Reducing the content of zinc in metallurgical waste in a rotary kiln

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Summary

Based on literature analysis, the design and subsequent implementation of the unique and experimental “Laboratory developed thermal equipment for treating metallurgical waste” was carried out. This experimental equipment is used for researching the heat treatment of metallurgical waste, especially in reducing the proportion of non-ferrous metals. This research work aids in the removal of harmful impurities in sludge and their possible reuse as charges in smelters or raw materials for other industries. Described here is the research work carried out on experimental equipment designed to reduce the content of zinc from sludge generated during steel production. Two methods for heat treating steelmaking sludge are described, the first without the addition of graphite and the second with the addition of graphite. Both thermal treatments show a high level of zinc removal, but in the case of adding graphite, the removal of zinc is several times higher compared to thermal treatment without graphite. The work was carried out as part of the project “Research on the processing of metallurgical waste, materials and by-products from metallurgical plants and related operations, number CZ.02.1.01/0.0/0.0/17_049/0008426”.

Keywords: *waste, slag, sludge, lead, zinc, thermal treatment*

Introduction

This work provides information on the removal of hazardous impurities from sludge. Hazardous impurities include Zn and Pb, which accumulate in the dust that occurs during the smelting of scrap metal, e.g. in an electric arc furnace. The dust contains a large proportion of iron oxides, from which iron is obtained in an electric arc furnace (EAF) by reduction processes. However, there is also an accumulation of the so-called circulating elements, namely Zn and Pb, because these evaporate from the charge material during melting and accumulate in the trapped dust, which is returned to the EAF as a charge. Zinc and lead also accumulate in the lining and in the furnace components that are in contact with the exhaust gases, such as the electrode contact components.

Hazardous waste is also generated during the production of liquid steel in oxygen converters (referred to as BOF), on average about 20 kg of dust and sludge per ton of liquid steel. Much of this dust is easily recycled by agglomeration or in blast furnaces, but dust with a high zinc content is usually put in landfills. Hydrometallurgical techniques like alkaline leaching, which are often used to remove zinc from the dust of electric arc furnaces, are unsuitable for recovering material from BOF dust because of the lower concentration of zinc present in it and the other actions for reprocessing the separated iron product. Pyrometallurgical treatment using a rotary hearth furnace (RHF), in processes such as FASTMET®, can be viewed as a commercially viable option for the processing and regeneration of iron and zinc if they are used as part of an integrated steelworks. The raw zinc oxide produced can be sold as a raw material containing zinc, and the reduced iron can be used in blast furnaces and to increase productivity.[1]

According to the authors [2] this residue zinc oxide, consisting mainly of iron oxide contaminated with other metal oxides (including zinc and lead), is usually put in landfills at great economic and environmental cost. The author has come up with an alternative based on the principles of industrial ecology, which involves incorporating Waelz slag into clay ceramic building bricks. Using slag is advantageous and ecological, because the bricks produced in this fashion are basically ordinary waste after use and are not hazardous.

At present rotary kilns are widely used to remove Zn and Pb. Rotary kilns are very efficient, but place high demands on flue gas cleaning technology, because in most cases, the material is also heavily contaminated with organic and inorganic components. Dioxins and furans are released during the process and an additional flue gas cleaning system needs to be installed.[3]

Rotary kilns

The principle of RHF equipment, which is used mainly for drying, sintering, roasting, producing metal, etc., is used to research the processing of waste from metallurgical operations. The rotary kiln is only one part of a large unit, which is much larger than the kiln itself, because it also contains charge preparation, equipment for gas blowing, for cleaning flue gas, for the processing of the product from the furnace, see Figure 1.[3]

Industrial rotary kilns are heated by natural gas. According to the contact of the gas with the heated material, we devide rotary furnaces into two basic types. The first type is a furnace with indirect heating, where the gas and its products are not in contact with the heated material, see Figure 2. The second type is a furnace with direct heating, where the gas and its products are in contact with the heated material, see Figure 3.

