

POSSIBILITIES OF FORMATION OF DIOXINS AND FURANS IN METALLURGICAL PROCESSES AS WELL AS METHODS OF THEIR REDUCTION

Received - Priljeno: 2006-06-20
Accepted - Prihvaćeno: 2006-11-03
Review Paper - Pregledni rad

The metallurgical industry, among others, generates various kinds of wastes: gaseous, dusts, wastes and sewage. Special attention of the European Union is directed towards the elimination or significant reduction of the gaseous-dust contamination emissions including the most hazardous compounds, such as dioxins and furans. In the article the sources of dioxins and furans in metallurgical industry are described along with the reduction methods of these pollutants. Particularly the activities recommended as the Best Available Techniques (BAT) in order to reduce the PCDD/PCDF emission from sintering processes, non-ferrous metallurgy and foundry engineering have been presented.

Key words: environmental protection, dioxin, furan, emission, metallurgical processes

Mogućnost formiranja deoksina i furana u metalurškim procesima kao i metode njihova smanjivanja.

Metalurška industrija, između ostalih, proizvodi različite vrste otpadaka: plinovite, prašinate, jalovinu i mulj. Posebna pozornost Europske unije usmjerena je prema eliminiranju i znatnom smanjenju plinovito-prašinate emisijske kontaminacije uključujući najopasnije spojeve, kao što su deoksini i furani. U članku su opisani izvori deoksina i furana u metalurškoj industriji zajedno s metodama smanjenja tih polutanata. Posebno su prikazane aktivnosti koje se preporučuju kao najdostupnije metode (BAT) radi smanjenja emisije PCDD/PCDF iz procesa sinteriranja, obojene metalurgije i ljevaoničkog inženjerstva.

Ključne riječi: zaštita okoliša, metalurški procesi, emisija, deoksin, furan

INTRODUCTION

Dioxins and furans are generally used names for polychlorinated dibenzoparadioxins (PCDD) and polychlorinated dibenzofurans (PCDF) of the general chemical formula given in Figure 1. Those chemical compounds are built from two benzene rings joined together either by one (PCDF) or by two oxygen atoms (PCDD), while in each benzene ring 1 to 4 hydrogen atoms can be substituted by chlorine. Dioxins and furans are very stable and biodegradation resistive, while simultaneously - due to a low solubility in water and a very good solubility in fats - undergoing bioaccumulation i.e. they are accumulating in fatty tissues of living organisms [1].

The most toxic are components containing 4 chlorine atoms substituted in positions: 2, 3, 7 and 8. Because of a diversified toxicity and the fact that we are usually dealing with the mixture of various dioxins and furans, the method of giving the total toxicity of PCDD/PCDF contained in

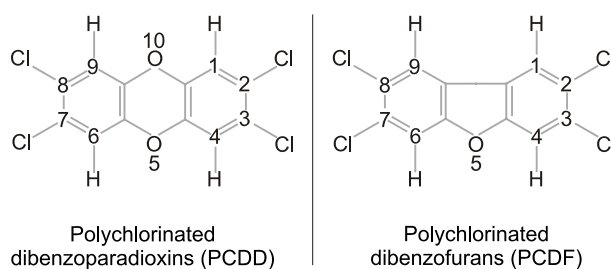


Figure 1. General chemical formula of dioxins and furans
Slika 1. Općenita kemijska formula deoksina i furana

the given sample is expressed by the International Toxic Equivalent (I-TEQ). For individual compounds belonging to this group the International Toxicity Equivalent Factor (I-TEF) was assessed. The I-TEF value for 2, 3, 7, 8 tetra-chlorodibenzo-p-dioxin, considered the most toxic from this group equals 1 [2].

