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THE USE OF AMMONIUM SULFATE AS AN INHIBITOR OF DIOXIN SYNTHESIS IN IRON ORE SINTERING PROCESS

WYKORZYSTANIE SIARCZANU AMONU JAKO INHIBITORA SYNTEZY DIOKSYN W PROCESIE SPIEKANIA RUDY ŻELAZA

Abstract: The main air pollutants in the sintering process of iron ore are polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and harmful dust. Ore sintering on sinter strands is one of the first technology steps in the ironworks. It is a process in which iron ore is crushed, subjected to annealing and mixed with appropriate additives, and then sintered in order to produce sinter which is the main component of iron in the blast furnace process. PCDD/Fs emissions were measured and the addition of ammonium sulfate as an inhibitor of the synthesis of dioxins in the sintering process of iron ore was studied.

Keywords: iron ore sintering, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, inhibitor, ammonium sulphate, de novo synthesis, emission reduction

Introduction

Iron and steel industry is very resource- and energy-intensive. The most important environmental impact of the iron and steel industry includes emissions into the atmosphere, most of which come from sinter plants. The main air pollutants in the sintering process of iron ore are polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and dust. The metallurgical processes provide in fact very good conditions conducive to the formation of PCDD/Fs dangerous to human health and the environment.

The Convention on Persistent Organic Pollutants (POPs), signed on 22 May 2001 in Stockholm, which came into force in Poland on 17 May 2004, aims at protecting human health and the environment against persistent organic pollutants. The Stockholm Convention provides for the elimination of production, use, import and export of the first twelve persistent organic pollutants, safe handling and disposal of such pollutants, and elimination or reduction of emissions of certain unintentional persistent organic pollutants. To this group belong not only polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) but also polychlorinated biphenyls (PCBs),

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hexachlorobenzene (HCBz) and pentachlorobenzene (PCBz). On the whole, the Convention applies to 22 substances. Dioxins are included in Annex C - their unintended release into the environment should be limited. Thus, in accordance with provisions of the Convention signed by Poland we are committed to reduce emissions of these pollutants, including dioxins.

The basic raw materials for steel production in blast furnaces are coke and iron ore. Ore sintering on the sinter strand is one of the first technological processes in the ironworks. Dioxin concentrations determined in two Polish sinter plants in 2004 [1] amounted to 1.2714 and 1.0539 ng I-TEQ/m³ in off-gases in the reference conditions and at the actual content of O₂, respectively, and were the highest concentrations of PCDD/Fs reported then in 20 installations tested in the steel sector.

To reduce dioxin emissions in the iron and steel industry to the required level, both primary and secondary methods are used. In recent years, research is carried out on the use of chemical inhibitors to reduce PCDD/Fs emissions. It is known that such an effect have the compounds containing sulfur or nitrogen in the molecule. For this purpose, in one of the Polish steel foundries tests were made with the use of ammonium sulfate as an inhibitor of dioxin synthesis which gave positive results.

Structure and properties of dioxins

The name "dioxins" usually refers to the entire group of 210 congeners (compounds with the same structure differing in the number and position of chlorine substituents), including 75 polychlorinated dibenzo-p-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs). Dioxins and furans are heterocyclic aromatic organic compounds. They are formed on the basis of two benzene rings, each consisting of 12 carbon atoms, connected to each other by one (as in the case of furans) or two oxygen atoms (as in dioxins). A numbering scheme is shown in Figure 1 [2].

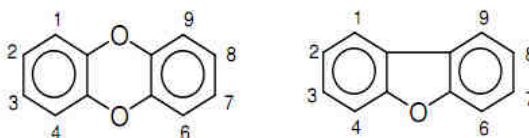


Fig. 1. Structure of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans [2]

Besides oxygen which binds benzene chains, in dioxin and furan molecules there are from 1 to 8 chlorine atoms attached to the benzene ring. The substitution of chlorine atoms in positions 2, 3, 7 and 8 is particularly important because such a system has the highest toxicity. Each subsequent chlorine atom attached to this structure causes reduction of toxicity, but the spectrum of side effects is similar [3].

