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HARMFUL ADMIXTURES ASSESSMENT IN SINTER MIXTURES USED IN IRON ORE SINTER PLANTS IN POLAND

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In this study composition of sinter mixtures used in Polish sinter plants were established. Seven sinter mixtures composition were examined, based on iron-bearing materials, admixtures and fuels. Contents of harmful admixtures were examined according to three kinds of environmental impacts: emissions of SO_x, heavy metals, polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/PCDFs).

Key words: iron ore, sintering process; sinter mixtures; chemical composition; harmful admixtures, Poland

INTRODUCTION

Steel production in Polish integrated steelworks (i.e. coking plants, sintering plants, blast furnaces, converters and rolling mills) in 2012 came to 4,23 million Mg of steel which corresponded to 50,6 % of the overall national output (the remaining 49,4 % accounted for steel production based on electric furnaces, i.e. 4,13 million Mg of steel) [1]. Polish metallurgical sector applies the Best Available Techniques (BATs) in order to reduce harmful emissions [2]. The iron ore sintering process is the largest source of pollutants generated by integrated steelworks (i.e. operating on a full production cycle). Gas and dust pollutants and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs / PCDFs) are generated from sintering process. According to the implementing decision of the European Union Commission of 28 February 2012, the BATs were applied in iron and steel industry to reduce major emissions from sinter belts by selection of appropriate raw materials (characterised by low content of harmful parameters) [3].

In the last few years increasing the importance and significance of environmental life cycle assessment (LCA) techniques for the iron and steel industry was observed [4]. The first environmental LCA for the steel production in Poland contained LCA analysis for the iron ore sintering process and alternative fuels for this process [5]. The LCA analysis results showed that the sinter plant had significant impacts on the environment due to fuel consumption, raw materials and waste generations. To reduce energy consumption and emission of pollutants a new method of the sinter mixture preparation was proposed (Figure 1) [6]. In Japan [7] and

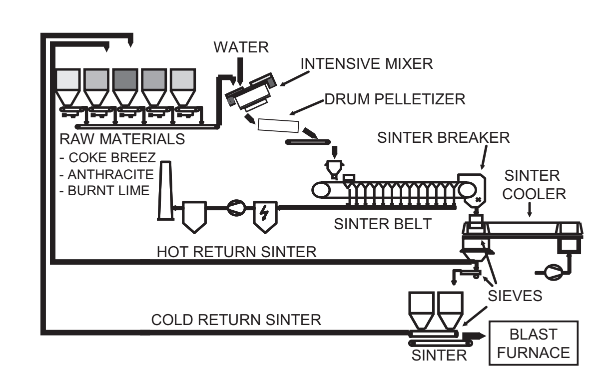

Figure 1 Sinter mixture preparation concept

Austria [8] intensive mixing and granulation of raw materials for sinter process were investigated. Intensive mixing and granulation can be used for other application [9].

In the previous works the PCDDs/PCDFs emissions from the iron ores sintering process was a crucial problem. Many studies were discussed the formation of dioxins in iron ore sintering process, where the main studies focused on the catalysts and precursors in the reaction of PCDDs/PCDFs formation. In Poland PCDDs/PCDFs studies in sinter plant were also described [10]. Cu is consider as the main catalyst in the PCDD/F formation reactions and Cl is consider as the main precursor. Inorganic parameters such as Al, Mg, Ca, K, Na, Zn and Mn were also mentioned as catalysts in the PCDD/PCDF formation reactions [11,12].

In many sintering plants, by-products containing iron were recycled to the sintering belt. This causes secondary emission of heavy metals contained in these raw materials which act as catalysts in the formation of PCDDs/PCDFs in the presence of precursors such as hydrocarbons, chlorine and organic compounds. The effect of harmful additives in blast furnace was examined [13].

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Table 1 **Share of iron-bearing materials and fuels in the studied sinter mixtures / wt. %**

Sinter mixture	Iron-bearing materials	Fuels
	hematite ore /magnetite/ mill scale	coke breeze/anthracite
S1	40/60/0	100/0
S2	20/80/0	100/0
S3	0/100/0	100/0
S4	0/91/9	100/0
S5	40/60/0	90/10
S6	20/80/0	80/20
S7	0/100/0	70/30

In national steelworks basic chemical composition of the raw materials (P_2O_5, Na_2O, K_2O, Zn, S, C, Pb, volatiles and ash) are performed in the sintering plants. However, there is lack of studies which determine influence of harmful admixtures contained in the raw materials and sinter mixtures on the gas pollution emissions, PCCDs/PCDFs and heave metals.

MATERIALS AND METHODS

In our study the analysis of chemical composition of chosen sinter mixtures were presented. Our study included measurements of the parameters in the raw materials: iron ores, fuels (coke breeze, anthracite, mill scale and admixtures (limestone, dolomite and burnt lime). Chemical composition of 30 parameters (C, S, Cl, Al, Fe, Ca, Mg, Na, K, Ti, P, Ag, As, Ba, Br, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn) in the raw materials used in Polish sinter mixtures were examined. The raw materials for sinter mixtures were obtained from Polish steelworks. The environmental analysis was performed for the sinter mixtures and harmful admixtures were examined according to three kinds of environmental impacts: emissions of SO_x, heavy metals and PCCDs/PCDFs.