PROPERTIES OF DIOXINS AND FURANS

Dioxins and furans are formed as undesirable side products in combustion processes and in some industrial

M. Holtzer, J. Dańko, R. Dańko, Faculty of Foundry Engineering University of Mining and Metallurgy, Cracow, Poland

processes such as industrial waste products and municipal wastes combustion, pesticide production, paper and cellulose manufacturing and also in metallurgical processes. It can be stated, that PCDD/PCDF can actually be formed in every thermal process, if any organic matter and chlorine are present within the combustion environment.

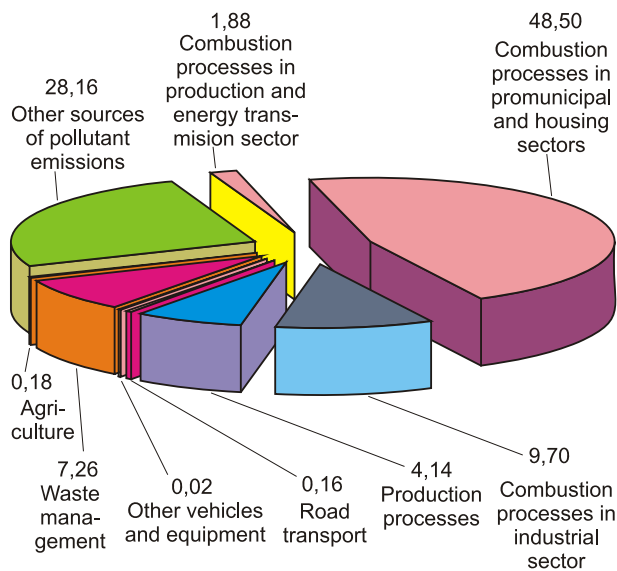


Figure 2. Share of individual sectors in the total dioxin and furan emission from the territory of Poland in 2004 (according to SNAP97 classification)

Slika 2. Udjel individualnog sektora u ukupnoj emisiji deoksina i furana na području Poljske u 2004. godini (prema klasifikaciji SNAP97)

The dominating sources of emission are combustion processes in municipal and housing sectors. Emission from these sectors was 187,7 g I-TEQ, which constitutes 48,5 % of the total emission (Figure 2.). The PCDD/PCDF emission from metallurgical processes in 2004 equalled 37,9 g I-TEQ, which is approximately 9,8 % of the total emission. However, as the result of economic and industry structural changes as well as introduction of new technologies dioxins and furans emission from the metallurgical sector declined significantly, in the last decade (Figure 3.). [3 - 5].

The largest share in the PCDD/PCDF emission in Poland has sintering. Secondary aluminium production, pig iron production and converter-oxygen steel plants have also a significant share (Table 1.). Dioxins

Table 1. Emission of dioxins and furans from the metallurgical sector including coke production in 2004

Tablica 1. Emisija deoksina i furana u metalurškom sektoru uključujući proizvodnju koksa u 2004. godini

Emission source	Activity / Gg	Emission index / mg I-TEQ/Gg	Emission / mg I-TEQ
Iron and steel production			
Sintering plant	7964,7	1,35	10752,3
Pig iron production	6400,0	0,01	64,0
Coke production (APC system/dust filters)	10213,9	0,30	3064,2
Basic oxygen steel plants	6858,0	0,02	137,2
Electric furnace steel plants	3720,9	3,00	11162,7
Production of non-ferrous metals			
Aluminium production (electrolysis)	58,9	2,00	117,9
Secondary lead production	39,4	8,00	315,3
Secondary zinc production (sample APCS)	31,1	100,00	3109,5
Secondary copper production (converter copper)	33,3	0,01	0,3
Secondary copper product. (remaining product.)	54,7	50,00	2733,9
Secondary aluminium production (including scrap processing)	251,5	4 - 150	6516,1
Source: National Emission Centre / Institute of Environmental Protection			

