**Danish Environmental Protection Agency**

**Ministry of the Environment**
**Institute of Environmental Protection**

# OPPORTUNITIES FOR REDUCTION OF DIOXIN EMISSIONS FROM THE METALLURGICAL SECTOR IN POLAND

Warsaw, 2005

This report on “Opportunities for Reduction of Dioxin Emissions from the Metallurgical Sector in Poland” presents the results of activities performed under the Polish-Danish project financed by the Danish Environmental Protection Agency from DANCEE resources.

Implementation of the project was supervised by the Project Steering Committee as follows: Stanisław Kamiński – Chairman (Ministry of the Environment, Dept. of Environmental Policy), Roman Głaz (Ministry of the Environment, Dept. of Environmental Protection Instruments), Adam Grochowalski (Cracow University of Technology), Mariusz Holtzer (AGH University of Science and Technology in Cracow), Wanda Kacprzyk (Institute of Environmental Protection), Mikala Klint (DANCEE, DEPA), Maria Kłokocka (Ministry of the Environment, Dept. of Environmental Policy), Carsten Lassen (COWI), Krzysztof Olendrzyński (Institute of Environmental Protection, National Emission Centre), Jarosław Ostrowski (Voivodship and Chief Inspectorate of Environmental Protection), Maciej Sadowski (Institute of Environmental Protection), Jerzy Wolski (National Fund for Environmental Protection and Water Management), Weronika Wziątek (Ministry of the Environment, Dept. of Environmental Policy).

The Danish Company – Consulting Engineers and Planners A/S (COWI), with Carsten Lassen as project manager, coordinated the project. The responsibilities of the National Project Co-ordinator were entrusted to the Institute of Environmental Protection with Maciej Sadowski as national project co-ordinator.

As foreign consultants Jens Apfel of the Badische Stahl-Engineering GmbH, Hans J. Keller of the ProVis GmbH and Carsten Lassen of the COWI were nominated.

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Thanks are due to Tinus Pulles, TNO-MEP (The Netherlands) and Ulrich Quass, Müller-BBM GmbH (Germany) for providing permission to use PCDD/PCDF analysis reporting forms developed as a part of the project "Dioxin emission in Candidate Countries".

# CONTENTS

# PREFACE

*Poland, within the framework of international obligations resulting from the EU membership, the Convention on Long-range Transboundary Air Pollution and its Aarhus Protocol on Persistent Organic Pollutants, as well as the Stockholm Convention on Persistent Organic Pollutants, is obliged to carry out emission inventories of substances subject to those agreements. During 2004, under the "Reduction of Dioxin Emission from the Metallurgical Sector in Poland" project, measurements were taken at the metallurgical sector, including the determination of, inter alia, dioxins, furans, polychlorinated biphenyls, hexachlorobenzene and 13 metals in flue gases.*

*This project was implemented under the agreement between the Danish Environmental Protection Agency and the Polish Ministry of the Environment by the Danish company COWI – the Consulting Engineers and Planners A/S together with the Institute of Environmental Protection, AGH University of Science and Technology in Cracow and the Cracow University of Technology on the Polish side.*

*The goal of the project was the quantitative assessment of dioxin and furan emissions from the metallurgical sector, development of foundations for action plans aimed at reduction of such emissions from specific facilities as well as verification of emission factors to be used for the purpose of the national inventory.*

*Denmark has a substantial scientific and technical potential concerning the reduction of dioxin emission to the air. Co-operation with the Danish Environmental Protection Agency, both in the implementation of this project as well as the preceding projects (for example "Survey of anthropogenic sources of dioxins in the Baltic Region", which was part of preparations for the development of the "National Implementation Plan for the Stockholm Convention on POPs"), was very successful. Efforts should be made to disseminate the results of the Polish-Danish project's recommendations and the proposed activities aimed at further reduction of dioxin and furan emissions.*

*I wish to convey the words of gratitude to the Danish Environmental Protection Agency for granting, within the DANCEE programme, the necessary financial support to this kind of a project in Poland. I wish also to express my thanks to the COWI Company and the foreign experts for their technical assistance and to the managers of individual plants of the metallurgical sector for their preparedness to participate in the project activities allowing the necessary measurements to be taken. Obviously, appreciation is being passed to the Polish project implementation team working under the skilful co-ordination of the Institute of Environmental Protection, to the members of the Project Steering Committee and all, who contributed to the project implementation and completion of the "Opportunities for Reduction of Dioxin Emissions from the Metallurgical Sector in Poland" report.*

*Tomasz Podgajniak*
*Minister of the Environment*

# 1. EXECUTIVE SUMMARY

The Polish-Danish “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project, covered by this report, was financed by the Danish Environmental Protection Agency (from DANCEE funds). Project activities were co-ordinated by the Consulting Engineers and Planners A/S (COWI). Implementation was based on sub-contracts made between COWI and the Institute of Environmental Protection in Warsaw, the Cracow University of Technology and the AGH University of Science and Technology in Cracow as well the Badishe Stahl-Engineering GmbH (Germany) and the ProVis GmbH (Germany). The responsibility of the National Co-ordinator was entrusted to the Institute of Environmental Protection.

The major goal of the project was to develop the foundations for further activities aimed at reduction of dioxins and furans from the metallurgical sector in Poland. Among the most important objectives the following must be mentioned:

- To measure primarily, the PCDD/PCDF emissions, to identify installations and sub-sectors having the decisive share in the emission of dioxins and furans from the metallurgical industry in Poland.
- To update the emission factors and using them to make a detailed inventory of dioxin and furan emission from the ferrous and non-ferrous metallurgy sector into the air.
- To carry out environmental reviews of selected installations in order to develop recommendations concerning opportunities for dioxin and furan emission reduction from the metallurgical sector.
- To formulate recommendations regarding follow-up actions.

The team of researchers selected installations in 20 different facilities of the metallurgical sector in Poland. They were chosen from those, who replied positively to the invitation to participate. Emission of selected pollutants from these installations was measured. Following this, several facilities were chosen and performance of environmental reviews concerning dioxin and furan emission, in the contexts of their possible reduction, was proposed. Participation of all the industries in the project was voluntary; the results obtained, as well as the names or facilities and their addresses are not revealed.

This report, prepared at the Institute of Environmental Protection, is based on fragmentary reports developed by individual task managers and presents the results achieved by the project in the following areas:

- measuring actual emissions of PCDDs/PCDFs, PCBs, HCB, and selected metals at 20 installations at industries producing: aluminium, zinc, copper, steel, castings from cast steel and cast iron, sinters of iron ore;
- carrying out the national inventory of dioxin emission for 2002 from the ferrous and non-ferrous metal production performed with the use of verified emission factors, as recommended by UNEP Chemicals;
- formulating recommendations concerning economically efficient activities and capital investments aimed at the reduction of emissions from the subject facilities.

The results obtained indicate that the largest dioxin and PCB concentrations occur during the iron ore sintering and aluminium scrap smelting processes.

Results of measurements taken confirm, in most cases, the emission factors used for inventory purposes in the past. Values of 7 emission factors were verified in result of the project implementation.

Inventory results of PCDD/PCDF emissions, including those concerning the metallurgical sector, differ between each other substantially. This is caused by the fact that the methods of emission estimation and classification of sources within the EMEP programme are different from the methodology recommended by UNEP Chemicals. The differences between the results obtained indicate also the degree of uncertainty in estimating the PCDD/PCDF emissions and releases, which may reach from several to hundreds percent.

The decline in dioxin and furan emissions from the metallurgical sector in Poland during 1995–2002 was caused on one hand by the reduction of production levels of some metallurgical products, and on the other by modernisation of technological processes, implementation of environmental protection projects and gradual introduction of iron and steel restructuring as well as improvement of methods for estimating the emission levels. Despite the considerable improvement in this respect, the share of the discussed sector in the total PCDD/PCDF emission is still substantial. According to results of the 2002 inventory, performed in accordance with the UNEP Chemicals recommendations, the share of the metallurgical sector in the total countrywide emission of dioxins and furans was 9%.

The factors and emissions resulting from the measurements performed indicate that among the sub-sectors of the metallurgical industry the greatest problems are caused by the iron ore sintering plants, the steel production in electric furnaces and the secondary copper production. However, it should be considered that the values measured at the electric arc furnaces refer to single installations and the results obtained cannot be regarded to be representative for the entire emissions from this sub-sector. Therefore continued efforts, aimed at the improvement of measuring methods are required to achieve results reflecting the actual emission levels, particularly with reference to installations with minimal or no air pollution control systems (APCS).

Results of the measurements carried out for the installations of secondary aluminium processing showing a considerable reduction of air pollutants' emission confirm the application of best available technologies at the plants concerned. Since no measurement results from plants applying poorer systems of older production technologies are available, the results presented by the report cannot be regarded as representative for the entire sub-sector.

For the fragmentary scope of the measurements their results cannot be used for updating or developing new standards of acceptable emissions from the metallurgical sector.

The results obtained will serve for the purposes of the national emission inventories for updating emission factors proposed by the Toolkit. However, further activities on the development of the national emission factors are needed.

Basing on the performed tests and the environmental reviews of selected plants recommendations were formulated for the reduction of generation or emission of these substances from iron ore sintering plants, electric arc furnace steel production processes, hot-blast furnace operations, secondary aluminium smelting in induction heaters and primary zinc production from zinc cathodes.

Having in mind that the results obtained from the project implementation allowed only for a preliminary recognition of the issue concerned, continuation of activities aimed at the reduction of dioxin and furan emissions from the metallurgical sector, including the costly emission measurements, is required. Such activities should include:

- evaluation of opportunities for reduction of PCDD/PCDF emission from the foundry industry (including production of pig iron, cast steel, copper alloys, aluminium, magnesium alloys) by systematic measurements of emissions at installations of that industry, with the aim of assessment of opportunities and methods of its reduction at instances of excessive releases;
- further verification of PCDD/PCDF emission factors for the metallurgical sector, inclusive primarily the aluminium metallurgy, based on results obtained from a larger group of installations;
- establishment of an information gathering system concerning technologies applied in the metallurgical sector (particularly in small and medium size plants).

The objectives envisaged by the project have been achieved and the results obtained were made available at the seminar held in Warsaw on 21st March 2005 and through the Internet.

# 2. INTRODUCTION

## 2.1. Origin of co-operation and formal project basis

Danish co-operation with the East European countries on the widely understood environmental protection has already quite a long history. The ecological projects implemented in Central Europe, including Poland, were financed by the Danish Environmental Protection Agency from the Danish Cooperation for Environment in Eastern Europe (DANCEE) resources. As examples of such cooperation can be mentioned an international project: “Survey of anthropogenic sources of dioxins in the Baltic Region” implemented in 2000–2001. The project included inventories of dioxin and furan releases in Estonia, Latvia, Lithuania and Poland. In Poland the inventory was implemented on the Polish side by the National Emission Centre at the Institute of Environmental Protection under supervision of the Steering Committee. Results of the project confirmed that one of the main dioxin emission sources in Poland is the metallurgical sector. In this connection, the need for better investigation on sources and categories of dioxin emissions from this sector was recognized [50].