The linings in the rotary kiln are made of refractory material, whether brick or cast.[2] When the material is heated directly by gas, the heat is transferred directly from the flame to the material. The temperature of the flame and its flue gases reaches 2100 °C.[4] The material is further heated by the radiation of the furnace itself and by heat conduction from the refractory material of the furnace, see Figure 4. When the material is indirectly heated, the heat is transferred to the material only by radiation from the inner shell of the furnace and by the conduction of heat from the inner part of the refractory lining of the furnace.

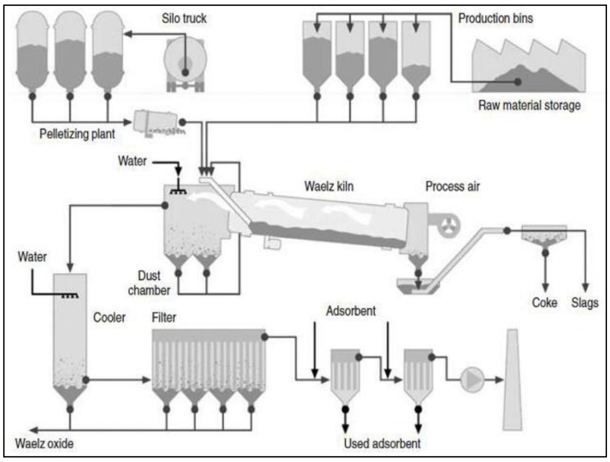

Figure 1: Flow chart of Waelz kiln process[3]

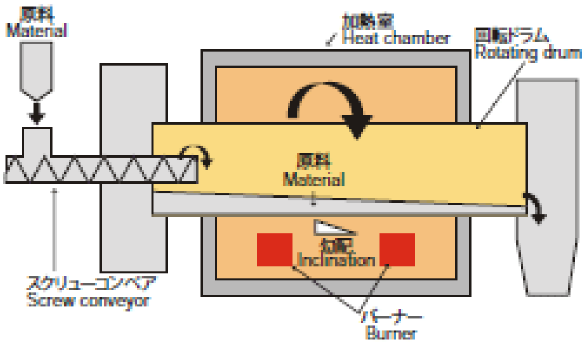

Figure 2: Rotary flame furnace with indirect heating[6]

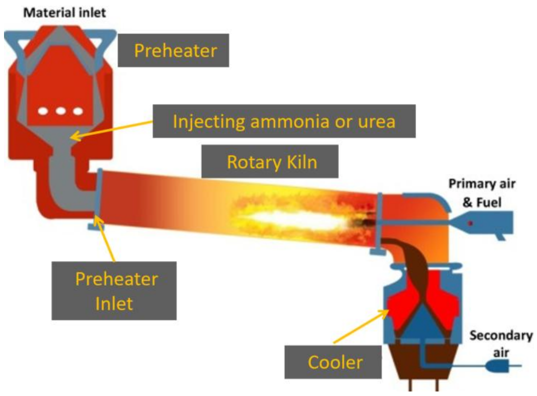

Figure 3: Rotary flame furnace with direct heating[5]

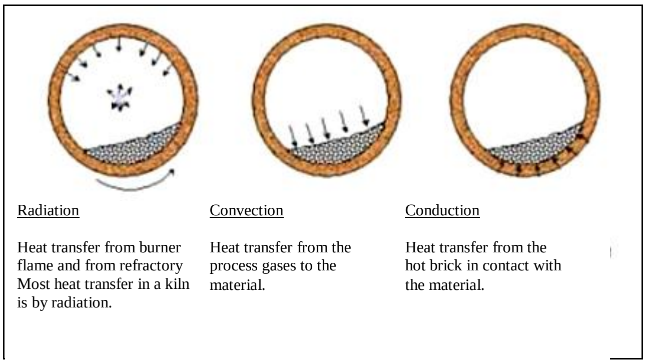

Figure 4: Heat transfer to the material in the furnace[8]