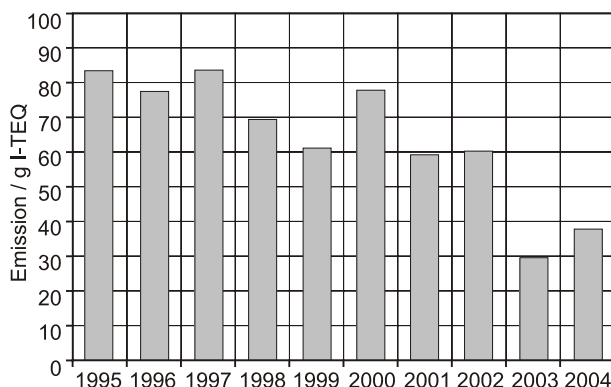


Figure 3. Emissions of dioxins and furans from the metallurgical sector in 1995 - 2004

Slika 3. Emisija deoksina i furana u metalurškom sektoru u razdoblju 1995. - 2004.

and furans are formed in thermal processes according to two basic mechanisms [6 - 8]:

1. As the result of not complete thermal decomposition of the so-called precursors, in which regrouping of atoms occur. The structure of precursors is similar to the one of dioxins and furans. Polychlorinated biphenyls (PCB), chlorophenols, chlorobenzenes, as well as PCV can be the precursors. This mechanism requires small oxygen content. The process of the PCDD/PCDF formation takes place on the surface of dust particles at a temperature between 250 - 400 °C and is catalysed by ions of certain metals, present there, e.g. Cu²⁺.

2. As the result of the so-called *de novo* synthesis, without the organic precursors participation. PCDD/PCDF are formed from C, O, H and Cl atoms in the presence of certain metals acting as catalysts (e.g. Cu, Fe). Chlorine can originate both from inorganic chlorides and organic compounds. Under those condition substances with aromatic rings are formed as intermediate products, which transfer later on into the PCDD/PCDF mixtures. Investigations of this mechanism bring the conclusion, that a significant role is played by aliphatic compounds, formed as products of not complete combustion, being next transformed into aromatic precursors of dioxin formation. The presence of carbon oxide and carbon black encourages *de novo* synthesis.

However, it has not yet been proved, which of these processes is a dominant one. The PCDD/PCDF formation processes, in accordance with the presented above mechanisms, occur in exhaust gases in the zone outside the furnace in the temperature range from 250 to 500 °C. The maximum of the formation takes place at a temperature of 350 °C.

Dioxins and furans can originate directly from the contaminated charging materials (e.g. metal scrap) containing those compounds, which - not being decomposed at a high temperature - enter into the stream of exhaust gases. Such process takes place in the oxygen lean atmosphere.

DIOXINS AND FURANS SOURCE IN METALLURGICAL INDUSTRY

Dioxins and furans can be formed in processes related to iron and steel metallurgy, non-ferrous metallurgy (production of Cu, Zn, Al) as well as in casting of iron alloys and non-ferrous metal casting (mainly aluminium alloys) [9 - 11].

Iron and steel metallurgy

The PCDD/PCDF emission can occur in ore sintering processes, pig iron production in blast-furnaces, steel production in converters and remelting of steel scrap. The emission coefficients of PCDD/PCDF in exhaust gases from steel plants in Germany, Belgium, Austria and Spain

Table 2. Concentrations of PCDD/PCDF in European steelworks emission factors are stated per tone of liquid steel [13]
Tablica 2. Koncentracija PCDD/PCDF u europskim željezarama; faktor emisije odnosi se na tonu tekućeg željeza [13]

Production sector	Concentration PCDD/PCDF / mg I-TEQ
Sintering plant	0,500 - 6,500
Blast-furnaces	0,001 - 0,004
Converter steel plant	0,001 - 0,006
Electric steewors	0,070 - 9,000

(calculated for 1 tonne of liquid steel) [12] are given in Table 2. The main, fully documented, source of PCDD/PCDF are processes occurring on a sinter strand [13, 14]. Maximum emission of those compounds, at the final segment of a sinter strand, can reach up to 6 ng I-TEQ/Nm³ [4] (Figure 4.). Relatively low dioxin concentration was found during pig iron production processes in blast-furnaces and in steel production processes in converters. In the majority of cases the PCDD/PCDF concentration does not exceed 0,1 ng I-TEQ/Nm³.