In connection with the introduction of the “EU Strategy on Dioxins, Furans and Polychlorinated Biphenyls” [1], and considering the results of the project mentioned above, the Danish side proposed in 2003 further co-operation on emissions in the metallurgical sector and the development of recommendations on opportunities and methods for dioxin emission reduction through a joint implementation of the project “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project. The Danish offer was accepted by the Ministry of the Environment in respect of the fact that Denmark has a considerable scientific and technical potential concerning reduction of dioxin air emission, as well as in view of the fruitful co-operation demonstrated so far.

The Ministry of the Environment performed the technical supervision upon implementation of the “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project. The leading body in this respect is the Department of Environmental Policy, responsible for technical supervision of the Stockholm Convention on Persistent Organic Pollutants and of the Geneva Convention on Long-range Transboundary Air Pollution and its Aarhus Protocol on Persistent Organic Pollutants. This department performs control on issues concerning dioxin emission and on inventories of those pollutants.

The Project Steering Committee was appointed by the decision of Marek Sobiecki, Director of the Department of Environmental Policy, and took responsibility for the preparation of the technical background of the “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project and for monitoring the project implementation progress. Members of the Project Steering Committee represented the following institutions: the Department of Environmental Policy of the MoE, the Department of Environmental Protection Instrument of the MoE, DEPA, COWI, the Institute of Environmental Protection, the Chief Inspectorate of Environmental Protection, the National Fund for Environmental Protection and Water Management, the AGH University of Science and Technology in Cracow and the Cracow University of Technology (the names of SC members are given on the editorial page).

The Polish-Danish “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project, covered by this report, was financed by the Danish Environmental Protection Agency (from DANCEE funds). Project activities were co-ordinated by the Consulting Engineers and Planners A/S (COWI).

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[1] Community Strategy for dioxins, furans and polychlorinated biphenyls, COM(2001)579 final [9].

Implementation was based on sub-contracts made between COWI and the Institute of Environmental Protection in Warsaw, the Cracow University of Technology and the AGH University of Science and Technology in Cracow as well the Badishe Stahl-Engineering GmbH (Germany) and the ProVis GmbH (Germany). The responsibility of the National Co-ordinator was entrusted to the Institute of Environmental Protection.

The goal of the project was to development the foundations for further activities aimed at dioxin and furan emission reduction from the metallurgical industries in Poland and to formulate proposals for different options of emission reduction based on examples from specific facilities. Additionally verification of emission factors for use in national emission inventories and correction of the existing inventory results with the use of the verified factors was also expected.

The team of researchers selected installations in 20 different facilities of the metallurgical sector in Poland. They were chosen from among those, which replied positively to the invitation to participate. Emission of selected pollutants from these installations was measured. Following this, 6 facilities were chosen and performance of environmental reviews concerning dioxin and furan emission, in the contexts of their reduction, was proposed. Participation of all the industries in the project was voluntary, the results obtained, the names or the facilities, and their addresses are confidential.

The goals of the project were attained and its results disseminated during a seminar held in Warsaw on March 21st, 2005. This report has been prepared at the Institute of Environmental Protection based on partial reports developed by the authors of particular tasks. It presents the results obtained from:

- measurements of actual emissions performed at the selected facilities (measurements of emission of PCDDs/PCDFs and other pollutants, including PCBs and HCB, for 20 installations at industries producing: aluminium, zinc, copper, steel, castings from cast steel and cast iron, sinters of iron ore);
- updating the national inventory of dioxin emission from the ferrous and non-ferrous metal production performed with the use of verified emission factors;
- formulation of recommendations concerning economically efficient activities and capital investments aimed at the reduction of emissions from the subject facilities.

## 2.2. Characteristics of dioxins and furans

Dioxins, but actually polychlorinated dioxins and furans (PCDDs/PCDFs) are the general term for an entire group of chemical compounds known as the chlorinated aromatic hydrocarbons. These compounds are structured from two benzene rings connected with each other by one (dibenzofurans – PCDFs) or two (dibenzodioxins – PCDDs) atoms of oxygen, at the same time in each of the benzene rings 1 to 4 hydrogen atoms can be replaced by chlorine. All compounds from that group are characterised by great thermal stability and resistance to physical and chemical effects. Dioxins and furans belong to very durable substances resistant to biodegradation, and at the same time, because of poor solubility in water and very good solubility in fats, they undergo bioaccumulation, hence gather in the fatty tissue of organisms. Because of these characteristics, the dioxins and furans are treated as persistent organic pollutants (POPs).

PCDDs/PCDFs are regarded as one of the most hazardous poisons among the currently known chemical compounds. This group encompasses 210 compounds (75 dibenzodioxins and

135 dibenzofurans) of a very much-differentiated toxicity. Most toxic are compounds containing 4 atoms of chlorine placed at positions 2,3,7 and 8, such as 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetradibenzofuran. Dioxins containing from 1 to 3 atoms of chlorine are relatively low toxic and are regarded as relatively harmless. Because of differentiated toxicity and because of the fact that usually we have to do with mixtures of various dioxins and furans, a method of presenting the total toxicity of PCDD/PCDF contained in a given sample by the use of the, so called, *International Toxic Equivalent* (I-TEQ). For single substances of that group *International Toxicity Equivalency Factors* (I-TEF) were determined. The value of I-TEF for the 2,3,7,8-tetrachlorodibenzo-p-dioxin, regarded as the most toxic dioxin, is equal to 1, and the values for all the remaining compounds of the PCDD/PCDF group are vary between 0 and 1 (Table 3.3). The total toxicity of dioxins and furans determined in a tested sample, for instance food, is calculated from the quantity and toxicity of individual compounds detected.

Despite of the high toxicity of some dioxins and furans, it is difficult to compare them with other strong poisons found in the environment, because their effects in concentrations, to which one usually is exposed, are not immediate. The harmful effects of PCDDs/PCDFs are demonstrated by endocrinal disturbance or organism functions resulting in fertility troubles, troubles in maintaining gestation or even infertility (the chemical structure of dioxins is similar to the structure of steroid hormones, under which the sexual hormones are counted). In this case, the disturbance in progesterone secretion, a hormone responsible for the maintenance and correct process of pregnancy, is the problem. Carcinogenic – teratogenic (causing damage to embryos) and allergenic effects of dioxins and furans were confirmed. They are brought to the organism primarily with food and accumulate in the fatty tissue of both animal (for instance, fish) and man. Thus, accumulation of dioxins takes place in tissues of a given organism as well as on the consecutive levels of the trophic chain. It should be kept in mind, that man is the last link in that chain. Unfavourable effects of dioxins and furans activity occur only after years of exposure and years of accumulation of these compounds in the body tissue.

Research on harmfulness, mechanisms of generation and action of dioxins and furans has been carried out for many years. During that period, great progress was made in analytical and diagnostic techniques allowing assessing the concentration of PCDDs/PCDFs both in the environment and their emission to the environment, as substances hazardous to the entire human population.

## 2.3. National situation

Environmental protection is performed in Poland in accordance with the “Second National Environmental Policy” adopted in 2001 [1]. This document contains the basic principles for making decisions on environmental protection issues and sets out priority activities for the period 2002–2010. Furthermore, in 2002 the Council of Ministers adopted a short-term “National Environmental Policy for 2003–2006 with due Account of the Perspectives for 2007–2010” [5].

The fundamental principle is the principle of sustainable development, the essence of which is based on equal treatment of social, economic and environmental rights. As air protection is concerned the national environmental police envisages widening the scope of pollution emission standards, introduction of product standards considering the entire cycle of product’s life and first of all aiming at elimination of generation of pollutants at their source, which consists also application of best available techniques (BAT).

The "Second National Environmental Policy Implementation Plan" prepared in 2002 [6] calls for implementation of a whole spectrum of activities of a capital and non-capital development character. The capital development activities, concerning reduction of air pollutants emission, included into the plan consist of modernisation or installation of air protection equipment and first of all a far going modernisation of production processes in a great deal of industrial branches. Non-capital activities of the plan envisage implementation of provisions of the Council Directive 96/61/EU on integrated pollution prevention and control (the so called IPPC Directive), which finally has formulated the complex of issues concerning application of BAT in industrial facilities.

Institutions responsible for the implementation of the tasks included into the said Implementation Plan is the Ministry of the Environment in relation to non-investment activities and in relation to capital development projects the Ministry for Economic Affairs and Labour as the government body directly responsible for the implementation of the necessary modifications and modernisations.

Responsibilities of the Minister of the Environment consist among others the formation of environmental policy and development of the legal, financial and organizational basis for environmental protection. The Minister of the Environment exercises the essential control over implementation of international environmental agreements in Poland. He initiates activities connected with elaboration of mechanisms stimulating acceleration of PCB removal from electrical equipment and determination of the permissible levels of environmental risk. In addition to that, the co-ordination of BAT implementation and tasks connected with the management of POP waste and residues and the control of POP emission (also from low power energy generators) lie within the competences of the Minister of the Environment.

The Minister for Economic Affairs and Labour is responsible for creating better and better conditions and legal basis for the economic development, including operation of enterprises and improvement of working conditions and elimination of the negative impact of hazardous substances, including POPs, on employees at their workplace.

At the regional level the voivodes are competent to supervise the control activities performed by the Voivodship Environmental Protection Inspectorates also concerning compliance of industrial enterprises with the requirements set out by the integrated environmental permits, including among others releases of pollutants into the environment.

One of the short-term goals related to air protection, mentioned by the Second National Environmental Policy was the development and implementation of the POPs, including dioxin and furan emission abatement programme. Such programme, known as the "National Strategy to Protect Environment Against Persistent Organic Pollutants" [7], was developed and adopted by the Council of Ministers in 2002. The Strategy sets out among others the main lines of activities, which should be initiated during the coming years in order to reduce the emission of the polycyclic aromatic hydrocarbons, dioxins and furans (PCDDs/PCDFs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs). These activities include the review of opportunities and advisability for introduction of BAT in the iron and steel industries, elimination use of open-hearth furnaces, development of national standards of pollutant emission from the ferrous and non-ferrous metal production and accomplish detailed inventory of that emission.

The basic international law concerning POP control include:

- EU legislation indirectly or directly referring to the reduction of PCDDs/PCDFs and dioxin-like substances,

- provisions of the Protocol on Persistent Organic Pollutants (referred to as the Aarhus Protocol) to the Convention on Long-range Transboundary Air Pollution,
- provisions of the Convention on Persistent Organic Pollutants (known as the Stockholm Convention) [4].

All the documents mentioned above are similarly oriented, though their essential scopes are somewhat different. The Stockholm Convention refers in principle to 12 persistent organic pollutants: aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, DDT, PCDDs and PCDFs. It imposes the ban on production and use of 9 of them and obliges to reduce production and use of DDT as well as restriction of its export and import and to reduction of environmental releases of 3 compounds PCBs, HCB, PCDDs and PCDFs. The general objective of the Convention, which took effect on May 17th, 2004, is the prevention of negative impacts of POPs on the environment and the human health as result of co-ordinated efforts made on the global scale aimed at neutralisation of POPs residues from their common use in the past.