Dioxins proved to be highly toxic for laboratory animals. In the course of long-term researches it was found that they caused birth defects, cancer, skin diseases, damages of liver and immune system. They had also very negative impact on the reproductive system. Their presence in the body caused birth defects in the offspring and induced spontaneous abortion [4].

The best known dioxin is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). It is highly toxic even in trace amounts. Experiments carried out on animals have demonstrated that TCDD is the strongest known toxic agent - it is about 10 000 times more toxic than potassium cyanide. Despite clear evidence of toxic effects of dioxins in animals, their equally strong toxicity for people is not so obvious. Although the World Health Organization declared dioxins the carcinogenic compounds, scientists are not unanimous on this issue [3, 5, 6]. The negative effect of dioxins on the human body is associated largely with their interference with endocrine functions. Therefore, dioxins and furans are among the so-called endocrine disrupters, or substances interfering with the action of the endocrine system. These results primarily in fertility problems related mainly to the maintenance of pregnancy and to infertility [7]. Other adverse health effects resulting from prolonged exposure to PCDD Fs may include [8]:

- reduced activity of the immune system,
- impaired psychomotor development of children,
- thyroid dysfunction,
- reduction of the quantity and quality of sperm in time,
- increased number of cases of ovarian cysts.

A prominent symptom of contact with dioxins is chloracne. It is a rash which often appears on the skin in people who had increased contact with chlorine.

Dioxin emissions from the sintering process

According to the Stockholm Convention [9], the sources highly responsible for the appearance of dioxins in the environment are as follows:

- a) waste incinerators, including co-incinerators of municipal, hazardous or medical waste or sewage sludge,
- b) cement kilns in which hazardous waste is burnt,
- c) production of paper pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching,
- d) the following thermal processes in the metallurgical industry:
 - secondary copper production,
 - sinter plants in the iron and steel works,
 - secondary aluminum production,
 - secondary zinc production.

According to the national inventory of emissions of dioxins the largest contribution to the national emissions has combustion processes outside the industry, in other words, municipal sector and heating plants. This is illustrated by the data shown in Figure 2 [10]. In 2010 it amounted to a total of 420.6 g I-TEQ per year.

The metallurgical sector (in the group of combustion processes in industry and production processes) emits about 8.2% of the national emissions of PCDD/Fs. Detailed information on the emission is given in Table 1 [10].

As follows from the Table, in the area of combustion in production processes in Poland the highest emissions of dioxins and furans into the air, including metallurgical processes, are caused by iron ore sintering - about 35.1%. High emissions of PCDD/Fs were also reported in the secondary copper production - 20.2%, and in the processes associated with the production of aluminum - about 24% of the emissions of dioxins and furans.

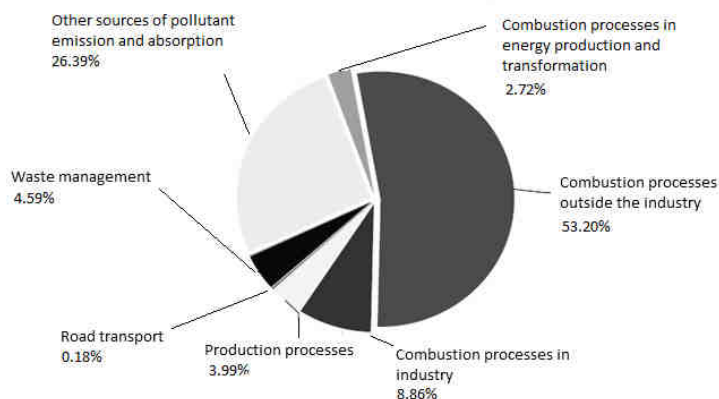


Fig. 2. The share of subsequent sectors (by SNAP - *Selected Nomenclature for Sources of Air Pollution* category) in the national dioxin emissions in 2011

Table 1
Sources of emissions of dioxins and furans into the air with reference to the metallurgical industry