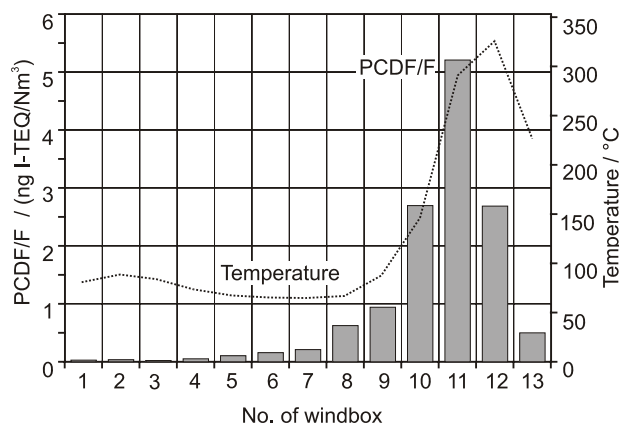


Figure 4. PCDD/F and temperature profile in the waste gas along the sinter strand

Slika 4. PCDD/F i temperaturni profili u otpadnom plinu uzduž žile smjera

In order to reduce the PCDD/PCDF emission from sintering processes the following activities are recommended as the Best Available Techniques (BAT) [14]:

- application of waste gases recirculation;
- treatment of waste gases from a sinter strand:
 - use of fine scrubbing systems, values < 0,4 ng I-TEQ/Nm³ have been achieved,
 - fabric filtration with addition of lignite coke powder also achieves low PCDD/PCDF emissions (> 98% reduction, 0,1 - 0,5 ng I-TEQ/Nm³).

Non-ferrous metallurgy

The possibility of the PCDD/PCDF formation within the non-ferrous metallurgy should be looked for mainly in sectors of the secondary production of copper, aluminium and zinc. In all those cases the major source of dioxins is a charge contaminated with oils or plastics. PCDD/PCDF compounds can be formed in the combustion zone, when the process is not running in optimal conditions, or in the system of gases treatment at their slow cooling (*de-novo* synthesis) [15]. Due to a high temperature, in processes of the primary copper production, decomposition of organic compounds occurs and the presence of SO₂ inhibits *de-novo* synthesis of dioxins. Application of gaseous mixtures

containing chlorine for degassing of liquid aluminium and removal of magnesium as well as the use of chlorides (salt flux) will provide a source of chlorine for a potential formation of dioxins.

Foundry engineering

Dioxins can be formed mainly in processes of melting of liquid casting alloys [16]. Dioxins or their precursors can be present in certain charge materials and also *de novo* synthesis is possible in furnaces or gas treatment systems. The PCDD/PCDF formation in other - than melting - stages of the casting process is rather not probable [17, 18].

Non-ferrous metal foundries: as long as only pigs and own scrap is being melted the risk of the PCDD/PCDF formation is very small. However, when the purchased scrap of non-ferrous metals is used the risk of the PCDD/PCDF formation exists. Dioxins or their precursors in the form of organic substances can be present in charge materials and the *de novo* synthesis in furnaces or in systems of waste gases treatment is possible. Application of mixtures containing chlorine for degassing and removal of magnesium as well as application of chlorides (as fluxing agents) can become the source of chlorine for a potential formation of dioxins. Preliminary purifying of scrap removes the majority of organic substances and improves effectiveness of the melting process.

Foundries of iron alloys: Taking into account that in melting furnaces there is a high temperature, the PCDD/PCDF emission (if they will be formed at all) will mainly originate as the result of *de novo* synthesis.

