STUDY OF ZINC AND LEAD THERMAL REDUCTION FROM A STEELMAKING SLUDGE

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https://doi.org/10.37904/metal.2023.4683

Abstract

The influence of varying thermal treatment conditions on reducing zinc and lead content from a steelmaking sludge was studied. The Waelz process in a laboratory rotary kiln was used for the experiments. It was found that the level of zinc and lead reduction strongly depends on used atmosphere and the reducing element used. A significant reduction of the zinc and lead content (well below 1 wt. %) was achieved at temperatures of 1,000 °C, respectively. A neutral atmosphere and high graphite content reduced the zinc and lead very efficiently. A nitrogen atmosphere caused the reduction of zinc and lead even without the use of an additional reducing agent; the carbon contained in the sludge was used for the reduction.

Keywords: Steelmaking sludge, laboratory rotary kiln, carbothermic reduction, zinc, lead

1. INTRODUCTION

Currently, waste is being more and more modified in such a way that, as a result, it replaces primary raw materials. The largest sources of waste include industrial activity (50 %), energy industry (40 %) and waste from the municipal sphere and agriculture from 10 %. Waste from industry is of various types, from gangue, through metallic and non-metallic waste, to highly toxic or otherwise dangerous substances.

Metallurgical production waste is divided based on its state into:

- solid (slag, scale, returnable steel waste, etc.),
- liquid (sludge, water, oil, lye liquor, etc.),
- gaseous (flue gas, exhalation).

Among the solid, metal-bearing wastes are included sludge and drifts from agglomeration and blast furnaces, scale, steelmaking dust and sludge, metal-bearing fractions from reprocessing of steelmaking slag [1].

Blast furnace sludge and dust are captured on some types of separators in the process of cleaning blast furnace gas by dry or wet methods [2, 3]. Some of the elements that these sludges contain (Cr, Pb, Cd, Zn, Na, K) are considered harmful, both for the environment and because they can cause problems in the blast furnace, especially by accumulating zinc on blast furnace lining, saturation in the molten metal and subsequent volume expansion that destroys the lining [4, 5]. For example, during the production of steel from scrap iron in an electric arc furnace, 11 - 20 kg of sludge is produced per t of steel. [6] Blast furnace sludge contains reduced iron, carbon, and blast furnace slag components such as calcium or magnesium oxide and zinc and lead in the form of oxides.

Table 1 shows an example of the chemical composition of blast furnace sludge [3] and **Table 2** of steelmaking sludge [6-11].

Table 1 An example of the chemical composition of blast furnace sludge (wt. %) [3]

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 An example of the chemical composition of steelmaking sludge (wt. %)

Fe	Ca	Mg	Mn	Pb	Zn	Ref.
61.0	-	-	-	-	1.59	[6]
50.16	-	-	-	-	2.4	[7]
-	-	-	-	-	4.8	[8]
50.0 - 80.0	3.0	0.20 - 5.0	0.40 - 2.20	0.20 - 1.80	1.7 - 6.5	[9]
50.65	4.18	1.49	-	0.07	4.37	[10]
49.87	5.5	2.68	-	0.24	9.37	[11]

The sludge can be landfilled after dewatering and pretreatment, which is very costly. The sludge particles contain large amounts of Fe and C that could be recycled in the furnace. However, the Zn content of the sludge is high, and the Zn input to the blast furnace must be limited, so Zn has to be removed. Another undesirable element in sludge is e.g. lead.

Therefore, the work deals with the study of influence of varying thermal treatment conditions on reducing zinc and lead content from a steelmaking sludge.

2. MATERIALS AND METHODS

The Waelz process in a laboratory rotary kiln was used for the experiment, see **Figure 1**. The experimental batch was poured into a ceramic shell of Al_2O_3 material (**Figure 2**). The shell was then inserted into a rotating ceramic tube of OD 90 mm/ID 80 mm and a length of 1,200 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 rotary mechanism drove a ceramic tube with a set speed of 0.5 - 4.0 rpm. In the rotary kiln, the experiments were prepared in the temperature range 700 - 1,200 °C with a heating rate and a cooling rate of 200 °C·h^{-1}, with a temperature control accuracy of 1 °C.

The chemical composition of the steelmaking sludge used for the experiment is shown in **Table 3**. The air or nitrogen atmosphere were used for zinc and lead reduction. Graphite fine powder extra pure with particle size < 50 μm (min. 99.5 %) was also used as reducing agent.