The basic goal of the Aarhus Protocol, the provisions of which took effect on October 23rd, 2003, is elimination or periodical abatement of production, emission and use of the 16 controlled POPs (aldrin, chlordane, chlordecone, DDT, dieldrin, PCDDs/PCDFs, endrin, heptachlor, hexabromobiphenyl, hexachlorobenzene, hexachlorocyclohexane, mirex, PCBs, toxaphene, PAHs) on a regional scale. Apart of that the Protocol determines the requirements concerning handling waste from products currently banned from production and use. It obliges Poland to reduce the emission of dioxins, furans, polycyclic aromatic hydrocarbons and HCB below the 1988 level. With reference to incineration of household, hazardous and hospital waste emission standards were introduced and application of BAT for POP emission reduction recommended together with a time schedule for compulsory application of emission standards and BAT for new and existing stationary sources. Measures for reduction of POP emission from mobile sources were recommended together with determination of main categories of stationary emission sources.

The EU legislation, in turn, does far exceed the scope of the Stockholm Convention and the Aarhus Protocol. They include provisions concerning a range of issues, such as production, use and environmental release of a large number of chemical substances, integrated environmental permits, management of hazardous waste, functioning of the, so called, large facilities of energetic combustion, environmental impact of industrial facilities, prevention of industrial accidents. As mentioned earlier, a great importance has in particular the IPPC Directive. The permissible threshold value of dioxins and furans, amounting to 0,1 ng I-TEQ/$Nm^3$ (for the oxygen content of 11%) within the EU countries, applies only to waste incineration plants [31].

Poland is the signatory to both the Stockholm Convention and to the Aarhus Protocol. Ratification processes for both of them are in progress. From May 1st, 2004, Poland is also a EU Member State. Hence, the provisions of the national environmental protection law are generally consistent with the EU requirements. The process of adjustment of the Polish law to the provisions of the Union is taking place since several years. In 2001, the fundamental legal Act - the “Environmental Protection Law” (O.J. 2001, No. 62, Item 627 with following amendments) was adopted. It regulates, among others, the issues of air quality protection and abatement of pollutant emission. This law has enacted the application of such solutions as the integrated environmental permits, which was a novelty in the Polish regulatory system. So far, the industrial enterprises were obtaining permits for disposal of pollutants to separate environmental media. Under the new law functioning of a plant, which substantially pollutes the environment in general, must obtain an integrated permit encompassing all releases to the environment. This duty also relates to enterprises of the metallurgical sector. Detailed rules for air protection are specified in executive acts to the Environmental Protection Law, among others in the Regulation of the Minister of the Environment of 4 August 2003 on emission standards from installations (O.J. No. 163, Item 1584) where the dioxin and furan emission standards from waste incineration plants are established. However, the emission standards for some significant industrial sources are still missing.

## 2.4. Characteristics of the metallurgical sector

Metallurgy, both ferrous and non-ferrous, has a long tradition in Poland. Since resources of iron ore are not too large in Poland, the iron and steel metallurgy was since mid of the XIX century based on imported ores. Mining of local ores is concentrated in the south of the country, around Częstochowa and Kłobuck.

Development of copper metallurgy was connected in Poland with the discovery of large deposits of that metal within the area of Lubin and Głogów. Exploitation of these resources begun in the sixties of the XX century. The copper strata in Poland are large but difficult to access. Despite of that four large copper mines (Lubin, Polkowice, Rudna and Sieroszowice) accompanied with the necessary processing plants were built. In Poland both the primary and secondary copper production is performed.

Zinc and lead metallurgy was developed in Poland basing on local deposits exploited as early as in the XIII century. Mining of zinc takes place mainly in the region of Olkusz town.

At the period after the II World War until 1989, in accordance with lines of the contemporary policy, a great emphasis was made on the development of heavy industry, including steel production and mining and copper metallurgy. The metallurgical sector was a leading sector in Poland. Similarly, as was the case with a number of other branches, it was characterised by excessive employment, high-energy consumption, low efficiency and law quality of products. The specific nature of the Polish metallurgy until 1989 was its concentration in the Upper Silesian region. Many plants have run a full process sequence, from the preparation of raw material (including coke) to the final rolled products. For this reason the metallurgical industry was exerting a heavy burden on the environment.

Table 2.1 shows the annual production of main metallurgical goods in selected years during 1980–2003 in Poland.

### *2.4.1. Ferrous metals production*

After the transformation of the political system in Poland, the importance of iron metals processing declined and the iron and steel metallurgy begun to face numerous problems. In this situation a restructuring programme was developed. Its key elements are the consolidation of mills into the holding Polskie Huty Stali S.A. (Polish Steel Works Inc.) and speeding up the privatisation process together with the use of financial resources obtained from issuing bonds for financial restructuring of the newly established company of the Polish Steel Works and the metallurgical works included into the governmental restructuring programme. According to expectations of that programme, full efficiency of entities subjected to the restructuring process should be attained until 2006. In result of activities performed, a reduction of employees has taken place with simultaneous decisive improvement of produce quality, now in line with the global standards. Process of decommissioning of open-hearth furnaces was finished in 2003 (Table. 2.1).

**Table 2.1.** Annual production of main metallurgical goods in selected years during 1980–2003 in Poland

| Year | Production of | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Crude steel [mln Mg] | | Pig iron [million Mg] | Hot rolled products[b] [million Mg] | Steel tubes [million Mg] | Unwrought, unalloyed refined copper [million Mg] | Zinc, technically pure [thousand Mg] | Unwrought, metallurgic aluminium, technically pure [thousand Mg] | Refined lead [thousand Mg] | Silver, technically pure [thousand Mg] |
| | total | out of which in open hearth furnaces | | | | | | | | |
| 1980 | 19.5 | 9.1 | 12.0 | 13.6 | 1.1 | 0.4[c] | 217 | 95.1 | 82.0 | 0.8 |
| 1985 | 16.1 | 6.9 | 9.8 | 11.8 | 1.0 | 0.4[c] | 180 | 47.0 | 87.3 | 0.8 |
| 1990 | 13.6 | 4.0 | 8.7 | 9.8 | 0.6 | 0.3[c] | 132 | 46.0 | 64.8 | 0.8 |
| 1991 | 10.4 | 2.6 | 6.5 | 8.0 | 0.5 | 0.4[c] | 126 | 45.8 | 50.8 | 0.9 |
| 1992 | 9.9 | 1.8 | 6.5 | 7.6 | 0.5 | 0.4[c] | 135 | 43.6 | 53.7 | 0.8 |
| 1993 | 9.9 | 1.7 | 6.3 | 7.6 | 0.5 | 0.4[c] | 149 | 46.9 | 62.3 | 0.8 |
| 1994 | 11.1 | 1.6 | 7.1 | 8.6 | 0.5 | 0.4[c] | 158 | 49.5 | 61.2 | 1.1 |
| 1995 | 11.9 | 1.5 | 7.5 | 9.0 | 0.6 | 0.4[c] | 166 | 55.7 | 66.4 | 1.0 |
| 1996 | 10.4 | 1.1 | 6.8 | 8.5 | 0.5 | 0.4[d] | 165 | 51.9 | 66.0 | 0.9 |
| 1997 | 11.6 | 1.1 | 7.5 | 9.3 | 0.5 | 0.4[c] | 173 | 53.6 | 64.7 | 1.0 |
| 1998 | 9.9 | 0.5 | 6.3 | 8.0 | 0.5 | 0.4[c] | 178 | 54.2 | 64.3 | 1.1 |
| 1999 | 8.9 | 0.4 | 5.3 | 7.0 | 0.5 | 0.5 | 178 | 51.0 | 64.0 | 1.1 |
| 2000 | 10.5[a] | 0.4[a] | 6.5[a] | 7.5[a] | 0.5[a] | 0.5 | 162 | 46.9 | 45.4 | 1.1 |
| 2001 | 8.8[a] | 0.2[a] | 5.4[a] | 6.4[a] | 0.4[a] | 0.5 | 160 | 44.7 | 44.7 | 1.2 |
| 2002 | 8.4[a] | 0.007[a] | 5.3[a] | 6.3[a] | 0.3[a] | 0.5 | 146 | 49.1 | 34.0 | 1.2 |
| 2003 | 9.1[a] | 0[a] | 5.6[a] | 6.8[a] | 0.3[a] | 0.5 | 132 | 45.4 | 55.6 | 1.2 |

Source: GUS

[a] data from specialistic surveys of the Ministry for Economic Affairs and Labour

[b] excluding semi-finished

[c] electrolytic copper

At present most of the steel works are situated in the south of the country (within the area of Upper Silesian Coal Basin, in Ostrowiec Świętokrzyski and in Stalowa Wola). The Lucchini Steel Works is an exception being situated in Warsaw. Among them the most important are the Mittal Steel Poland S.A., previously known as ISPAT Polska Stal S.A., a company that was the legal successor of the Polskie Huty Stali S.A. Company, the latter being part of the Mittal Steel Co. This enterprise is grouping four largest Polish steel works located: in Cracow (former Sendzimira Steel Works), Dąbrowa Górnicza (former Katowice Steel Plant), Sosnowiec (former Cedler Steel Plant) and Świętochłowice (former Florian Steel Plant).

These steel plants, having in hand the entire technological sequence are concentrating approximately 70% of the Polish potential of the metallurgical industry. Their joint capacity amounts to 7.6 million Mg of raw steel and about 6.6 million Mg of rolled products.

The iron and steel mills have a significant effect on the level of the national dioxin and furan emission, as well as dusts and heavy metals. They affect also the emission size of polycyclic aromatic hydrocarbons in result of manufacturing coke for use in blast-furnace processes. The reconstruction of iron and steel industries in Poland during the resent years consisted of shutting part of the blast furnaces, which produced crude iron and ferroalloys of chromium and manganese. In result the burden of gases and dusts from those furnaces, containing primarily heavy metals, onto the environment was substantially eased. Shutting off part of the blast furnaces allowed for restructuring the steel production processes, based primarily on elimination of open-hearth furnaces from being used. Their production capacities decreased from 6.9 million Mg of steel in 1985 to 0.007 million Mg in 2002 (Table 2.1). The open-hearth furnaces were fired with heating oil and, in principle, did not require preliminary processing of scrap. They were difficult to airtight sealing, and their construction allows for secondary generation of dioxins and furans in tubing carrying off gases. The basic oxygen process, mainly because of higher production capacity and energy efficiency, has replaced open-hearth process. Decommissioning of open-hearth furnaces was justified exclusively by environmental protection reasons, too.

The second factor reducing PCDD/PCDF emission is the reduced steel production, which fell during the period 1980–2003 from 19.5 million Mg down to about 9.1 million Mg (Table 2.1).

### *2.4.2. Non-ferrous metals production*

The non-ferrous metallurgy in Poland is represented by the industry processing of copper, zinc, lead, aluminium and silver. There is a particularly intensive use of metal scrap from various sources in this industry, which in turn leads to the use of a large variety of recycled raw materials. As sources of non-ferrous metals the metal scrap, dross and scum, furnace and post filtration dusts and scrum, which contain quite large amounts of metals or their compounds. Recycled raw materials are used also in some primary processes. For these reasons the non-ferrous metallurgy represents a serious source of pollutants, including dioxins and furans. In order to reduce the content of organic substances in the charge material removal of coatings and deoiling is applied through washing and pyrolysis processes. Centrifugation can also be applied for oil recovery and reduction of load on the heating system. Knowledge about the sources of recycled raw material may be useful information on potential emissions connected with its utilisation.