Cupolas: Chlorine and carbon originated from coke are present in cupolas. In addition carbon can be introduced together with a bad quality scrap (oiled-up scrap, contaminated with cooling liquids). In special cases of a cupola process the conditions favouring the PCDD/PCDF formation occur. Since *de novo* synthesis occurs mainly during cooling of exhaust gases. In the case, when gas scrubbing by means of the desintegrator is applied, exhaust gases pass through the critical temperature range of dioxins formation (250 - 450 °C) already after dedusting, i.e. at small dust content. In addition chlorides are washed out. This situation lowers significantly the risk of *de novo* synthesis occurrence.

Rotary furnaces: Due to the limited possibilities of the introduction of alloy additives, the charge generally consists of pure materials only. Because of the high temperature of the flame, exhaust gases are in the temperature range from 1000 to 1300 °C. Combustion occurs inside the furnace. *De novo* synthesis is possible when gases are cooling slowly.

Induction furnaces: Due to the limited possibilities of the introduction of alloy additives, the charge also consists mostly of pure materials. In addition no stream of hot

exhaust gases, which might be slowly cooled, is formed in the furnace.

Arc furnaces: This type of furnaces with alkaline lining, allows introduction of alloy additives and performing the refining of a metal bath. Due to this feature it is possible to use a contaminated scrap. If a charge contains organic compounds and/or chlorinated substances, then during cooling of exhaust gases some amount of PCDD/PCDF can be formed.

METHODS OF REDUCTION OF DIOXINS AND FURANS EMISSION IN METALLURGICAL PROCESSES

Even small amount of chlorine in paints, plastics or other organic material can cause the PCDD/PCDF formation. It is not practically possible to lower the chlorine content in metallurgical processes. One can only attempt to carry on the process in such a way that:

- unfavourable conditions for the PCDD/PCDF formation will be created,
- PCDD/PCDF will be effectively removed from exhaust gases.

Methods of the PCDD/PCDF reduction can be divided into two groups: primary and secondary methods [9].

Primary methods are techniques preventing the formation of contamination, which encompass reduction or elimination of the PCDD/PCDF formation in the installation. The following activities are here included:

- selection of charge materials together with their preliminary purification,
- optimisation and inspection of the technological processes,
- application of combustion and water spraying of exhaust gases.

Secondary methods are techniques limiting the emission of contamination by means of their decomposition or adsorption. Those methods do not prevent the PCDD/PCDF formation at sources, but provide the limitation of their emission to the atmosphere. The following methods should be mentioned here:

- highly effective installations for dust removal,
- adsorption on active carbon or lignite in a solid bed or applied as an addition to the stream of gases, combined with fabric filters.
- catalytic decomposition of PCDD/PCDF in the gas treatment system,
- prevention of PCDD/PCDF being formed again, by means of a rapid cooling of combustion gases to a temperature below 250 °C. The amount of PCDD/PCDF being formed is inversely proportional to the gas cooling rate.

Regardless of the fact that dioxins are thermally decomposed at a high temperature ($> 800 - 850\text{ }^{\circ}\text{C}$) in the presence of oxygen, the possibility of *de novo* synthesis still exists, when gases being cooled are passing through the temperature range, at which PCDD/PCDF can be formed again ($250 - 650\text{ }^{\circ}\text{C}$). Such temperature range can occur in heat exchangers or in systems of gas treatment in the cooler parts of the furnace, e.g. in the place of its charging.

When exhaust gases contain dust particles, on which dioxins can adsorb, their decomposition can occur not earlier than when a temperature is above $1000\text{ }^{\circ}\text{C}$.