Current knowledge of removing Zn from dust

First the method of removing Zn using CO and O_2 is described, with the basic reaction in a rotary kiln presented in Figure 5. Due to the low boiling point, Zn evaporates at 907°C. The description of chemical reactions between Zn gas and oxygen is described by equations (1), (2) and (3) and in the charge by equations (4) to (9). [7]

The author [7] also mentions the removal of zinc from liquid slag in the furnace for producing lead with excess air and coal or coke. The reactions taking place in the furnace are clearly presented in Figure 6, and are occurring at a temperature of 1300-1500°C. When removing Zn in rotary kilns, the flame heats the atmosphere in the kiln up to a temperature of 2000°C and the material is heated from gas heated up to a temperature of 1500°C, see Figure 7[9]

Reaction in the gas phase (oxidizing):

$\{Zn\} + ½ \{O_2\} \rightarrow ZnO$ (1)

$\{CO\} + ½ \{O_2\} \rightarrow \{CO2\}$ (2)

$\{Zn\} + \{CO\} + \{O_2\} \rightarrow ZnO + \{CO_2\}$ (3)

Reaction in the charge (reducing):

$(ZnO) + \{CO\} \rightarrow \{Zn\} + \{CO_2\}$ (4)

$\{CO_2\} + C \rightarrow 2\{CO\}$ (5)

$(ZnO) + C \rightarrow \{Zn\} + \{CO\}$ (6)

$(FeO) + \{CO\} \rightarrow Fe + \{CO_2\}$ (7)

$\{CO_2\} + C \rightarrow 2\{CO\}$ (8)

$(FeO) + C \rightarrow Fe + \{CO\}$ (9)

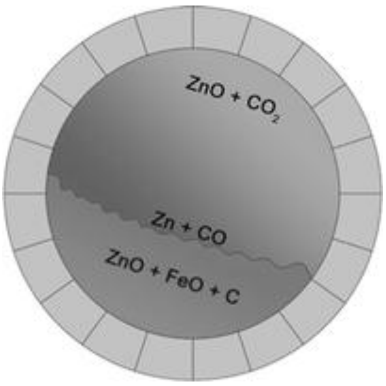

Figure 5: Main reactions in the Waelz kiln, reduction Zn[7]

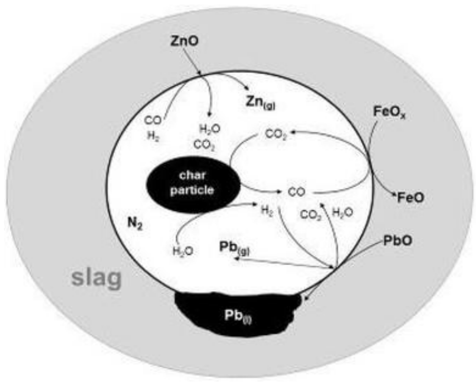

Figure 6: Reaction system occurring in the slag fuming process[7]