The copper metallurgy is distinguished by characteristic technologies, form which the type and level of emission depend. In case of secondary production the basic cause for dioxin and furan emission are the pollutions of copper scrap by plastics containing chlorine, lubrication oils, paints and varnishes etc. The most significant emission sources are concerned with the processing of scrap, melting and refining. In cases of adding scrap polluted by organic material to the converter, the process of melting secondary copper presents a potential source of emission.

Production and processing of copper is performed by the KGHM Polska Miedź S.A. (KGHM Polish Copper Inc.) company, consisting of two integrated raw material mills. These are the Huta Miedzi "Głogów" (Copper Mill "Glogow") and Huta Miedzi "Legnica" (Copper Mill "Legnica") plus the Huta "Cedynia" ("Cedynia" Mill), the latter manufacturing rolled products. The total capacity of the Polish metallurgical plants amounts annually to 540 thousand Mg of electrolytic copper, 220 thousand Mg of rolled products and 1200 Mg of silver, which places the production potential of the KGHM Polska Miedź S.A among the largest manufacturers of that sector in the world. The copper scrap is processed, among others by the Zakłady Hutmen S.A. (Hutmen Works Inc.) in Wroclaw. Originally, this factory had 7 furnace sets for scrap processing of a total production capacity of 10 thousand Mg of copper. Because of significant emission of pollutants from those furnaces, a deep modernisation of scrap processing was carried out. The environmentally burdensome sets were replaced by one rotary furnace with the over grate blast, in which the process is hermetically sealed. This action eliminated the troublesome emission. Presumably, the emission of PCDDs/PCDFs has also been considerably reduced. Potential sources of dioxin and furan emission are also the electric cable manufacturing plants, where copper is recovered from worn out cables. Such factories have special equipment to separate the insulating material from the metal, the latter being the actual conducting element. This operation prevents decisively the generation of dioxins and furans in copper processing furnaces.

With reference to secondary aluminium production, a great potential of dioxin and furan emission exists. There are two main reasons for the generation of PCDDs and PCDFs. The first one is the application of hexachloroethane for extraction of magnesium and other undesirable components from aluminium and second, inaccurate separation of the insulation material (or its abandoning), lubrication oils and oils containing chlorine from the surface of the aluminium scrap melted in furnaces. Despite of that a considerable progress has been achieved in that industry in respect of emission reduction. In addition to that, the parameters of the collected scrap are very strictly determined by the processing industry. In result of standardisation of scrap quality, the raw material put for processing is relatively clean.

During the eighties of the last century, two aluminium-processing plants were present in Poland in Skawina and in Konin. Before 1985, the aluminium production in Skawina was abandoned. Nowadays this plant, under a changed name Zakłady Metalurgiczne Skawina S.A (Metallugical Work Skawina Inc.) is involved in secondary aluminium production and processing. The plant in Konin, now know as Aluminium Konin-Impexmetal S.A. is primarily producing rolled products (sheets and strips), of which about 70 thousand Mg are sold annually. It is also the only producer of metallurgical aluminium in Poland with a capacity of 53 thousand Mg/annum. The Konin plant meets the requirements of the EU directive concerning heavy metals and hazardous substances. During recent years far going technological changes were made by the Konin works resulting in reduced emission of polycyclic aromatic hydrocarbons and allowed to attain the standard level of benzo-a-pyrene emission. The secondary production of aluminium, apart from the Skawina and Konin plants takes also place at the Alumetal Grupa "Kęty S.A. (Alumental Group Kety Inc.). Both, the aluminium mill and the plant of secondary processing do not apply hexachlorethane for the melting process, and the treatment of the heat, if it takes place, is carried out with application of adequate mixture of neutral gases and chlorine with preliminary and final washing of the product in the furnace with the use of hydrogen.

Implementation of the BAT in the industry of secondary aluminium processing has been to a great extent accomplished.

Some potential of dioxin and furan emission is connected also with the zinc production industry, and with the secondary production in particular. The processes of zinc production may generate dioxins and furans first of all during the phases of roasting, sintering and melting and, to a lesser extent, also during casting. In some processes PCDD/PCDF generation is possible in the combustion zone and in the section of cooling the flue gas cleaning system (synthesis *de-novo*), specifically when the recycled material used in the process contained plastic components.

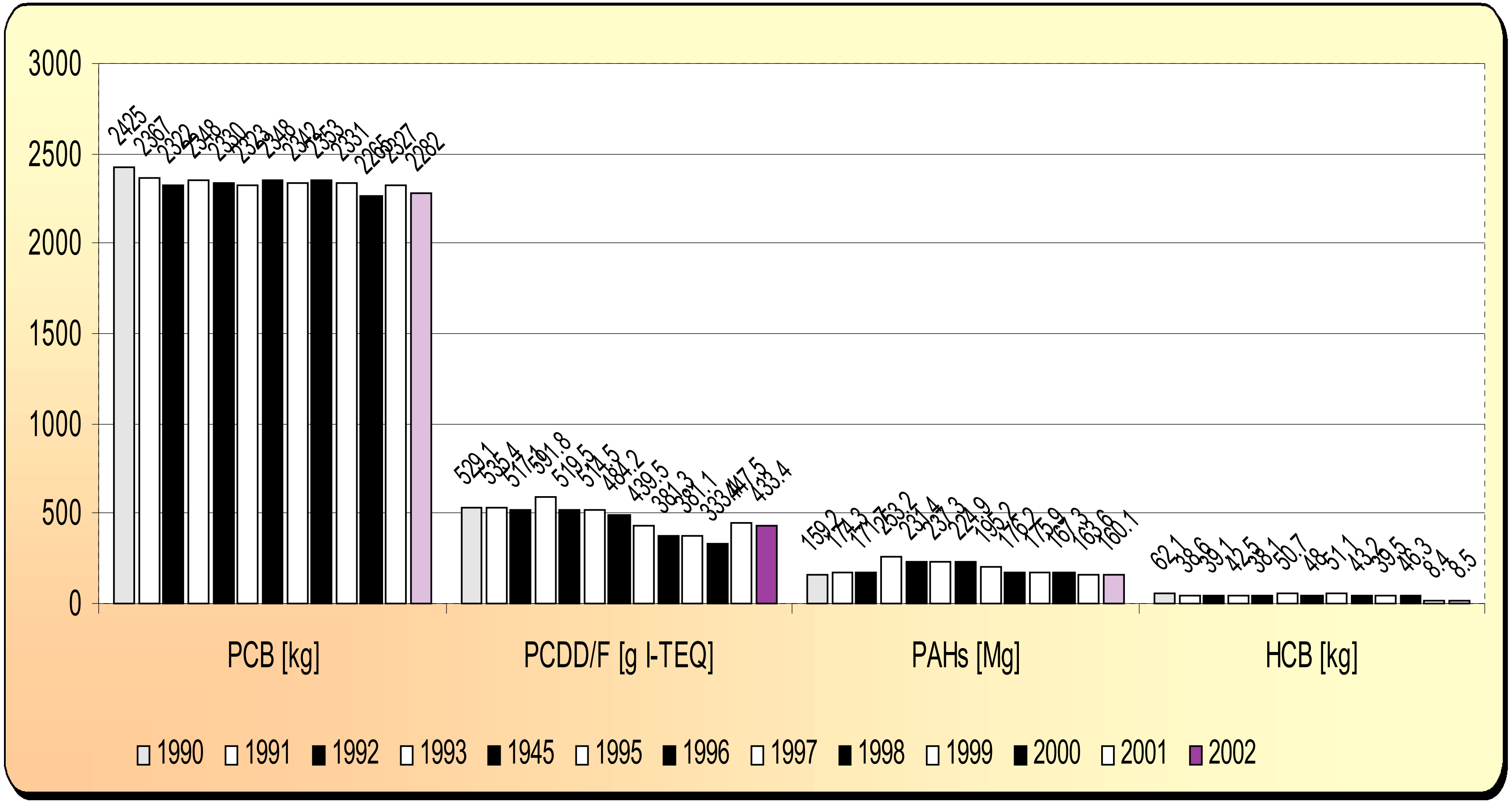
The largest producers of zinc and lead is the Huta Cynku "Miasteczko Śląskie" ("Miasteczko Slaskie" Zinc Mill), producing 80 thousand Mg of zinc and 28 thousand Mg of lead per year. It is a modern metallurgical plant, in which the production process is performed by the method of a shaft furnace allowing obtaining zinc and leading within one technological sequence. This facility was during the seventies and eighties of the last century one of the major sources of air pollution emission within the northern area of the Katowice region. Successive implementation of an environmental protection programme right from the commencement of the nineties, aimed at closure of the most worn-out sections, construction of new dust catching equipment and modernisation of the old ones provided for the reduction of heavy metal emission and a simultaneous increase of production output.

## 2.5. Emission of dioxins and furans

Dioxins and furans are generated as undesirable by-products during combustion processes and some industrial production processes, such as industrial and household waste incineration, production of pesticides, manufacturing of paper and pulp and also in iron and steel metallurgy and during production of non-ferrous metals. During the seventies and eighties of the XX century household waste incineration plants were still the main source of PCDD/PCDF emission. At present, in result of sharpening the emission standards and thanks to the development of new combustion techniques, the situation has changed, and the modern incineration plants are exhausting flue gases containing dioxins and furans in such concentration as found in the polluted air of the cities [59]. Abandoning production of chloroorganic pesticides from and bleaching paper with chlorine has cause considerable reduction of dioxin and furan emission from those processes. However, the uncontrolled burning of household waste in domestic fireplaces (individual heating boilers) remains still a serious problem, since this is the main source of dioxin emission to the air in Poland.

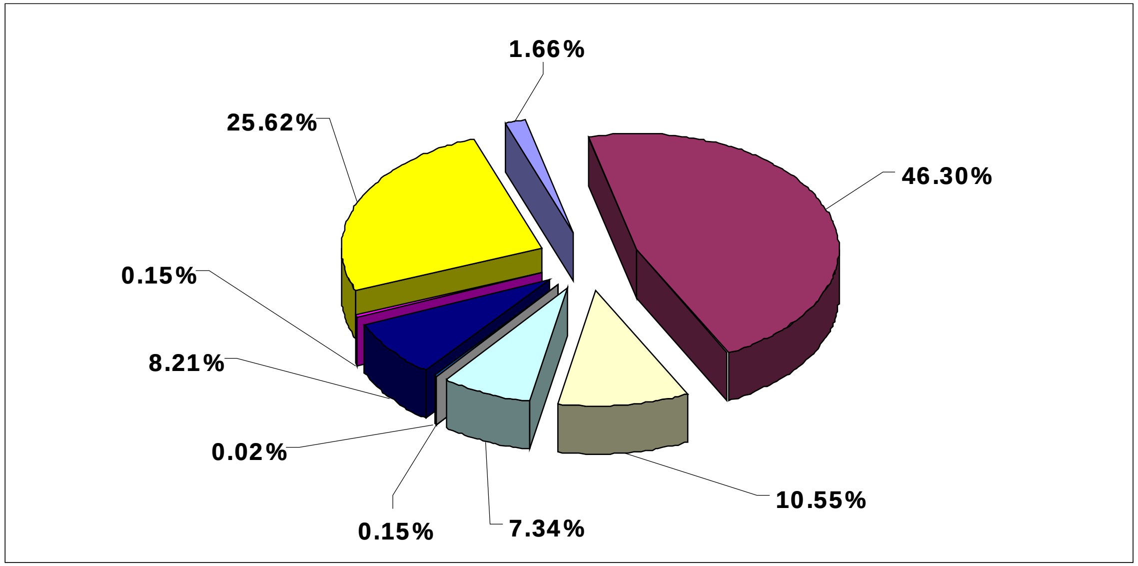
Emissions of persistent organic pollutants (dioxins and furans, polycyclic aromatic hydrocarbons, PCBs and HCB) from the Polish territory are reported annually to the UN Economic Commission for Europe and used for the purposes of EMEP [11]. Those activities belong to the European co-operation programme implementing the duties imposed by the Convention on Long Range Transboundary Air Pollution. The reports are being prepared at the National Emission Centre located at the Institute of Environmental Protection. Until the year 1999, the SNAP97 classification with its 11 main categories, was in use. At present, the NFR classification is applied, which consists of 7 sections and various main source categories. Results of POP emission from the Polish territory during 1990–2002, based on data of the National Emission Centre are presented in Table 2.1.