Process	Total atmospheric emission	Percentage of total emission
	[mg TEQ]	[%]
Total	420 634,45	-
01. Combustion processes in the production and transformation of energy	11 446.47	2.7212
02. Combustion processes outside the industry	223 798.39	53.2050
03. Combustion processes outside the industry, including:	37 253.05	8.8564
Iron ore sinter (agglomerate)	7 880.29	1.8734
Secondary lead production	354.49	0.0843
Secondary zinc production	3 495.80	0.8311
Secondary copper production (converter copper)	0.784	0.0002
Secondary copper production (copper smelted in other furnaces)	4 540.75	1.0795
Secondary aluminum production (including scrap metal processing, cleaning systems with lower performance)	5 372.71	1.2773
Secondary aluminum production (scrap metal processing, cleaning systems with higher efficiency, better charge control)	811.88	0.1930
04. Production processes	16 774.99	3.9880
Iron blast furnace - smelting	36.38	0.0086
Processes in basic oxygen steel plants	81.61	0.0194
Electric furnaces	11 941.43	2.8389
Production of aluminum	31.91	0.0076
07. Road transport	764.74	0.1818
08. Other vehicles and equipment	81.54	0.0194
09. Waste management	19 292.11	4.5864
10. Agriculture	234.56	0.0558
11. Other sources of pollutant emissions and absorption	110 988.58	26.3860

In iron and steel industry the process of iron ore sintering is identified as the most important source of dioxin emissions. So far, research centers in Europe have carried out a few studies in this field.

Dioxins are formed in thermal processes following three mechanisms. They can be formed from chemical substances which are their precursors, *eg* chlorobenzenes and chlorophenols or can be a result of PAH decomposition. The third pathway is the formation of PCDD/Fs from incompletely burnt compounds containing carbon in their structure, *eg* soot and hydrocarbons. This is a so called *de novo* synthesis [11].

The *de novo* synthesis covers formation of dioxins outside the area of combustion of particulate carbon as well as organic and inorganic chlorine in the presence of fly ash at about 200-400°C in the presence of a catalyst, *eg*, copper, aluminum or zinc, and iron. The fastest reaction occurs at about 300°C. The mechanism of the *de novo* synthesis has a decisive effect on the amount of dioxins formed in thermal processes.

The purpose of iron ore sintering is to prepare a charge to blast furnaces. In the process of sintering fine-grained ferruginous material is used. This may be fine iron ore, ore concentrate powder, ferruginous powder and mill scale, which due to their form cannot be charged directly into the blast furnace. As a result of sintering of fine iron-bearing material a sinter is formed with appropriate parameters, grain size and chemical composition. The use of sinter being the major element of mix charged to the blast furnace improves permeability and uniformity of chemical composition of the charge, thus increasing productivity and, consequently, decreasing energy consumption and the amount of wastes [12]. A flow diagram of ore sintering is shown in Figure 3.

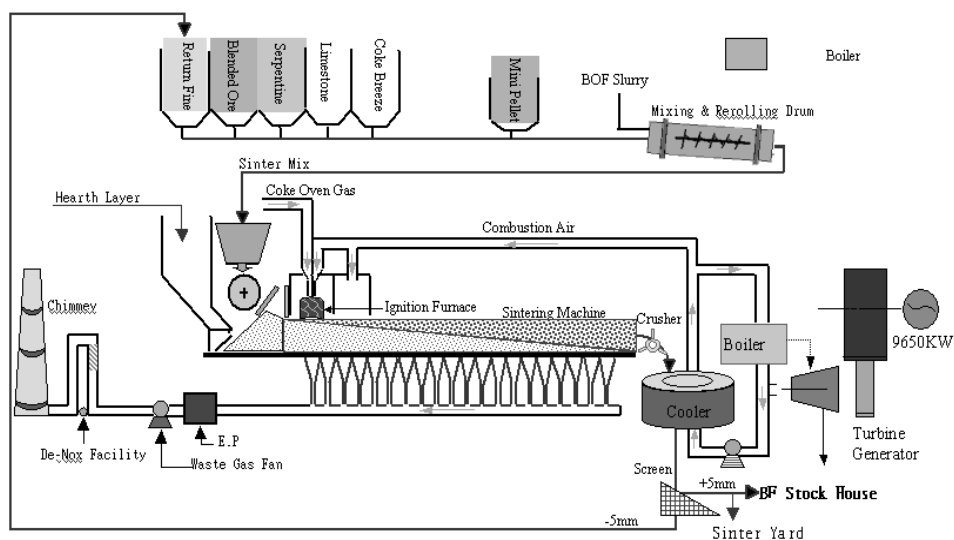


Fig. 3. Flow diagram of iron ore sintering process [13]