Figure 1 Laboratory rotary kiln

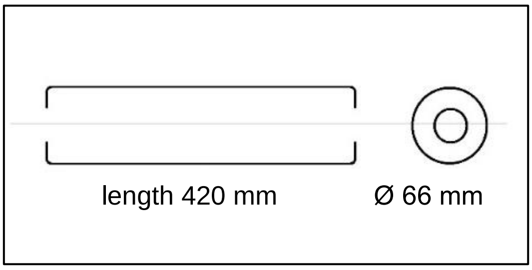

Figure 2 Schematic - Ceramic shell

Table 3 The chemical composition of experimental steelmaking sludge (wt. %)

	C	S	Fe_{metal}	FeO	Fe_2O_3	$Fe_{summary}$	Al_2O_3	CaO	SiO_2	Cr_2O_3
Steelmaking Sludge (S)	4.3	0.11	0.21	11.65	55.63	48.17	0.880	1.800	2.200	0.230
	MgO	**MnO**	**P_2O_5**	**TiO_2**	**V_2O_5**	**BaO**	**CdO**	**CuO**	**PbO**	**ZnO**
	1.650	1.120	0.230	0.030	0.010	<0.01	<0.01	0.100	0.430	13.900

The weights in one experimental batch, processing atmosphere and eventually reducing agent were as follows:

- SN - 50 g of steelmaking sludge (S) processed in a nitrogen atmosphere (N),
- SA - 50 g of steelmaking sludge (S) processed in an air atmosphere (A),
- SNG - 50 g of steelmaking sludge (S) with the addition of 50 g of graphite (G) processed in a nitrogen atmosphere (N).

3. EXPERIMENTAL RESULTS

The steel sludge was subjected to thermal treatment and subsequently the change in Zn content was evaluated. During processing, there was also a change in the content of Fe_2O_3, FeO, metallic Fe and C. The all Zn oxides in the sludge were analyzed. The Fe_2O_3 content decreased in experimental batches that contained the reducing agent graphite or were treated in a neutral nitrogen atmosphere, see **Figure 3**. The Fe_2O_3 content decreased already at temperatures above 900 °C and the most pronounced is the reduction of the Fe_2O_3 content at a temperature of 1,100 °C, see **Figures 3-6**. The Fe_2O_3 content increased in the experimental batches that were thermally treated in an oxidizing air environment and a graphite reducing agent wasn't used. The change in the content of FeO and Fe_2O_3 was also evidenced by the sludge colour change due to thermal treatment, see **Figures 7-9**. No changes in sludge content occurred after treatment at 700 °C, see **Figure 7**. The increase in Fe_2O_3 content, the decrease in FeO content and the colour change after treatment at 800 °C is shown in Figure 8. The changes in Fe, FeO, Fe_2O_3 content and colour after treatment at 1,100 °C are shown in Figure 9. The carbon contained in the sludge was also used to reduce oxygen from the sludge, the content of which decreased after thermal treatment, see **Figure 6.** However, if an external source of carbon was added, this external source was used first and then the carbon contained in the sludge. In the same thermally treated experimental batch, a decrease in zinc and lead content and an increase in Fe metal content was achieved.

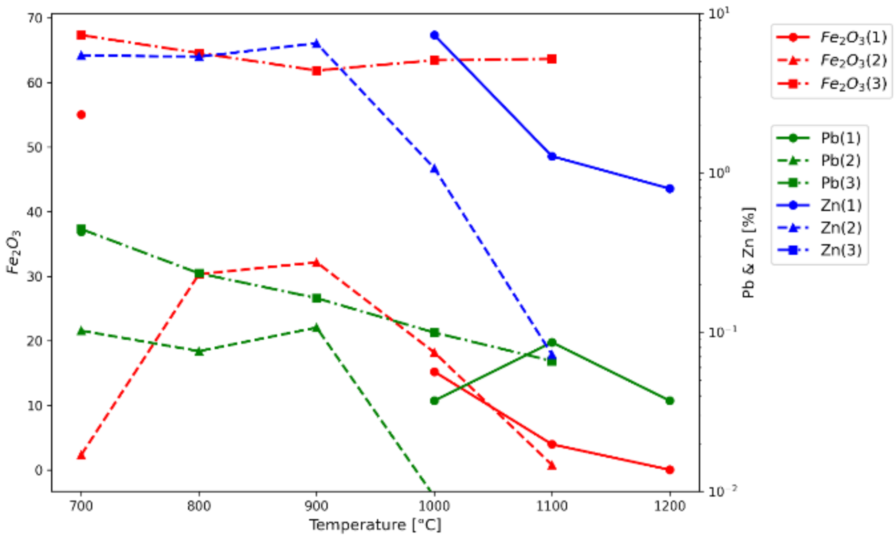

Figure 3 The Effect of temperature, atmosphere and reducing element on Fe_2O_3, Zn and Pb content in steelmaking sludges; (1) SN, (2) SNG and (3) SA.