Air emission of PCDDs/PCDFs from the Polish territory in the year 2002 has been estimated at 433.4 g I-TEQ. Combustion processes within the municipal and housing sectors are the dominating source of emission (Figure 2.2). In 2002 the emission from these sectors amounted to 200.6 g I-TEQ,



Source: National Emission Centre/ Institute of Environmental Protection

**Figure 2.1.** Annual POP emissions from Polish territory during 1990–2002



Source: National Emission Centre/ Institute of Environmental Protection

1.66 % - Combustion processes in production and energy transformation sectors
46.30 % - Combustion processes in municipal and housing sectors
10.55 % - Combustion processes in the industrial sector
7.34 % - Production processes
0.15 % - Road transport
0.02 % - Other vehicles and equipment 0,01%
8.21 % - Waste management
0.15 % - Agriculture
25.62 % - Other sources of pollutant emission

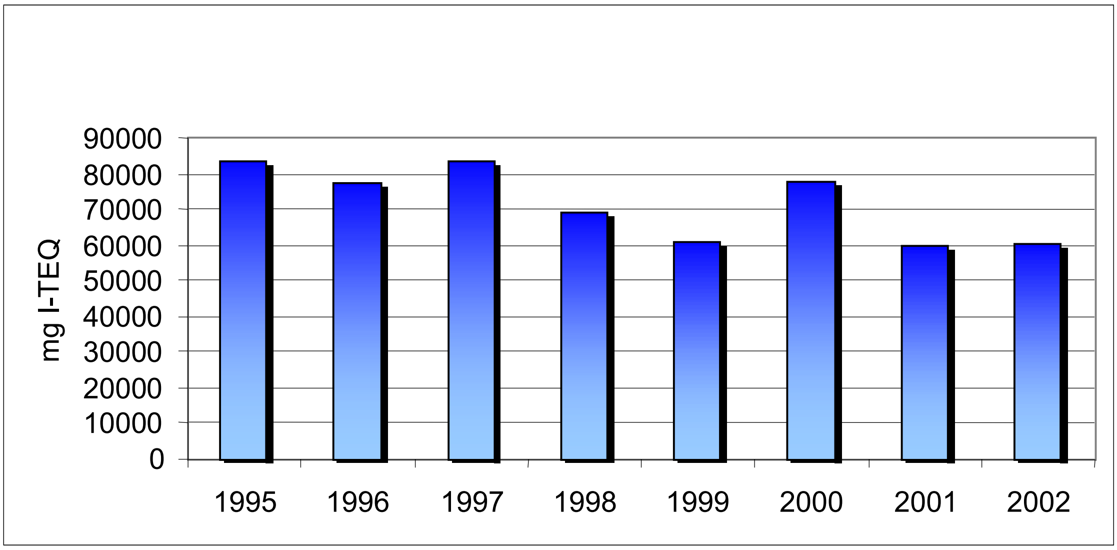
**Figure 2.2.** Share of individual sectors in the total dioxin and furan emission from the territory of Poland in 2002 (according to SNAP97 classification)

thus to 46.3% of the total emission. This is two and a half times more than the total emission from production processes (31.8 g I-TEQ) plus industrial combustion processes (45.7 g I-TEQ). A substantial share in that emission belongs to uncontrolled burning of domestic waste. However, prevention of such practices is not easy for the lack of legal regulations and control possibilities, and also for poor public awareness about the threats posed by such activities. Therefore, efforts have to be made to improve control and abatement of emission also from this sector.

Emission from metallurgical processes was estimated in the year 2002 at 62.76 g I-TEQ (Table 2.2). It is 14.5% of the total country's emission.

Clearly, both in case of PCDD/PCDF emissions as well as releases together with disposed waste the share of the metallurgical sector in total emission is substantial. It should, however, be noted that during the last decade, in result of economic transformation, restructuring of industry and implementation of new technologies, emission of dioxins and furans from the production of ferrous and non-ferrous metals has been considerably reduced. The level of emission during 1995–2002 from the metallurgical sector (estimated in accordance with the SNAP97 and the NFR classifications) is presented in Figure 2.3.

The increase of emission in the year 2000 presented in Figure 2.3 is primarily the result of the change of classification, mentioned earlier, from SNAP97 to NFR. Until the year 1999 the metallurgical sector was regarded as: pig-iron, open heart furnace plants, basic oxygen steel plant, electric steel plants, sintering plants and aluminium production. Since the year 2000 secondary production of lead, zinc, copper and aluminium were added. Despite of this change the emission for 2002 was estimated at a similar level as in 1999 and much lower than in the preceding years.



Source: National Emission Centre/ Institute of Environmental Protection

**Figure 2.3.** Emission of dioxins and furans from the metallurgical sector in 1995–2002

As far as the structure of emission from the metallurgical sector is concerned, the highest share of emission comes from aluminium production. This is attributed to a great extent to the use of poorly pre-treated aluminium scrap. A large share in the total emission is credited to sintering plants, pig iron and the basic oxygen steel plant. Table 2.2. presents the emission of dioxins and furans from the metallurgical industry and from coke production in 2002 (inventory made according to SNAP97 classification).

**Table 2.2.** Emission of dioxins and furans from the metallurgical sector including coke production in 2002

| Emission source | Activity [Mg] | Emission [mg I-TEQ] |
|---|---|---|
| ***Iron and steel production*** | | |
| Sintering plants | 6591.3 | 9557.4 |
| Pig iron production | 5296.4 | 10592.8 |
| Coke production (APC systems/dust filters) | 8787.9 | 2636.4 |
| Open hearth furnace steel plants | 7.2 | 14.4 |
| Basic oxygen steel plants | 5799 | 11598 |
| Electric furnace steel plants | 2561.2 | 5122.4 |
| ***Production of non-ferrous metals*** | | |
| Aluminium production (electrolysis) | 58.8 | 117.6 |
| Secondary lead production | 66.5 | 532 |
| Secondary zinc production (simple APCS) | 12.7 | 1270 |
| Secondary copper production (converter copper) | 29.4 | 0.3 |
| Secondary copper production (remaining furnaces) | 69 | 3450 |
| Secondary aluminium production (including scrap processing) | 119.1 | 17865 |

Source: National Emission Centre/ Institute of Environmental Protection

## 2.6. Objectives and scope of the project

Among the most important objectives of the Polish-Danish “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” project the following must be mentioned:

- Measurement of emission, primary PCDDs/PCDFs, to identify installations and sectors having the decisive share in the emission of dioxins and furans from the metallurgical industry in Poland.
- Updating the emission factors and using them make a detailed inventory of dioxin and furan emission from the ferrous and non-ferrous metallurgy sector into the air.

- Carrying out environmental reviews of selected installation in order to develop recommendations concerning opportunities for dioxin and furan emission reduction from the metallurgical sector in Poland.
- Provide recommendation regarding follow up actions.

The first stage of the project was used for the measurement of real dioxin and furan emissions at selected installations representing different processes applied in the metallurgical industry. Measurements were taken from June to August 2004 at 20 installations. Apart from PCDD/PCDF emission the emission of PCBs, HCB, total organic carbon, particulate matter, hydrogen chloride, hydrogen fluoride, sulphur dioxide, carbon dioxide, carbon oxide, hydrogen oxides, oxygen and 13 metals: Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V and Sn was measured.

Subsequently, basing on the data gathered, updated emission factors for dioxins and furans were established in relation to each individual process, which than were used for updating the inventory of dioxin and furan emission for 2002 from the metallurgical sector in Poland, according to recommendations of UNEP Chemicals [40].

Simultaneously at 6 selected installations: iron ore sintering plant, installation fro steel production in an electric arc furnace, installation for secondary aluminium melting, installation for the primary zinc production and installation for the secondary aluminium production plant environmental reviews were carried out. On their basis, after consultations of the local and foreign experts with the management of all facilities covered by the project, proposals were made on methods of reducing of PCDD/PCDF emission, and in broader terms, for the particular branch of the metallurgical sector with the use of experience of the EU Member States and with due regard of the BREF recommendations (reference documents concerning BAT, developed for the purpose of obtaining the integrated permit, the documents thereto do not present a legalised standard).

# 3. ANALYSIS OF DIOXIN EMISSION FROM THE METALLURGICAL SECTOR

Within the framework of the project[2] investigations were performed, in which the concentrations of PCDDs, PCDFs, PCBs, and HCB in flue gases from processes taking place in the metallurgical industry in Poland were determined. Tests[3] were carried out in 20 selected installations at plants involved in metallurgy of iron and steel, copper, aluminium and zinc between the 15 June and the 11 August in 2004. Results of analyses from these measurements are presented in Tables 3.6 and 3.8 as well in Table B of Annex 2.

The following substances were subject of measurement:

- 17 single congeners of PCDDs and PCDFs expressed as total I-TEQ values, according to the EN–1948 EU standard [25],
- Polychlorinated biphenyls (PCBs) – as a sum of 7 indicator congeners,
- Hexachlorobenzene (HCB),
- in addition to that the total organic carbon (TOC, $C_{org}$), particulate matter (PM 0.2), HCl, HF, $SO_2$, $CO_2$, CO, $NO_x$, $O_2$ and 13 metals: Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V and Sn.

## 3.1. Selection of plants and installations

In selection of plants and installations, an effort was made to include into investigations each of the production process and ensure that the tested installation was typical emission standard for the given industrial process. The technological process at time of measurement had to be run with maintenance of typical, nominal load of production standards.

### *3.1.1. Steel and iron metallurgy*

There are four different processes performed in this sector:

Sintering of iron ore. This process is commonly known as generating high concentrations of dioxins and PCBs. As can be drawn from technical literature 2–4 g of I-TEQ of these substances are released annually into air by the European countries.

Iron production (blast furnace) and steel production (basic oxygen furnace). In both of these processes, a relatively low dioxin concentration was measured, which may be the result in the presence of a high

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[2] The study, results of which are presented in this chapter, is also the subject of the scientific paper submitted to: *Environmental Science and Technology.*

[3] All studies, tests, calculations and the final report [53] was carried out by the team of the Laboratory of Trace Analysis of the Krakow University of Technology staff, under supervision of Prof. Adam Grochowalski, PhD., Eng. Sampling at the installations was performed by the EMPIRO Ltd. in Krakow, permanently co-operating in this respect with the Krakow University of Technology.