The mix is sintered on a continuous, traveling grate called a sinter strand, which consists of multiple trolleys whose number is specific for the given sinter strand [14] (Fig. 4). In the heat zone, where the temperature is from 1250 to 1320°C on average, fine grains

of the mix are completely reacted, and bigger ones are subject to partial surface melting [15].

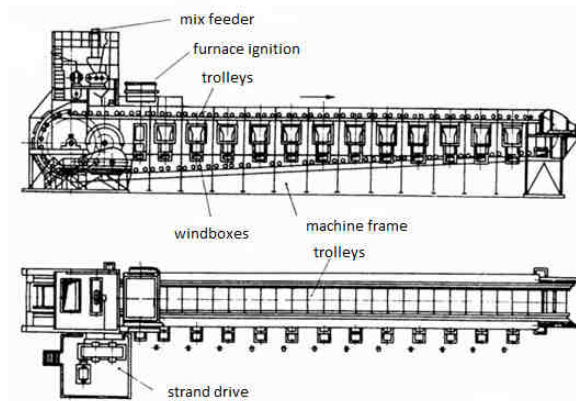


Fig. 4. Diagram of the sinter strand

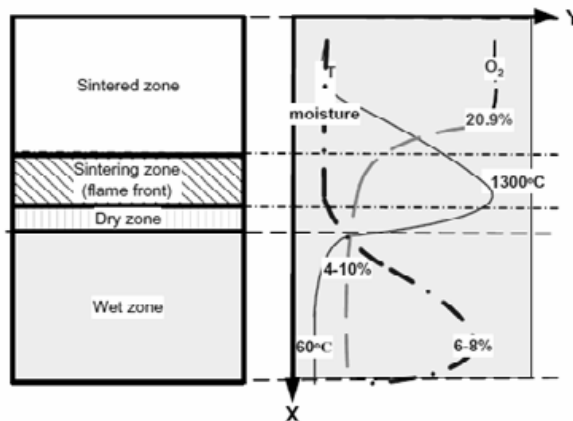


Fig. 5. Schematic arrangement of zones on the sinter strand

With reference to the flame front which causes sintering and basing on the physical and chemical changes of the mix during sintering, the strand can be divided into four main zones (from the top), as shown in Figure 5:

- ready sinter,
- sintering zone - the flame zone,
- dry (firing) zone,
- wet zone.

A layer where combustion of coke particles takes place is called the flame zone. As a result of downward combustion moisture evaporates from the sintered mix, which leads to the formation of a dry zone at the flame front. The wet zone develops due to

condensation of water vapor entrained with the air stream which moves from the dry zone. In the wet zone the temperature, humidity and oxygen concentration change slightly [16-18].

The above division into zones helps to clarify the location of space where PCDD/Fs can form. An experiment conducted by Fisher and co-workers in 1997 [19] was to test the hypothesis whether dioxins are formed inside the sintering zone on the strand, or maybe directly behind it. It was observed that when urea was added directly to the sintering zone the concentration of dioxins decreased significantly, while its addition outside the sintering zone did not produce significant results. Nakano [20, 21] found high concentrations of PCDD/Fs in the dry zone, at a distance of 10-30 mm in the flame front. This suggests that dioxins in the iron ore sintering are formed just in this zone where temperatures reach values in the range of 200-650°C. In addition, due to the fact that the compounds present in the upper phase tend to escape, it is more likely that dioxins are formed in the lower dry layer, where near the flame front a so-called temperature window and good oxygen conditions appear. While the flame front moves downward the zone some chlorinated congeners are thermally decomposed due to their proximity to the flame, while the lower chlorinated congeners escape.