Activities, related to the technological process interference or the primary methods undertaken in order to prevent the dioxins formation, are listed below [9, 15, 17]:

- combustion of exhaust gases from the furnace in the cold-blast cupola shaft or in the combustion chamber of the hot-blast cupola,
- continuous monitoring and the temperature control in the combustion chamber of the hot-blast cupola (temperature $> 850\text{ }^{\circ}\text{C}$) and maximising the holding time at that temperature (recommended time > 2 seconds),
- maintaining the dust particles concentration in the recuperator, if possible at the level $< 20\text{ mg/Nm}^3$, for the hot-blast cupola at an application of wet dedusting,
- rapid cooling of exhaust gases in the temperature range $250 - 450\text{ }^{\circ}\text{C}$,
- prevention or minimising of a dust collection in the cooling system of combustion gases, especially in heat exchangers (e.g. by using heat exchangers with vertical pipes), effective purifying of the system interior,
- melting of a pure charge, (in order to prevent the dioxins formation in the aluminium secondary metallurgy, oils and organic substances should be removed prior to melting),
- oxygen blowing-in for ensuring complete combustion.

Significant reduction of PCDD/PCDF by primary methods is difficult and often even impossible. Therefore, apart from the primary methods, the secondary ones should be considered. The PCDD/PCDF emission level of the order of $0,5\text{ ng I-TEQ/Nm}^3$ can be achieved at the primary methods, while the secondary methods employment allows lowering this level to below $0,1\text{ ng I-TEQ/Nm}^3$.

Secondary methods, being applied in the case of casting furnaces comprise - among others - *effective dedusting*, e.g. with the application of fabric filters¹. The dedusting procedure should be carried on at the lowest possible temperature. Though PCDD/PCDF express the tendency of adsorbing on dust particles, but at the temperature above $100\text{ }^{\circ}\text{C}$ they undergo desorption and can permeate through fabric filters. This process can be supported by an *introduc-*

tion to the gas stream powdered additives (active carbon, lignite, zeolites), on which PCDD/PCDF are adsorbing. Those powders, together with the adsorbed dioxins are later removed by dry methods. Since the captured dust can have a high PCDD/PCDF concentration it requires either special methods of storage or some earlier treatment. However, as the result of such procedures, dioxins are not destroyed but only transferred into other places in the environment. When carbon related additives are blown into the dedusting system special safety measures should be adhered to, to prevent the risk of ignition or explosion in fabric filters. Thus, together with active carbon a quicklime is also blown in. Blowing in of active carbon can be also applied at *wet dedusting* [19]. Methods of the catalytic decomposition on the appropriate catalyst are applied for the PCDD/PCDF removal. To achieve that, the fabric filters containing catalytic layers are utilised. This technique has been successfully applied in steel industry and its utilising in the foundry industry is also possible [7, 21]. In order to prevent the deactivation of the catalyst layer, the prior removal of more coarse dust particles and heavy metals from the stream of gases is necessary. Catalytic oxidation allows 95 - 99 % dioxin reduction.

CONCLUSIONS

The selection of the most effective and economic method depends on the accessibility of the place, safety aspects, process stability, and economic factors. Prior to the implementation of any secondary methods the contamination reduction possibility by the primary methods, such as effective combustion, furnace construction improvement and scrap quality control - for new and existing plants - should be considered. The primary methods of the PCDD/PCDF reduction do not require additional investments.

Total costs of purifying the exhaust gases (dust, heavy metals, acid gases etc.) are often attributed to the dioxin reduction only. Therefore the costs of the recommended ways of dioxin emission seem too high. However, if at the selection of the method of the dioxin emission reduction one takes into account the simultaneous reduction of other contamination, the additionally incurred costs resulting from dioxin removal are relatively small.

REFERENCES

- [1] A. Grochowalski: Dioksyny. Cz. I - Szkodliwe działanie, Analityka (2001) 1, 13 - 17.
- [2] B.J. Alloway, D.C. Ayres: Chemical Principles of Environmental Protection. Second Ed. Stanley Thornes Ltd. 1998.
- [3] K. Olendrzyński, B. Dębski, J. Skońkiewicz, I. Kargulewicz: Inventory of PCDD/F emission from the metallurgical sector. KCIE/IOŚ, Warsaw 2005.
- [4] C. Lassen, E. Hansen, I. Kargulewicz, M. Holtzer i in.: Survey of Dioxin Source in the Baltic Region, Environmental Science and Pollution Research 10 (2003) 1, 49 - 56.