$SO_2$ concentration causing blockage of the chlorination of aromatic compounds. This phenomena (however still disputable) results from the mechanism of the, so-called, *de-novo* synthesis, in which dioxins are created during the reaction of atomic chlorine with molecules of atomic carbon. In most cases the dioxin concentration is less than 0.1 ng I-TEQ/$m^3$ in stack gases from these processes.

Melting of iron and steel scraps. Because of the high content of plastics, coatings, paintings and sealing as well as other non-ferrous materials in the charge during preliminary thermal operations concerned with heating up the iron and steel scrap a strong emission of pollutants, including dioxins and PCBs takes place.

### 3.1.2. *Copper metallurgy*

Two basic processes are being implemented in the Polish copper metallurgy described below.

Sintering and enrichment of copper ore – is connected with high emission of $SO_2$, which is used directly for sulphuric acid production (SOLINOX plant). Because of the extremely high of $SO_2$ concentration, reaching up to 250 g/$m^3$, the dioxins formation in this process is negligible. Moreover, the process of $H_2SO_4$ production requires multi-step scrubbing of process gases leading to a very effective removal of dioxins and PCBs traces. The investigations performed had to confirm this theory.

Recovery of copper from slag of thermal processes requires application of various additives and represents a high temperature process. The copper oxide is a known catalyser for the formation of dioxins in thermal processes.

In both cases the concentration values for dioxins, PCBs and HCB from these processes are unknown. Reactions of dioxins formation under such circumstances are not recognised and only measurements may confirm the actual values of their concentrations.

### 3.1.3. *Aluminium metallurgy*

In all cases (four installations) the thermal process was concerned with melting aluminium scrap using different technologies: electric furnace, gas chamber furnace, gas and oil fired rotary furnace and electric furnace with preheating to remove plastics and decoration coatings (aluminium beverage tins).

### 3.1.4. *Zinc metallurgy*

Two processes taking place in two technological operations in zinc metallurgy were subject of examination.

Enrichment and sintering zinc ore connected release of a high $SO_2$ concentration. Similarly to copper ore the process gases in this case contain a high concentration of $SO_2$, which is used also for production of sulphuric acid. Low concentration of dioxins and PCBs confirms the theory of dioxin formation inhibition in presence of high $SO_2$ concentrations and that the process of sulphuric acid production reduces dioxins from process gases to trace values, below 0.1 ng I-TEQ/$m^3$.

Zinc casting from zinc cathodes. In this process, an additive of ammonium chloride ($NH_4Cl$) is applied, which presents a potential source of dioxin formation because of chlorine content.

### *3.1.5. Installations tested*

Measurements were conducted in the 20 metal industry installations, which agreed to allow the stack gases to be tested. For confidential reasons no names of installation or company has been revealed. Table 3.1 shows installations with their identification numbers, to facilitate the use of the measurement results presented in Tables 3.6 – 3.9 and in Annex 2.

**Table 3.1.** List of examined installations

| Installation examined and its allocated identity number | |
|---|---|
| 1. Foundry of spheroid and cast iron | 11. Aluminium scrap melting-natural gas furnace |
| 2. Iron ore sintering plant | 12. Aluminium scrap and cans melting-electric furnace |
| 3. Enrichment of copper ore | 13. Zinc ore roasting (sphalerite)-$H_2SO_4$ production from stack gases |
| 4. Copper smelting (production of sulphuric acid) | 14. Zinc casting from zinc cathodes |
| 5. Copper smelting (de-coppering of slag) | 15. Steel scrap melting-steel production in an electric arc furnace ** |
| 6. Copper smelting (production of sulphuric acid) | 16. Production of primary iron in a blast furnace |
| 7. Foundry of cast iron * | 17. Steel production in a basic oxygen furnace |
| 8. Foundry of cast steel-electric arc furnace | 18. Grey and spheroidal graphite iron production-gas rotary furnace |
| 9. Aluminium scrap melting-electric furnace | 19. Iron ore sintering plant |
| 10. Aluminium scrap melting-rotary furnace | 20. Steel scrap melting-steel production in an electric arc furnace ** |

Source: Laboratory of Trace Analyses, Cracow University of Technology

* Measured upstream the APCS - measurements downstream the APCS were not possible.

** For these installations, measurements were performed on the secondary off-gas for technical reasons preventing measurement on primary off-gas.

## 3.2. Sampling and analysis methodology

### *3.2.1. Methods of PCDD/ PCDF determination*

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are collected on quartz fibre filter (dust fraction) fixed on glass sinters and after removal of the solid fraction by filtration, on a solid sorbent – polyurethane foam (gas fraction) in an isokinetic manner with the use of EMIOTEST 2594 with a heated filtration chamber. In addition to that, the water condensate was collected after cooling down the flux of gases. Schematic presentation of the apparatus is given in Figure 3.1.

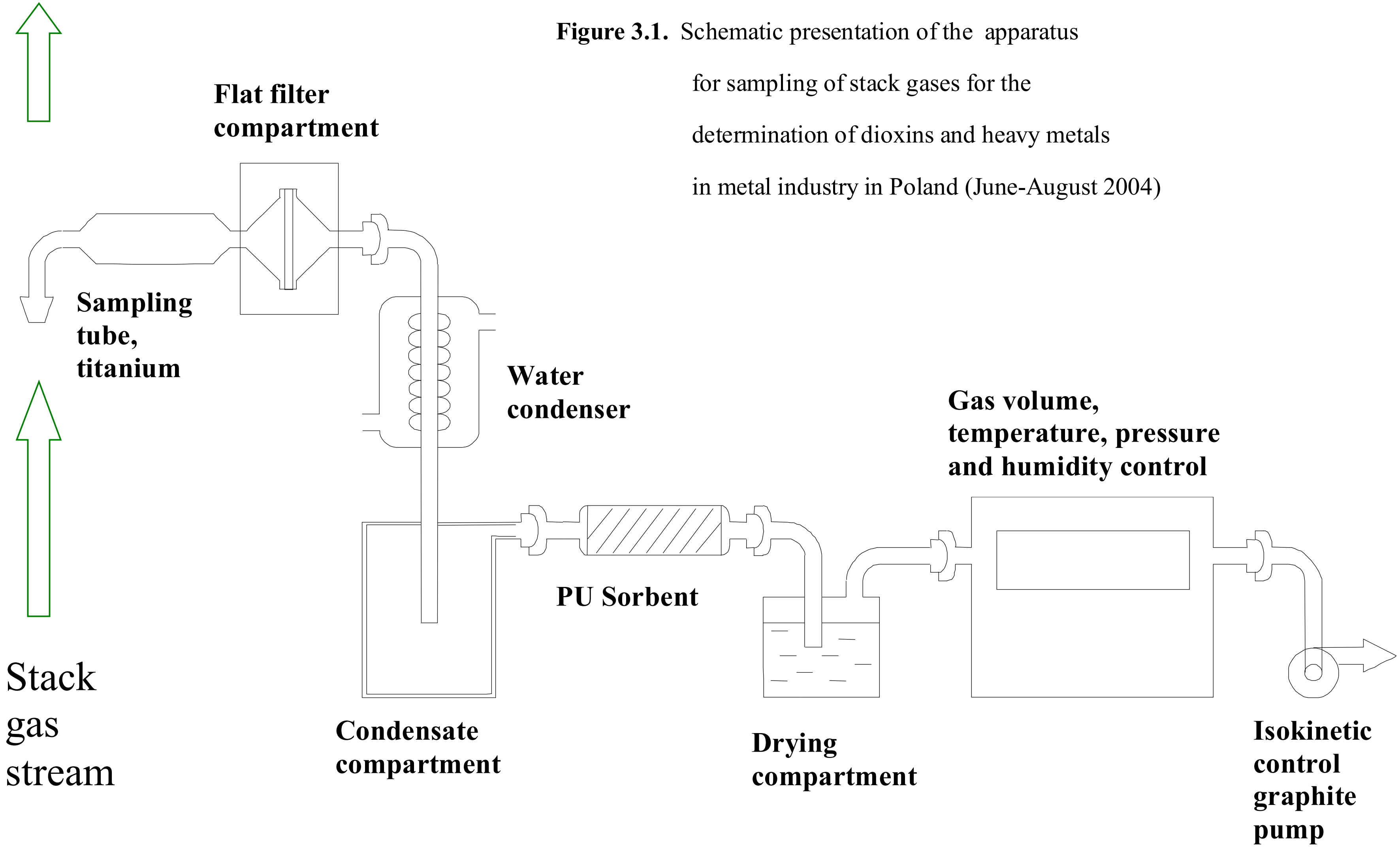

**Figure 3.1.** Schematic presentation of the apparatus for sampling of stack gases for the determination of dioxins and heavy metals in metal industry in Poland (June-August 2004)

Samples are prepared in accordance with the developed procedures[4] based on techniques of extraction in a liquid-solid body system and the techniques of multi-step liquid chromatography. The standard titrimetric substance compliant with the standard EN–1948 [25], being the mixtures of 2,3,7,8-PCDD and PCDF labelled with stabilised isotopes $^{13}$C, and 2,3,7,8-TCDD labelled with $^{37}$Cl were introduced to the samples of ashes fixed on an earlier prepared filter of quartz fibre and of sorbents and water condensate. These substances are inserted as internal standards in order to calculate the recovered analyte after a long lasting (over 6 hours) collection of samples and after a complicated and time consuming process of sample preparation for quantitative analyses. A proven analytical procedure has been applied for analytical examination being a modification of standard procedures, applied for testing of gas, dust, ash and other substances originating from waste incineration and other thermal processes. Samples were placed into the Soxhlet apparatus and extracted by toluene. The extracts were cleaned by preparative liquid chromatography techniques. Prior to instrumental analysis, the sample is being brought to the adequate volume (50–500µl) with use of nonan as solvent. Analyses are performed by the gas chromatography technique combined with mass spectrometry with double fragmentation of the tested molecule with use of equipment of Finnigan MAT GCQplus GC-MS/MS type. Calculation of the analyte recovery is performed basing on standards labelled prior to extraction by isotopes $^{13}$C-PCDD, $^{13}$C-PCDF.

### *3.2.2. Calculation of concentration of HCB and of PCDD/PCDF and PCB congeners*

Calculation of PCDD, PCDF, PCB and HCB concentrations in the samples was based on the determination of the peak areas (height or size of areas of surfaces peaks) of identified congeners referred to the standard substances, including $^{13}$C-PCDD/PCDF retention times. Choice of the area surface of the peak or its height depended from the quality of the analytical signal obtained. In determination of dioxins and PCBs by the GC-HRMS or GC-MS/MS techniques performance of calculations with use the peak height measurement is recommended. It was confirmed by the international inter-laboratory comparative tests (1996–2004) that the measurement of the area surface of integrated peaks is discriminated by a larger incidental error than the measurement of its peak. Calculations of dioxin and PCB concentrations were based on the measurement of the peak of the substance under examination.