It is also likely that the resulting PCDD/Fs are strongly adsorbed on the sintered material or finished products of combustion (*eg* porous carbon or fine ash particles). Dioxins in the gas phase move toward the regions closer to the wet zone where the temperature is about 60°C. This process is still progressing, and finally, when the flame front reaches the bottom of the sinter, released PCDD/Fs are observed in the off-gas.

At the same time, air is supplied to the sinter bed. The vertical downward airflow is due to pressure drop caused by windboxes installed below the sinter strand. Gas velocity in the windbox is 0.3-0.5 m/s on average. Gas stream falling with the combustion zone is directed to the windboxes, where in the last ones located on the discharge side, it is for a short time at a temperature favorable for the *de novo* synthesis (Figs. 6 and 7).

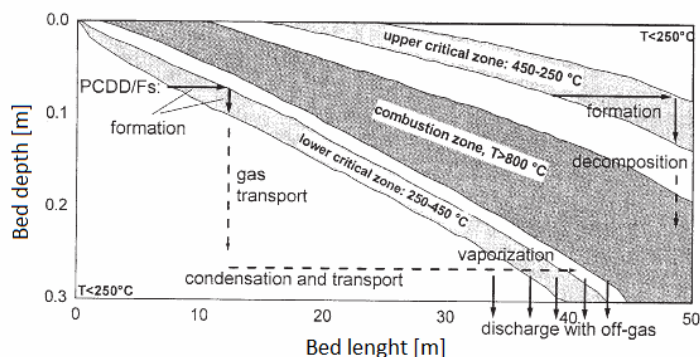


Fig. 6. Temperature distribution in sintering zones along the strand

In the initial part of the strand up to about 60-70% of its length, the temperature prevailing in the windboxes is about 80°C which is too low to form PCDD/Fs. However, in the windboxes at the strand end where flame front approaches the bed bottom, temperature rise is sufficient to obtain conditions favorable for the *de novo* synthesis. The *de novo*

synthesis can take place on the surface of fly ash suspended in the off-gas. Thus, the concentration of dioxins measured under the sinter strand should be the lowest in the first windboxes and with the increasing off-gas temperature should reach its maximum in the windboxes located at 80-90% of the strand length [20].

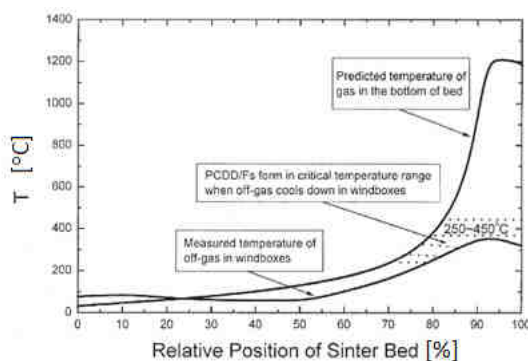


Fig. 7. Areas of dioxin formation in the sinter strand

While leaving the strand, the sinter cooled to approximately 150°C gets into the crusher where it is broken into smaller pieces and next transported on belt conveyors to the blast furnace [21]. The sintering process can also be carried out in the system with recirculation of the off-gas to the sinter strand [22].

Dioxin inhibitors

From the literature it is known that compounds present in the off-gas can have various effects on the course and speed of dioxin formation. For example, copper chloride, CuCl and CuCl_2 , accelerate the dioxin formation. Therefore, it is obvious that the metallurgical processes associated with copper casting and processing are potentially important sources of dioxin emissions to the atmosphere. It was also shown that the addition of $\text{Mg}(\text{OH})_2$ and CaO caused an increase of PCDD/Fs concentration [23, 24].

However, there are both inorganic and organic compounds which inhibit the formation of dioxins. PCDD/Fs inhibitors act by removing chlorine or disrupting catalytic reactions of dioxin formation in the presence of such metals as Cu. The inhibitors are nitrogen and sulfur compounds as well as oxides and hydroxides of alkali metals. Nitrogen and sulphur contain free pairs of electrons due to which they are capable of forming stable catalytic complexes with metals, delaying in this way the catalyst activity, while the alkali metals and ammonia compounds reduce the concentrations of hydrogen chloride used in the formation of PCDD/Fs [16].