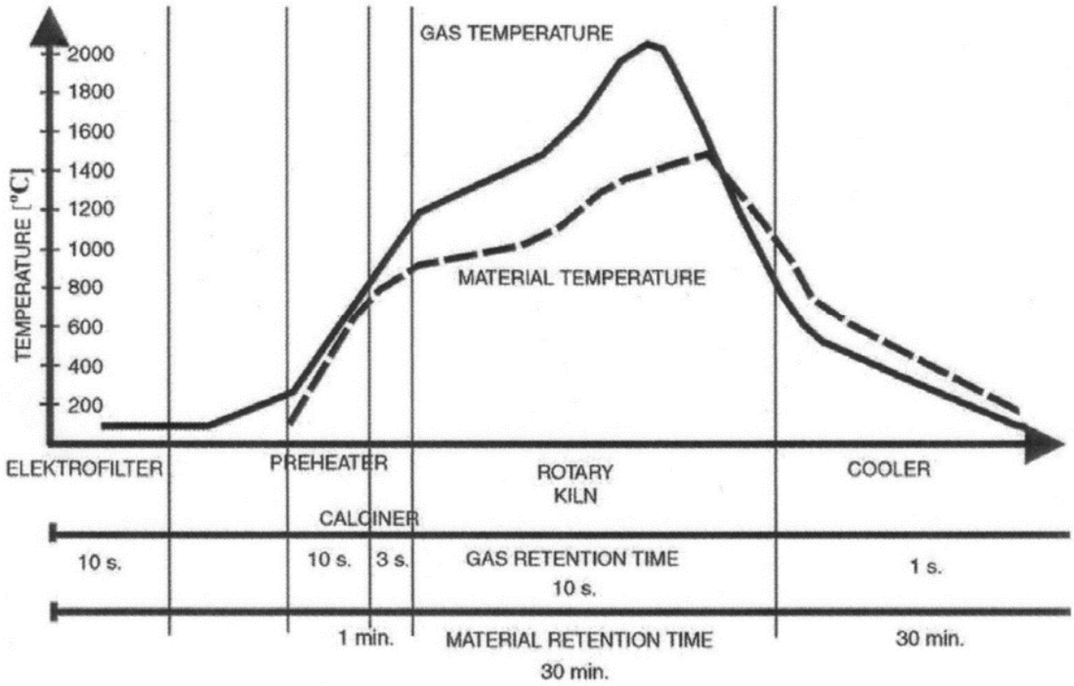

Figure 7: Diagram showing entrance points of AFR in the cement plant as well as temperature profile and retention time of gas and solids[9]

The second way to remove Zn is to use Cl at high temperatures. When removing Zn, the author [10] recommends using chlorides together with high temperature. Where Zn can be completely removed at temperatures in the range of 650 – 900 °C with the addition of 10 wt.% Cl, preferably at 1000 °C, the Zn is left in the form of $ZnCl_2$. The author also points out the negative effect of H_2O in the flue gas during the removal of Zn and, conversely, the positive effect of Si in the input raw material. The average composition of the atmosphere during the experiments was 3.0% CO_2, 18% O_2, 74% N_2 and 5% H_2O with an average gas flow of 12.7 $Nm^3.h^{-1}$ of CH_4 and 19.0 $Nm^3.h^{-1}$ of O_2.

According to the author [10], another very harmful element, Pb, is released in the form of the oxide PbO at above 850°C and without chlorination. When Cl is used, all lead components in the form of $PbCl_2$ are captured. If we increase the temperature to 1000 °C, up to 100% of Pb can be removed using only temperature control. The effect of temperature, the addition of Cl and other additives to remove undesirable elements have been grouped together by the author [9] in Table 1.

Table 1: Relevant parameters influencing the removal of heavy metals from sewage sludge ash by chlorination[10]

Heavy metals	Temperature	Cl addition	Cl availability	Major elements in the ash				Gas composition	
				Al	Ca	Fe	Si	H_2O	O_2
Cd	+	0	0	0	(+)	0	-	++	0
Cr	+	++	++	0	(-)	0	++	-	++
Cu	++	+	+	(+)	0	-	++	0	0
Ni	++	++	++	0	0	-	(-)	-	(-)
Pb	+	(+)	0	0	+	0	+	0	0
Zn	++	++	++	(-)	+	(-)	+	-	0

Note: ++ strongly positive influence; + positive influence; (+) low positive influence; 0 no influence; (-) low negative influence; - negative influence; -- strongly negative influence.

Design and implementation of the experimental equipment

The classic rotary kiln places high demands on temperature control in the kiln, on content control and flue gas cleaning, on the size of the furnace, reaction possibilities (oxidation and reduction), and especially on additional equipment for fuel gas preparation, extraction, etc. From the point of view of the experimental equipment, control and monitoring and accurate evaluations, better results are achievable using rotation using electricity and electricity as heat sources. Such a furnace makes it possible to very precisely control the temperature in the furnace, to control the composition of the gases entering the process, and to evaluate and monitor the output composition of the gases and their contents.