Zinc reduction was always started when the experimental batches (SN) were heated above 900 °C. The lowest content of 0.07 % Zn and lead 0.01 % Pb was achieved at SNG batch treated at a temperature of 1,200 °C. On the other hand, the batch that did not contain a reducing agent and was treated in an air atmosphere showed almost no reduction of Zn content, see **Figure 3**. It can be seen from **Figure 3** that the main influence on the reduction of Zn in the sludge is the content of reducing agent and the secondary effect has the atmosphere in the rotary kiln. In contrast, the reduction of lead content is temperature-dependent and decreases already at 800 °C. The obtained experimental results showed that the limiting temperature for the Zn reduction is 900 °C and for Pb is 800 °C.

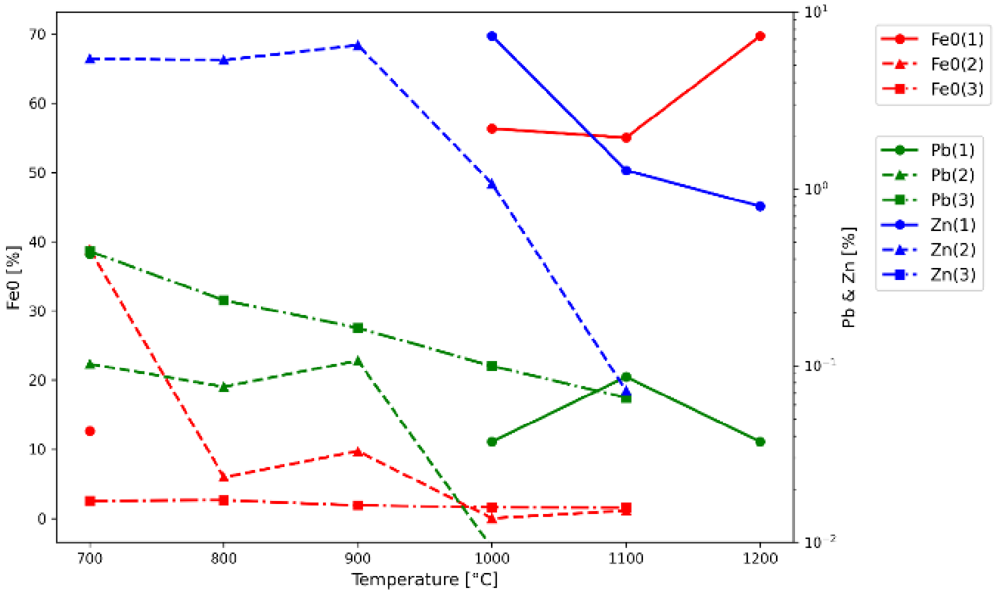

Figure 4 The Effect of temperature, atmosphere and reducing element on FeO, Zn and Pb content in steelmaking sludges; (1) SN, (2) SNG and (3) SA.

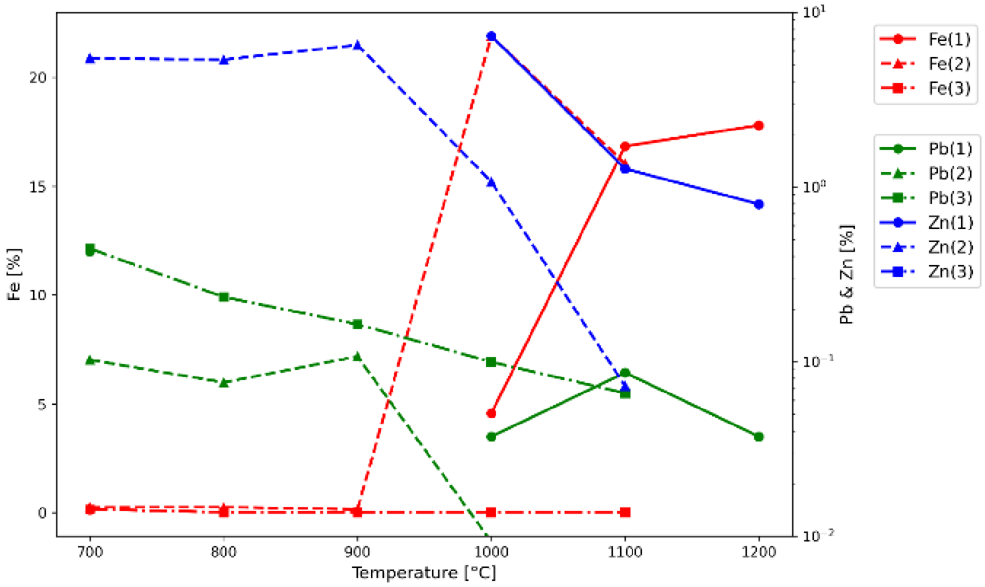

Figure 5 The Effect of temperature, atmosphere and reducing element on Fe, Zn and Pb content in steelmaking sludges;(1) SN, (2) SNG and (3) SA.