The mass of the determined congener $m_i$ in the tested sample was calculated according to the following algorithm: the final volume of the extract of the tested sample, gushed onto the chromatographic column was calculated on the introduced syringe standard, which was the solution of $^{37}$Cl-2,3,7,8-TCDD. A strictly measured volume of this solution was put into the purified sample extract before its evaporation to 20 µl. The exact volume of the final extract $V_{EK}$ was calculated from the formula (3.1).

$$V_{EK} = \frac{H_{37-WZ} \times V_{EK}^{IN} \times V_{37-WZ}}{H_{37-EK} \times V_{37-WZ}^{IN}} \qquad (3.1)$$

where:

$V_{EK}$ - final volume of the tested sample extract [µl],

$V^{IN}_{EK}$ - volume of the gush onto the column of the final tested sample extract [µl],

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[4] developed by Adam Grochowalski, PhD., Eng. Professor of the Krakow University of Technology, Laboratory of Trace Analyses and Inorganic Technologies and published in the "*Zeszyty Naukowe Politechniki Krakowskiej*".

$V^{IN}_{37\text{-}WZ}$ - volume of the gush onto the column of the syringe standard solution $^{37}$Cl-2,3,7,8-TCDD [μl],

$V_{37\text{-}WZ}$ - volume of the syringe standard solution $^{37}$Cl-2,3,7,8-TCDD introduced into extract of the tested sample before its evaporation to the final volume [μl],

$H_{37\text{-}WZ}$ - height of the peak $^{37}$Cl-2,3,7,8-TCDD in the syringe standard solution,

$H_{37\text{-}EK}$ - height of the peak $^{37}$Cl-2,3,7,8-TCDD in the final extract of the tested sample.

The value of the analyte recovery was calculated in relation to signals obtained from the internal standard. Calculations were carried out basing on measurement of peak height of substances labelled by isotopes $^{13}$C, introduced into the samples before commencement of the analytical procedures, in relation to values obtained for standard substances $^{13}$C-PCDD, $^{13}$C-PCDF and $^{13}$C-PCB. These substances were also applied for calibration of the chromatographic equipment and for the assessment of column efficiency as well as to check the responses of the detector. The computati0on of the recovery level $R_{Vi}$ was carried out according to formula (3.2).

$$R_{Vi} = \frac{H_{13-i} \times C_{13-WZ\,i} \times V_{EK} \times V_{13-WZ}^{IN}}{H_{13-WZ\,i} \times m^{13}{}_{i} \times V_{EK}^{IN}} \times 100\% \tag{3.2}$$

where:

$R_{Vi}$ - level of analyte recovery [%],

$H_{13\text{-}i}$ - peak height of individual congeners of the internal standard $^{13}$C-PCDD/PCDF/PCB in the sample,

$H_{13\text{-}WZi}$ - peak height of individual congeners of the internal standard $^{13}$C-PCDD/PCDF/PCB in the standard calibration solution,

$C_{13\text{-}WZi}$ - concentration of individual congeners of the internal standard $^{13}$C-PCDD/PCDF/PCB in the standard calibration solution [pg/μl],

$V_{EK}$ - final volume of extract of the tested sample [μl] calculated as per formula (3.1),

$V^{IN}_{EK}$ - volume of the gosh onto the column of final extract of the tested sample [μl],

$V^{IN}_{13\text{-}WZ}$ - volume of the gosh onto the column of solution of the internal calibration standard solution $^{13}$C-PCDD/PCDF/PCB [μl],

$m^{13}{}_{i}$ - mass of individual congeners of the internal standard $^{13}$C-PCDD/PCDF/PCB introduced into the tested sample [pg].

The masses of individual congeners were calculated according the formula (3.3), using the measurement of peak height.

$$m_i = \frac{H_{ANi} \times C_{AN-WZi} \times V_{EK} \times V_{AN-WZ}^{IN}}{H_{AN-WZi} \times m_{PR} \times R_{Vi} \times V_{EK}^{IN}} \times 100\% \tag{3.3}$$

where:

$m_i$ - mass of the subject congener [pg/g or respectively in ng/kg] of the sample,

$m_{PR}$ - mass of the sample in [g],

$H_{ANi}$ - height of peak of the tested congener in the final extract of the sample,

$H_{AN\text{-}WZi}$ - height of peak of the congener concerned in the standard mixture of natural PCDD/PCDF/PCB,

$C_{AN\text{-}Wzi}$ - concentration of the tested congener in the standard mixture of natural PCDD/PCDF/PCB [pg/μl],

$V_{EK}$ - the final volume of the tested sample's extract [μl], calculated according to formula (3.1),

$V^{IN}_{EK}$ - volume of the gosh on the column of the tested sample's final extract [μl],

$V^{IN}_{AN\text{-}WZ}$ - volume of the gosh on the column of the standard mixture of natural PCDD/PCDF/PCB [μl],

$R_{Vi}$ - level of recovery of the subject congener [%], calculated by the formula (3.2).

In that way the mass of each of the 17 PCDD/PCDF congeners and 12 PCB congeners (Table 3.2) in the tested sample were calculated. In all cases the result of the analysis is presented in relation to the summary mass level of the sample's toxicity level (I-TEQ) related to 1 $m^3$ of flue gases under standard conditions and for the actual $O_2$ content.

**Table 3.2.** List of measured congeners for: dioxins (PCDDs/PCDFs) as polychlorinated dibenzodioxins - column I and polychlorinated dibenzofurans - column II, coplanar non-ortho and mono-ortho PCBs (so called WHO-PCB) – column III and so called marker PCBs – column IV.

| PCDD congener | PCDF congener | WHO-PCB congener | Marker PCB congener |
|---|---|---|---|
| I | II | III | IV |
| 2,3,7,8-TCDD | 2,3,7,8-TCDF | PCB 77 | PCB 28 |
| 1,2,3,7,8-PeCDD | 1,2,3,7,8-PeCDF | PCB 81 | PCB 52 |
| 1,2,3,4,7,8-HxCDD | 2,3,4,7,8-PeCDF | PCB 105 | PCB 101 |
| 1,2,3,6,7,8-HxCDD | 1,2,3,4,7,8-HxCDF | PCB 114 | PCB 118 |
| 1,2,3,7,8,9-HxCDD | 1,2,3,6,7,8-HxCDF | PCB 118 | PCB 138 |
| 1,2,3,4,6,7,8-HpCDD | 2,3,4,6,7,8-HxCDF | PCB 123 | PCB 153 |
| OCDD | 1,2,3,7,8,9-HxCDF | PCB 126 | PCB 180 |
|  | 1,2,3,4,6,7,8-HpCDF | PCB 156 |  |
|  | 1,2,3,4,7,8,9-HpCDF | PCB 157 |  |
|  | OCDF | PCB 167 |  |
|  |  | PCB 169 |  |
|  |  | PCB 189 |  |

The number: e.g. PCB 118 is an IUPAC name for the individual 2,3',4,5,5'-pentachlorobiphenyl congener, the one from 209 of all PCB congeners from monochlorobiphenyl to decachlorobiphenyl.

### *3.2.3. Calculation of the PCDD/PCDF toxic equivalent*

Calculation of toxic equivalency of the sample (expressed as a value of International Toxic Equivalent: I-TEQ) is based on the, so-called, International Toxicity Equivalency Factor of 2,3,7,8-TCDD (I-TEF). I-TEQ is the value, which is calculated from the result of analyses for mass concentration of all congeners of PCDDs and PCDFs in which 2,3,7,8 positions in the molecule are substituted by chlorine atoms. The numerical value of I-TEQ is a total of partial parameters obtained by multiplication of an analytical result of mass concentration of an individual congener by respective I-TEF value. The numerical values of those factors are compiled in Table 3.3. From these values, the potential toxicity of exhaust gases in terms of dioxins can be calculated. In all currently binding legal legislation concerning dioxins content, the unit of measure is the total w ng I-TEQ/m$^3$. The EU EN-1948 standard [25] and the respective regulation of the European Union are applicable in this respect.

Calculation of the I-TEQ mass value was performed in accordance with the formula 3.4:

$$I - TEQ = \sum_{i=17}^{i=1} (m_i \times I - TEF_i) \qquad (3.4)$$

where:

I-TEQ - International Toxic Equivalent of the tested sample expressed in mass measure units [usually in ng], expressed only for PCDDs/PCDFs

$m_i$ - mass of individual i-congener of PCDD and PCDF (according to Table 3.2) [ng],

I-TEF$_i$ - International Toxicity Equivalency Factor for the i-congener of PCDD/PCDF, in relation to the toxicity of 2,3,7,8-TCDD (according to Table 3.3).

**Table 3.3.** List of individual PCDD/PCDF congeners and their respective I-TEFi values (according to NATO CCMS and UE EN–1948) established and used mainly for instances of thermal processes

| PCDD i-congener | Value of I-TEFi | PCDF i-congener | Value of I-TEFi |
|---|---|---|---|
| 2,3,7,8-TCDD | **1** | 2,3,7,8-TCDF | 0.1 |
| 1,2,3,7,8-$P_5$CDD | 0.5 | 2,3,4,7,8-$P_5$CDF | 0.5 |
| 1,2,3,4,7,8-$H_6$CDD | 0.1 | 1,2,3,7,8-$P_5$CDF | 0.05 |
| 1,2,3,6,7,8-$H_6$CDD | 0.1 | 1,2,3,4,7,8-$H_6$CDF | 0.1 |
| 1,2,3,7,8,9-$H_6$CDD | 0.1 | 1,2,3,6,7,8-$H_6$CDF | 0.1 |
| 1,2,3,4,6,7,8-$H_7$CDD | 0.01 | 1,2,3,7,8,9-$H_6$CDF | 0.1 |
| OCDD | 0.001 | 2,3,4,6,7,8-$H_6$CDF | 0.1 |
| | | 1,2,3,4,6,7,8-$H_7$CDF | 0.01 |
| | | 1,2,3,4,6,7,8-$H_7$CDF | 0.01 |
| | | OCDF | 0.001 |

### *3.2.4. Calculation of PCB toxic equivalent*

All of the PCB congeners were measured from the same samples as PCDDs/PCDFs. Sampling method was exactly the same as is presented in Chapter 3.2.1. However, there are some differences in sample clean-up procedures for separation of PCDDs/PCDFs from WHO-PCB and marker PCBs. PCB congeners are divided into the two groups as it is shown in Table 3.2:

1. So called: "WHO-PCB", also called "coplanar non-ortho and mono-ortho congeners" (12 selected congeners).
2. So-called "marker PCBs" being the mixture of 7 individual congeners.

For purpose of calculation of sum of PCBs are used "marker PCBs" (see Table 3.2). Column 5 of Table 3.6 presents calculation of Σ PCBs in exhaust gases for 20 analysed installations. Table 3.4 shows the example of calculation of sum of PCBs express as the sum of marker PCBs analysed in samples taken from exhaust gases under standard conditions and actual content of O2 for installation of No. 2.