All analysed sinter mixtures were prepared in the intensive mixer. The tests were conducted within a range of concentrates share in the sinter mixture from 60 to 100 %. The share of the iron-bearing materials and fuels used in the studied sinter mixtures was presented in Table 1.

The sinter mixtures differ amount of hematite ores, magnetite concentrates, mill scale and fuels (anthracite and coke breeze). The maximum share of anthracite in the fuel (mixture of coke breeze and anthracite) was 30 % and the maximum share of mill scale in the iron-bearing mixture was 9 %. The composition of the sinter mixtures used in the study was presented in Table 2.

Sinter mixture S3 and S4 did not contain hematite ores and the iron-bearing material was magnetite concentrates. Anthracite was used as fuel in S5, S6 and S7 in three share (10 – 30 wt. %). Mill scale was added in sinter mixture S4.

RESULTS AND DISCUSSION

Seven sinter mixtures were identified (Table 2) and chemical analysis was conducted for these mixtures.

Table 2 **Composition of the studied sinter mixtures / wt. %**

Raw materials	S1	S2	S3	S4	S5	S6	S7
Hematite	31,12	15,74	0,00	0,00	30,91	15,63	0,00
Magnetite 1	24,78	33,44	42,32	39,35	24,62	33,20	41,99
Magnetite 2	24,86	33,54	42,47	39,49	24,69	33,31	42,14
Mill scale	0,00	0,00	0,00	7,66	0,00	0,00	0,00
Burnt lime	2,96	3,00	3,04	3,11	2,95	2,98	3,01
Dolomite	1,22	1,24	1,25	1,27	1,21	1,23	1,24
Lime stone	10,69	8,69	6,63	4,85	10,90	8,90	6,85
Coke breeze	4,37	4,35	4,29	4,27	4,25	3,80	3,34
Anthracite	0,00	0,00	0,00	0,00	0,47	0,95	1,43

Table 3 **Heavy metals and S in the studied sinter mixtures / kg/Mg**

Mixtures	S	Hg	Zn	Pb
S1	0,31	$0,09\cdot10^{-6}$	$1,19\cdot10^{-3}$	$0,15\cdot10^{-3}$
S2	0,35	$0,08\cdot10^{-6}$	$0,87\cdot10^{-3}$	$0,13\cdot10^{-3}$
S3	0,38	$0,07\cdot10^{-6}$	$0,54\cdot10^{-3}$	$0,11\cdot10^{-3}$
S4	0,36	$0,07\cdot10^{-6}$	$0,59\cdot10^{-3}$	$0,12\cdot10^{-3}$
S5	0,37	$0,13\cdot10^{-6}$	$1,19\cdot10^{-3}$	$0,15\cdot10^{-3}$
S6	0,44	$0,15\cdot10^{-6}$	$0,87\cdot10^{-3}$	$0,13\cdot10^{-3}$
S7	0,52	$0,17\cdot10^{-6}$	$0,54\cdot10^{-3}$	$0,11\cdot10^{-3}$

Table 4 **Alkali and main catalyst and precursor of PCDDs/PCDFs in the studied sinter mixtures / kg/Mg**

Sinter mixtures	Na	K	Cu	Cl
S1	0,28	0,54	$0,37\cdot10^{-3}$	0,59
S2	0,28	0,44	$0,37\cdot10^{-3}$	0,59
S3	0,28	0,31	$0,35\cdot10^{-3}$	0,59
S4	0,26	0,31	$0,48\cdot10^{-3}$	0,57
S5	0,28	0,54	$0,37\cdot10^{-3}$	0,58
S6	0,28	0,45	$0,36\cdot10^{-3}$	0,59
S7	0,27	0,31	$0,35\cdot10^{-3}$	0,58

Figures 2 a-h presented contents of main harmful admixtures, such as S, Hg, Zn, Pb, Na and K, Cu and Cl in each raw material used in studied sinter mixtures. List of harmful admixtures in terms of environmental impact was presented in Tables 3, 4 respectively.

Sinter mixture S7 was characterized by the highest content of S and Hg (Figures 2a, 2b respectively). The highest content of S and Hg in S7 was caused by the highest amount of anthracite as fuel in this studied mixture. Magnetite concentrates, coke breeze and anthracite introduced the highest amount of S and Hg in the sinter mixtures (including the content of harmful admixtures and amount of raw materials in sinter mixture). Hg contents in the sinter mixture increased even up to 0,172 mg/Mg of sinter in fuel with 30 % share of anthracite. The highest content of Zn was in sinter mixtures S1 and S5 (Figure 2c). It was connected with the highest amount of hematite ores in these sinter mixtures. The same sinter mixtures were characterized by the highest amount of Pb (Figure 2d). Burnt lime, dolomite, limestone and hematite ores introduced high amount of Pb in the sinter mixtures (including the content of harmful admixtures and amount of raw materials in sinter