Experimental

The research was conducted in one of the local steel mills, in the iron ore sintering plant. About $120 \text{ dm}^3/\text{h}$ of aqueous inhibitor solution was supplied by a pneumatic nozzle to the last 3 windboxes (sections of the off-gas extraction from the sinter strand), where the off-gas temperature exceeded 250°C . Off-gas samples to determine PCDD/Fs concentration

were collected from the total off-gas stream (from all 15 windboxes) in accordance with the methodology described in the standard EN-1948-1. The collected samples were purified in accordance with EN-1948-2, and then the concentration of PCDD/Fs was determined by the chromatographic method described in the standard EN-1948-3 specifying the concentration of 17 congeners of PCDD and PCDF.

Result and discussion

Results of the measurement are given in Tables 2 and 3. Figure 8 shows a graphical representation of the results (dependence of the reduction of PCDD/Fs emission on the inhibitor concentration in the off-gas duct).

Table 2

Results of studies on the use of ammonium sulfate as an inhibitor

No.	Date	T	Q	V	t	c_D	$c_{PCDD/Fs}$	c_{inh}	α
		[K]	[m ³ /h]	[m ³]	[s]	[mg/m ³]	[ng/m ³]	[mmol/m ³]	[%]
1	26-10-2011	360	410 256	3.03	7231	0.638	28.90	0.0000	0.00
2	27-10-2011	360	392 515	2.93	7232	0.647	28.99	0.0706	4.02
3	28-10-2011	360	403 603	2.81	7246	0.643	26.74	0.1375	8.97
4	02-11-2011	348	334 858	3.05	7497	0.631	30.28	0.2486	14.47

Table 3

PCDD/Fs concentration in the off-gas from the sinter strand (control - water)

No.	Date	T	Q	V	t	c_D	$c_{PCDD/Fs}$
		[K]	[m ³ /h]	[m ³]	[s]	[mg/m ³]	[ng/m ³]
1	26-10-2011	360	410 256	3.03	7231	0.638	28.90
2	16-11-2011	361	405 821	3.01	7245	0.636	29.46

Symbols in the tables:

T - off-gas temperature [K], Q - volumetric flow rate of inlet gas [m³/h], V - volume of the off-gas sample taken to determine PCDD/Fs concentration [m³], t - aspiration time of the off-gas samples to determine PCDD/Fs concentration [s], c_D - dust concentration in the off-gas stream [mg/m³], $c_{PCDD/Fs}$ - PCDD/Fs concentration (total weight of all 17 congeners) in the off-gas stream [ng/m³], c_{inh} - the inhibitor concentration in the off-gas stream during the test [mmol/m³], α - reduction of PCDD/Fs emission calculated from PCDD/Fs stream ratio [mg/s] in the test with the inhibitor and the test without the inhibitor (with pure water) [%]

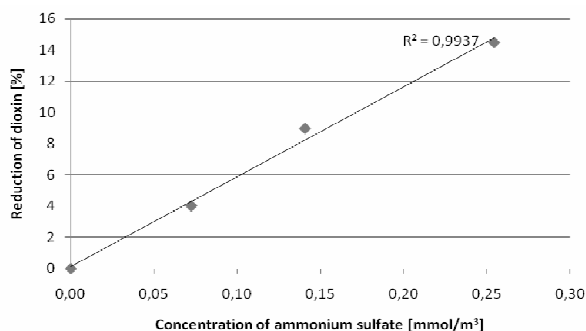


Fig. 8. Dependence of the reduction of dioxin emissions on the inhibitor concentration

In none of the so far published studies systematic research was performed on the reduction of PCDD/Fs depending on the inhibitor concentration in the off-gas stream. Usually, various inhibitors dosed into the inlet gas stream at various concentrations were compared. In studies described in the literature, the reduction of PCDD/Fs emissions reached up to 95% for certain inhibitors.

In our study a practically linear effect of the inhibitor concentration in the off-gas duct on the achieved reduction of dioxin emissions was observed for ammonium sulfate. However, at applied concentrations of the inhibitor the reduction of PCDD/Fs was approximately 14.5% and significantly differed from the values reported in the literature.

