities is not a concern, or for ceramic applications as a flux or property modifier. Overall, it can be concluded that the pyrometallurgical processing of converter sludge enables the simultaneous production of metallic iron and concentrated zinc oxide, which represents a significant technological advancement for the utilization of this waste material from the perspective of the circular economy.

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