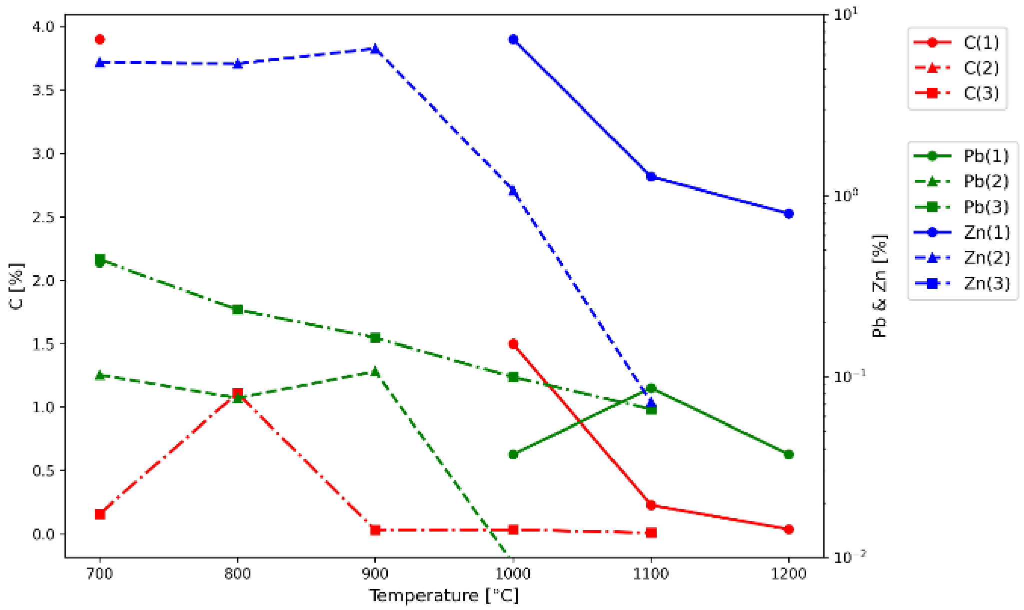

Figure 6 The Effect of temperature, atmosphere and reducing element on C, Zn and Pb content in steelmaking sludges; (1) SN, (2) SNG and (3) SA.

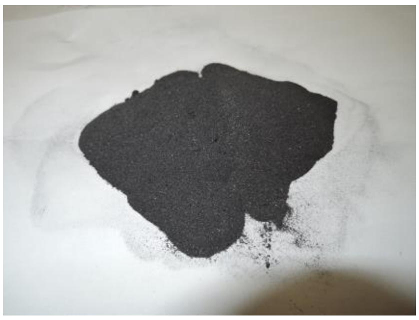

Figure 7 Effect of temperature on the colour change of steelmaking sludge (SNG), processed in a nitrogen atmosphere with graphite at 700 °C

Figure 8 Effect of temperature on the colour change of steelmaking sludge (SNG), processed in a nitrogen atmosphere with graphite at 800 °C

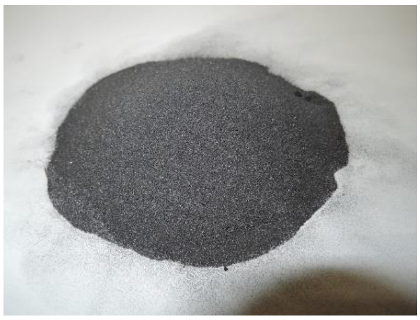

Figure 9 Effect of temperature on the colour change of steelmaking sludge (SNG), processed in a nitrogen atmosphere with graphite at 1,100 °C

4. CONCLUSION

The influence of varying thermal treatment conditions on reducing zinc and lead content from a steelmaking sludge was studied. The Waelz process in a laboratory rotary kiln was used for the experiments. It was found that the level of zinc and lead reduction depends strongly on the atmosphere and the reducing element used. A neutral atmosphere and high content of the graphite in combination with high temperature can reduce the content of Zn in the sludge to 0.06 wt. % and almost completely reduce the Pb at 1,200 °C. A significant reduction in the Zn content to 0.66 wt. % and Pb to 0.06 wt.% already occurs at temperatures of 1,100 °C. It was also verified that the speed change in the range of 0.5-4 rpm has no effect on reducing the Zn content in steelmaking sludge. Obtained results showed that the baseline temperature for reducing the Zn content is 900 °C, respectively 800 °C for Pb.

ACKNOWLEDGEMENTS

This work was created as part of drawing and using institutional support for the Long-term and conceptual development of a research organization in 2023, provided by the Ministry of Industry and Trade of the Czech Republic.

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