Based on the facts above and analyses of the processes taking place in rotary kilns, a design was made and a tender and subsequent production of the research equipment were carried out. The new equipment is officially called “Laboratory developed thermal equipment for treating metallurgical waste” (referred to as the rotary kiln) and it is shown in Figure 8. The rotary kiln is lined with fibrous ceramics with excellent thermal insulation properties and low heat accumulation. The inner space of the furnace is used for the placement of a sample of up to 400 mm long. The furnace is equipped with a removable corundum or quartz tube. The working environment of the furnace (tube) permits the choice of different types of atmospheres, including creating a vacuum inside it. The machine is equipped with a rotating mechanism driving the inserted tube with the option of setting the speed. The research samples can be inserted into a special ceramic cartridge, see Figure 9, which is then placed inside the tube and the tube itself inserted completely into the furnace. The furnace contains mass flow meters for the input agent with the possibility of switching and mixing gases. The furnace is equipped with an automatic control system to program increases and decreases in temperature, in vacuum, filling the furnace with gases and purging it with inert gas.

Figure 8: Laboratory refining equipment for the thermal treatment of metallurgical waste

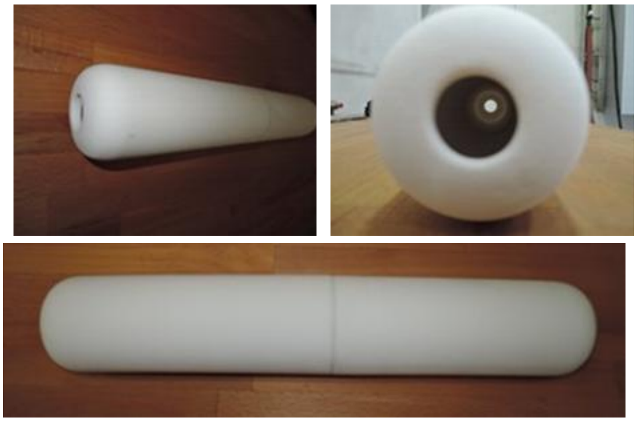

Figure 9: Special ceramic tube

The basic technical parameters of the rotary kiln are as follows:

- The internal diameter of the corundum tube is ϕ 80 mm and the length is 1200 mm,
- Indirect electric heating of the charge,
- Operating temperature range 400-1650°C, with the heating rate 50 – 200 $°C \cdot h^{-1}$,
- The weight of the charge based on granulate, briquettes, pellets ϕ 0.1 – 25 mm is 0.1 – 0.6 kg,
- The obtainable vacuum, more precisely the suction of the atmosphere, is below 50 Pa,
- The rotation of the tube varies continuously in the speed range of 0.1 – 20 min^{-1}, or samples can be heated without rotation,
- Gases are used that can be mixed in different proportions and blown into the furnace: CO, CO_2, O_2, air, N_2, Ar with a flow rate of 10 – 500 $ml \cdot min^{-1}$.

Experimental part

In the rotary kiln at MATERIAL AND METALLURGICAL RESEARCH Ltd., experiments were performed to reduce the content of undesirable impurities in steelmaking sludge generated during the production of steel in oxygen converters. The focus of the experiments was on the removal of Zn from sludge using a thermal process. The experiments were divided into two parts, where in the first series of experiments the samples of steel sludge were only thermally treated, and in the second series of experiments the samples were treated both thermally and at the same time graphite was added as a reduction element. The graphite was in the form of extra pure fine powder with a granulometry of 50 µm. In order to ensure a full reduction environment, a charge to graphite ratio of 1:1 was chosen for the first step.

Both series of experiments were performed with the same 100 g weight of steel sludge and a heating rate of the metal sample of 170°C.h^{-1}, holding at that temperature for 60 min, and a cooling rate of 170°C.h^{-1}. In order to maintain the same starting conditions for all experiments and the heating of the charge, the entire interior of the furnace was evacuated to 50 Pa after inserting the charge into the furnace and closing it. The entire interior of the furnace was then filled with an inert atmosphere composed only of nitrogen.