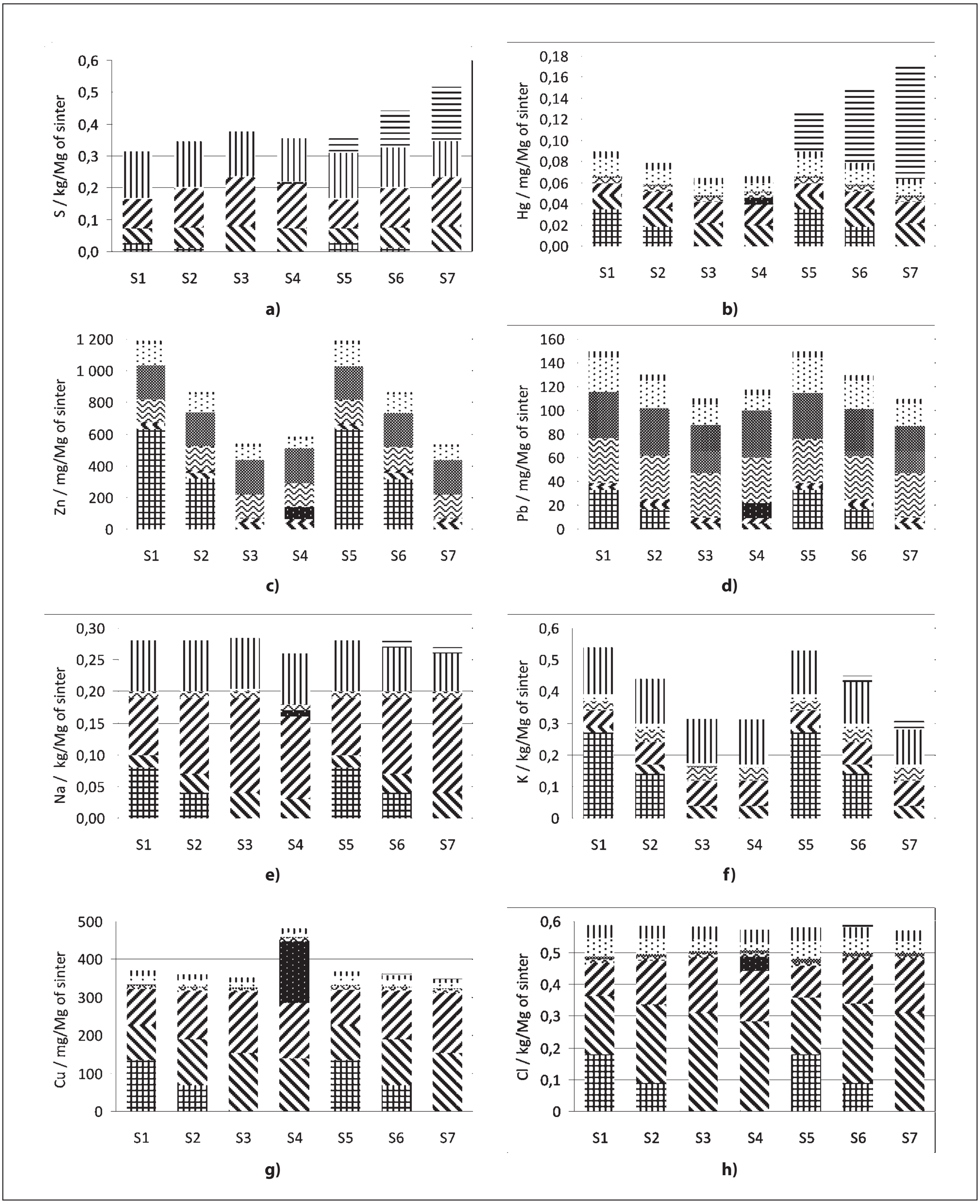

Figure 2 Content of main harmful admixtures in the studied sinter mixtures (a) S, (b) Hg, (c) Zn (d) Pb, (e) Na, (f) K, (g) Cu, (h) Cl

mixture). The higher content of Na in sinter mixtures was caused by the magnetite concentrates (Figure 2e) and content of K was caused by the hematite ores (Figure 2f). Sinter mixture S4 was characterized by the highest amount of main catalyst of PCDDs/PCDFs (Figure 2g). The highest content of Cu was caused by the highest amount of mill scale in this studied sinter mixture. The high amount of Cu was introduced by the iron-bearing materials. Cl content in each sinter mixture had the same level (Figure 2h). The highest amount of

Cl was introduced by the hematite ores and magnetite concentrates.

CONCLUSIONS

Contents of harmful admixtures in the sinter mixtures were assessed according to chosen kinds of environmental impacts: emissions of SO_x (content of S), heavy metals (content of Hg, Zn, Pb), alkali (content of K, Na) and PCDDs/PCDFs (content of the main catalyst - Cu and the main precursor - Cl).

Low content of harmful additives was in the sinter mixtures, where 100% of iron-bearing materials were only magnetite concentrates, the fuel was coke breeze and mill scale was not.

These obtained results can provide useful information for identifying the source of environmental pollution produced by iron ore sintering process and can be the primary step in achieving source reduction.

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Note: I. Golczyk is responsible for English language, Katowice, Poland