¹ PCDD/PCDF in a temperature below $300\text{ }^{\circ}\text{C}$ are liquids of a high viscosity and therefore are easily adsorbing on dust particle surfaces.

- [5] C. Lassen, E. Hansen, J. Żurek, M. Holtzer i in.: Inventory of dioxin and furan releases in Poland. DANCEE and Ministry of Environment Poland, Warsaw 2002. Final Report.
- [6] B. Gullett, E. Altwicker, Wikström, A. Touati: PCDD/F Formation Rates from Fly Ash and Methane Combustion Carbon Sources, *Organohalogen Compd.* (2001) 50, 292 - 296.
- [7] A. Grochowalski: Dioskyny. Cz. II - Źródła, drogi skażenia, *Analityka* (2001) 2, 4 - 10.
- [8] W. Kolsut: Metody redukcji emisji trwałych zanieczyszczeń organicznych ze szczególnym uwzględnieniem procesów przemysłowych. Proceedings, Implementacja Konwencji Sztokholmskiej, Warsaw 2002.
- [9] Report "Reduction of Dioxin and Furan Emission from the Metallurgical Sector in Poland". DANCEE, Danish Environmental Protection Agency, Ministry of Environment Poland. Warsaw 2005.
- [10] M. Holtzer, I. Kargulewicz: Dioksyny i możliwości ich powstawania w procesach metalurgicznych, *Hutnik - Wiadomości Hutnicze* (1996) 8, 274 - 279.
- [11] M. Holtzer, I. Kargulewicz: The formation of Dioxins in Metallurgical Processes, *Acta Metallurgica Slovaca* 3 (1997), 233 - 237.
- [12] D. Burchart-Korol: Persistent organic pollutants (POPs) in the iron and steel industry, *Hutnik* (2005) 7-8, 412 - 416.
- [13] D. Burchart, R. Sosnowski: Emission of dioxins in the process of iron ores sintering. Proceedings, VII Conference Dioxins in Industry and Environment, Kraków-Tomaszowice 2004, p. 89 - 95.
- [14] Reference Documents on the Best Available Techniques in the Production of Iron and Steel. December 2001. . European IPPC Bureau, Sevilla.
- [15] Reference Documents on the Best Available Techniques in the Non-Ferrous Metals Industry. December 2001. European IPPC Bureau Sevilla.
- [16] M. Holtzer: Possibilities of Formation of Dioxins and Furans as well as Methods of Reducing it, *Przegląd Odlewnictwa* (2005) 7-8, 474 - 482.
- [17] Reference Documents on the Best Available Techniques in the Smitheries and Foundries Industry. July 2005. European IPPC Bureau, Sevilla.
- [18] Techniken zur Regenerierung von Mono- und Mischsandten aus Giessereien. Umweltbundesamt, personal communication.
- [19] Process Guidance Note Draft Electrical, Crucible and Reverberatory Furnaces. UK Environmental Agency, PG 2/3 (2002).
- [20] B. Duquet: Dioxin Emissions from Cupolas Influence on the Fume Treatment Process. Proceedings, 2nd International Cupola Conference. Trier 2004.
- [21] G. Wielgosiński, A. Grochowalski i in.: Katalityczny rozkład polichlorowanych dibenzo-p-dioksyn i polichlorowanych dibenzofuranów. Badania nad rozkładem odchlorobenzenu na katalizatorze $V_2O_5 - WO_3 / Al_2O_3 - TiO_2$. Proceedings, VII Conference Dioxins in Industry and Environment, Kraków-Tomaszowice 2004, p. 54 - 60.