The steelmaking sludge was subjected to chemical analysis according to QI-ISO-LAB1-10-09 and according to QI-ISO-LAB1-10-04 on LECO CS 230, ARL X-ray and ADVANT´X devices.: 4.3% C, 0.11% S, 48.17% Fe overall, 1.12% MnO, 0.23% Cr_2O_3, 1.8% CaO, 2.20% SiO_2, 1,65% MgO, 3.33% Na_2O, 13.9% ZnO. The experiments showed there was a significant reduction in the content of C and ZnO, see Table 2. Table 2 shows the values of ZnO for 100 g of the charge, i.e. without the graphite reducing element. Table 2 also shows that during the thermal treatment of steelmaking sludge, the ZnO content decreases both without the addition of graphite and with the addition of graphite. In the first series of experiments without the addition of graphite, carbon is consumed in the reduction of ZnO and is subsequently evaporated. In the second series of experiments with the addition of graphite, the reduction in the ZnO content is more drastic even at low temperatures compared to the experiments where graphite was not added. At 700°C, the reduction in ZnO is almost twofold.

Table 2: Chemical composition of steel sludge samples after experiments

	Content C [wt.%]			ZnO content [wt.%]		
Temperature [°C]	700	1000	1100	700	1000	1100
1st series without graphite	3.9	1.5	0.04	13.66	9.11	0.99
2nd series with graphite	-	-	-	6.78	1.33	0.09

Results and discussion

The experimental work shows that the reduction of the content of ZnO can be achieved already during thermal treatment, at a temperature of 1100 °C. From an energy point of view, and therefore also from an economic point of view, the final ZnO content depends on the requirements that the company wants to establish in steelmaking sludge. At a temperature of 1000 °C, the addition of graphite makes it possible to remove seven times more ZnO than without the addition of graphite. The addition of graphite significantly increases the process of removing ZnO from steelmaking sludge, and a certain level of ZnO content can be obtained by using a control element together with temperature control. In a rotary flame furnace, graphite can be replaced by imperfect combustion, or by the addition of graphite or another suitable carbon-containing charge.

Conclusions

This work presents a literature analysis of the issue of reducing undesirable impurities in metallurgical waste, especially the reduction of Zn and Pb. Also presented is the project within which this work and investment have been carried out, the investment being called “Laboratory thermal equipment for treating metallurgical waste” (referred to as rotary kiln). The experimental work described in this work was focused on the reduction of ZnO content in steelmaking sludge in the production of steel in oxygen converters. Based on two experimental series of thermally treating sludge, the first without the addition of graphite and the second with the addition of graphite, it was found that with increasing temperature the effect of removing ZnO from sludge increases and this effect is significantly supported by the addition of graphite, which increases the effect at 1000 °C by up to 7 times.

Acknowledgements

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Možnosti snížení obsahu zinku v metalurgických odpadech v rotační peci

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Souhrn

Na základě literárního rozboru byl proveden návrh a následně realizace jedinečného experimentálního zařízení „Laboratorní termické zařízení pro hutní zpracování odpadů“. Experimentální zařízení slouží pro výzkum tepelného zpracování metalurgického odpadu, zejména při snižování podílu neželezných kovů. Výzkumné práce vedou k odstranění škodlivých příměsových prvků v kalech, aby bylo možné jejich následné využití jednak opětovně v hutích jakožto vsázky, nebo jako vstupní suroviny pro jiné průmyslové odvětví.

Jsou popsány výzkumné práce realizované na experimentálním zařízení, které vedly ke snížení obsahu zinku z ocelárenských kalů vzniklých při výrobě oceli. Popsány jsou dva způsoby termického zpracování ocelárenského kalu, první bez přídavku grafitu a druhý s přídavkem grafitu. Oba termické způsoby zpracování vykazují vysoký stupeň odstranění zinku, ale v případě přídavku grafitu je odstranění zinku několikanásobně vyšší oproti termickému zpracování bez grafitu. Práce byly realizovány v rámci projektového záměru s názvem „Výzkum zpracování hutního odpadu, materiálů a vedlejších produktů z metalurgických a souvisejících provozů číslo CZ.02.1.01/0.0/0.0/17_049/0008426“.

Klíčová slova: *odpad, struska, kaly, olovo, zinek, tepelné zpracování.*