A characteristic feature of the inhibitor selected for the tests, *ie* ammonium sulfate, is that it has both nitrogen and sulfur (in N : S atomic ratio 2 : 1) in its molecule. Both of these elements are considered to be effective inhibitors of PCDD/Fs synthesis. Previous studies [16] proved that nitrogen compounds added to the charged material in the combustion process have their optimum efficiency. The best reducing power is obtained by adding 0.042 wt % of the inhibitor while achieving 50-70% reduction of dioxins. Above this value an increase in the efficiency of PCDD/Fs reduction is not observed. On the other hand, SO₂ inhibits dioxin formation by reacting with Cl₂ in the off-gas duct, creating a less reactive HCl molecule. Although this has not been fully confirmed, it is believed that an increase of sulfur content in the fuel can potentially result in a reduction of PCDD/Fs emission from the sintering process. However, the introduction of sulfur compounds directly to the raw sinter mix will inevitably lead to an increase in already high sulfur emission.

Conclusions

It was found in the research that addition of inhibitors made it possible to reduce dioxin emissions from metallurgical processes. However, this method has many limitations. The main one is the construction of metallurgical equipment and temperature distribution in the off-gas discharge system. However, experimental data collected in the research made it possible to carry out experiments on reducing dioxin emissions in accordance with the provisions of the Stockholm Convention of which Poland is a signatory.

It should also be noted that today no regulations - either national or EU, oblige the steel industry to reduce PCDD/Fs emissions. In several EU countries, there is a limit on dioxin emissions from metallurgical processes - the allowable PCDD/Fs concentration in the emitter cannot be higher than 0.1-0.4 ng TEQ/m_u³ (Table 4).

Table 4

Limit values of PCDD/Fs emissions from the metallurgical industry in some countries [25]

Country	Limit [ng I-TEQ/Nm ³]
Austria	0.4
Canada	0.20-1.35
Germany	0.1-0.4
Japan	0.1-1.0
The Netherlands	0.1
United Kingdom	0.5-2.0
Italy	0.4

A separate issue is cost-effectiveness of the reduction of dioxin emissions from off-gas streams with the use of inhibitors. Analysis of the results leads to a conclusion that the addition of more ammonium sulfate (approaching the optimum effectiveness of N atoms) could result in increased effectiveness of dioxin reduction in a sinter plant. On the other hand, it would definitely increase the costs and at higher off-gas streams reaching 400 000 m³/h the method would be not only unprofitable but would also increase significantly sulfur emissions. The cost of dosing system and current operating costs (the cost of reagents-inhibitors) for such plants are so high that they become comparable with the costs of other methods for reducing dioxin emissions, for example the filtration and catalytic method. The developed method to reduce dioxin emissions can find application in small plants only.

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WYKORZYSTANIE SIARCZANU AMONU JAKO INHIBITORA SYNTEZY DIOKSYN W PROCESIE SPIEKANIA RUDY ŻELAZA

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Abstrakt: Do głównych substancji zanieczyszczających powietrze w procesie spiekania rud żelaza należą polichlorowane dibenzodiodksyny i polichlorowane dibenzofurany (PCDD/PCDF), a także szkodliwe pyły. Spiekanie rud na taśmach jest jednym z pierwszych węzłów technologicznych huty o profilu surowcowym. Jest to proces, w którym ruda żelaza jest kruszona, poddawana wyżarzaniu i mieszana z odpowiednimi dodatkami, a następnie spiekana w celu otrzymania spieku, który stanowi główny składnik żelazowy w procesie wielkopiecowym. W aglomerowni wykonano pomiary emisji PCDD/Fs, a także badano dodatek siarczanu amonu jako inhibitora syntezy dioksyn w procesie spiekania rudy żelaza.

Słowa kluczowe: spiekanie rudy żelaza, polichlorowane dibenzo-p-dioksyny, polichlorowane dibenzofurany, inhibitor, siarczan amonu, synteza *de novo*, ograniczanie emisji