**Table 3.4.** Sum of PCBs are calculated as a sum of concentrations of 7 individual marker PCB masses determined in samples taken from exhaust gases under standard conditions and actual content of $O_2$

| No. | Indicator PCB congener | $m_i$ – mass of the congener PCB [ng/m$^3$] |
|---|---|---|
| 1 | PCB28 | 16.56 |
| 2 | PCB52 | 20.02 |
| 3 | PCB101 | 4.40 |
| 4 | PCB118 | 4.21 |
| 5 | PCB153 | 11.97 |
| 6 | PCB138 | 17.82 |
| 7 | PCB180 | 0.18 |
| 8 | Σ PCBs | 75.16 |

Source: Laboratory of Trace Analyses, Cracow University of Technology

Calculation of the WHO-TEQ mass value was performed in accordance with the formula 3.5:

$$WHO - TEQ = \sum_{i=12}^{i=1} (m_j \times TEF_j) \qquad (3.5)$$

where:

WHO-TEQ - Toxic Equivalent of the tested sample expressed in mass measure units [ng], <u>only for WHO-PCB</u>

$m_j$ - mass of individual WHO-PCB j-congener (see Table 3.2) [ng],

$TEF_j$ - Toxicity Equivalency Factor for the j-congener of WHO-PCB , in relation to the toxicity of 2,3,7,8-TCDD (according to Table 3.5).

**Table 3.5.** List of individual WHO-PCB congeners and their respective TEF values, however, expressed mostly for food analysis.

| WHO-PCB j-congener | Value of WHO-TEFj | WHO-PCB j-congener | Value of WHO-TEFj |
|---|---|---|---|
| PCB77 | 0.0001 | PCB126 | 0.1 |
| PCB81 | 0.00001 | PCB156 | 0.0005 |
| PCB105 | 0.0001 | PCB157 | 0.0005 |
| PCB114 | 0.0005 | PCB167 | 0.00001 |
| PCB118 | 0.0001 | PCB169 | 0.01 |
| PCB123 | 0.0001 | PCB189 | 0.001 |

### *3.2.5. Calculation of total toxic equivalent*

Total mass value of PCDDs/PCDFs and PCBs is calculated as a sum of I-TEQ obtained from the formula (3.4) and WHO-TEQ obtained from the formula (3.5):

$$\sum TEQ = I - TEQ + WHO - TEQ \qquad (3.6)$$

Total values of Σ TEQ [in ng TEQ/m$^3$] are given in Table 3.6.

### *3.2.6. Method validation*

Method validation for dioxin determination in exhaust gas samples was carried out basing on specially prepared standard ash samples. The precision of determination was considered acceptable when the relative standard deviation for single measurement is lower than 10% for 2,3,7,8-TCDD and TCDF. For OCDD and OCDF this value must be lower than 20%.

For the purpose of ash, testing the relative standard deviation for single of 2,3,7,8-TCDD amounted to 6% and for 2,3,7,8-TCDF was equal to 10%. As for OCDD the standard deviations for single measurement did not exceed 15% and for OCDF 20%. Mean values were calculated on the result of eight independently performed tests of the standard sample of ash.

Testing of ash samples was performed under strictly equal conditions, using the same batch of solvents and the reagents from the same production batches. All analyses were carried out using the GC-MS/MS system equipped with auto-sampler. Precision of injection for this method was calculated as ±2% on the base of a series of twenty performed analyses. For this purpose, 2 μl portions of 2,3,7,8-TCDD standard solution of 10 pg/μl concentration were injected. The signal to noise ratio obtained was $S/N \geq 65$.

The sensitivity of the method was accepted when the limit of detection was at a level allowing to detect each of the seventeen 2,3,7,8 chlorine-substituted PCDDs and PCDFs and the twelve coplanar and mono-orto PCBs. In case of the examined bottom ash sample, the limit of detection for 2,3,7,8-TCDD was 1 ng/kg. The detection limit for OCDD and OCDF was 5 ng/kg.

The method's limit of detection determinability was calculated for the instance when the signal to noise ratio was S/N = 3. In cases of a tested sample where the signal was below that value or when no peak of the examined congener was found, the limit of detectability was calculated from the formula (3.7).

$$L_{ODi} = \frac{H_N \times C_{AN-WZ_i} \times V_{EK}}{H_{AN-WZi} \times m_{PR} \times R_{Vi}} \times 300 \qquad (3.7)$$

where:

$L_{Odi}$ - detectability level of the i- congener of PCDD, PCDF or PCB [pg/g],

$H_N$ - mean signal noise value measured as the *height of peak to inter-peak valley* ratio in the region of the analyte retention time

$C_{AN-WZi}$ - concentration of that congener in the standard calibration solution [pg/µl],

$V_{EK}$ - final volume of sample solution extract [µl]

$H_{AN-WZi}$ - peak height of the analyte in the standard calibration mixture solution

$m_{PR}$ - sample mass [g],

$R_{Vi}$ - level of analyte recovery [%], calculated according to formula (3.2).

For gas samples the result of analyses was related to 1 $m^3$ of gas in relation to standard conditions (i.e. corrected to 273K of temperature and 0,1 MPa of pressure).

### 3.3. Results obtained

The result from the determination of PCDDs, PCDFs, PCBs and HCB and their respective emission values as well as emission factors is presented in Tables 3.6. and 3.7. Additional data concerning PCDD/PCDF and PCB emission from 20 metallurgical installations are included in Table B of Annex 2. Table 3.8 shows the values of metals concentration. Metal emission factors are presented in Table 3.9.

**Table 3.6.** PCDD/PCDF, PCB and HCB concentrations in flue gases from 20 metallurgical installations investigated in Poland during the period June–August 2004. Values are given in ng/m$^3$ for flue gases under standard conditions and for the actual O$_2$ concentration

| Inst. No | Concentrations in flue gas | | | | | |
|---|---|---|---|---|---|---|
| | PCDD/PCDF [ng I-TEQ/m$^3$] | PCB [ng WHO-TEQ/m$^3$] | Total* [ng TEQ/m$^3$] | ΣPCB [ng/m$^3$] ** | HCB [ng/m$^3$] | O$_2$ [level %] |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | 0.0240 | 0.0004 | 0.0244 | 2.935 | 12 | 19.5 |
| 2 | 1.2714 | 0.0481 | 1.3195 | 75.16 | 1491 | 13.1 |
| 3 | 0.0774 | 0.0043 | 0.0817 | 2.806 | 1.391 | 18.2 |
| 4 | 0.0101 | 0.0009 | 0.011 | 0.269 | 17.05 | 9 |
| 5 | 0.0025 | 0.0004 | 0.0029 | 12.74 | 3.691 | 19.2 |
| 6 | 0.0028 | 0.0035 | 0.0063 | 0.211 | 1.57 | 10.3 |
| 7 | 1.1757 | 0.1614 | 1.3371 | 947.8 | 140.2 | 18.8 |
| 8 | 0.0042 | 0.0025 | 0.0067 | 34.19 | 4.608 | 20.9 |
| 9 | 0.5809 | 0.0546 | 0.6355 | 0.417 | 17.51 | 20.7 |
| 10 | 0.0314 | 0.0034 | 0.0348 | 4.169 | 10.87 | 17.4 |
| 11 | 0.1259 | 0.0115 | 0.1374 | 10.09 | 12.25 | 20 |
| 12 | 0.1185 | 0.0086 | 0.1271 | 112.1 | 22.69 | 20.3 |
| 13 | 0.0175 | 0.0002 | 0.0177 | 1.257 | 4.415 | 8.8 |
| 14 | 0.006 | 0.0003 | 0.0063 | 36.15 | 7.814 | 20.9 |
| 15*** | 0.0035 | 0.0019 | 0.0054 | 1208 | 7.822 | 19.8 |
| 16 | 0.0029 | 0.0002 | 0.0031 | 1.328 | 0.304 | 18 |
| 17 | 0.0177 | 0.0008 | 0.0185 | 5.311 | 1.941 | 17.9 |
| 18 | 0.0024 | 0.0011 | 0.0035 | 1.904 | 0.472 | 13.6 |
| 19 | 1.0539 | 0.0464 | 1.1003 | 278.8 | 613.1 | 17.4 |
| 20*** | 0.0539 | 0.0272 | 0.0811 | 108.4 | 51.58 | 20.4 |

Source: Laboratory of Trace Analyses, Cracow University of Technology

* Values are a sum of data from column 2 and 3 calculated from the formula (3.6) and are a total ng TEQ/m$^3$ value expressed as a sum of: PCDDs/PCDFs in ng I-TEQ/m$^3$ calculated from the formula (3.4) and PCBs in ng WHO-TEQ/m$^3$ calculated from the formula (3.5).

** Sum of PCB calculated as a sum of the total 7 marker PCB congeners, as given in the last column of Table 3.2.

*** For these installations, measurements were performed on the secondary off-gas for technical reasons preventing measurement on primary off-gas.

## 3.4. Summary

Measurements were carried out under typical operational conditions, nominal capacity of the plant (information at each time obtained from the plant operator). In case of installations, No. 16 and 17 sampling had to be completed in less than 6 hours, which was caused by the specific operation conditions for those plants. For installations No. 15 and 20, measurements were taken for the secondary off-gas as for technical reasons it was not possible to perform measurements for the primary off-gas. In the installation No. 7, the measuring was performed on the gas stream prior to their final cleaning in the water scrubber system. The reason for such a procedure was that gas is released directly into the atmosphere, without any opportunity for the sampling port to be installed. To meet the desirable sampling procedure an extension (hood) would have to be installed to extend the stream of fluxes enabling isokinetic sampling. Under the existing circumstances, an approximate value of cleaning efficiency, defined by the equipment producer, can be taken for granted.

The highest dioxin and PCB concentration was recorded for sintering of iron ore plants (installations No. 2 and 19). Relatively high dioxin concentration was also revealed for aluminium scrap melting installation No. 9, 11 and 12), although for the installations No. 11 and 12 the concentrations remain within the permissible levels recommended by UNEP (0.1 ng I-TEQ/m$^3$). High concentration of dioxins in flue gases from the installation No. 7 was, as mentioned above, the result of taking samples for testing from gases prior to their cleaning.

Dioxins, as most organic substances, undergo thermal decomposition in temperatures exceeding 800$^o$C. In specific instances, when the reaction gases of the combustion process contain dusts, on which dioxins are adsorbed, the destruction of dioxins may be effected only when the temperature is raised above 1000$^o$C. Under the temperature above 1000$^o$C, the matter occurs in the form of radicals or even free atoms. At the moment of cooling down the hot flue gases, a recombination of radicals takes place. In that way the thermodynamically stable molecules are formed, for instance water, $CO_2$ or HCl. Also, PCDDs, PCDFs and PCBs belong to such chemical substances, which form or replicate (*de-novo*) during the gases cooling process. Hence, dioxins are formed in high temperature processes from radicals during cool down of flue gases. Therefore, there is no possibility to avoid the dioxin formation in metallurgical processes, where beside the pure metal other organic compounds are found in the form of ore components or protective coatings and plastics present in the melted metal scrap.

Even a small amount of chlorine in paints, plastics or other organic materials causes generation of dioxins and PCBs. It must be taken into account that dioxins are formed in nanogram concentrations, and the content of chlorine in organic pollutants is by several orders higher. Practically no means are available to reduce the chlorine content in metallurgical processes. Only efforts can be made to manage the process in such a manner that would create unfavourable conditions for dioxin formation and remove them efficiently from exhaust gases.

**Table 3.7**. Emission values and emission factor values for PCDDs/PCDFs, PCBs and HCB from 20 metallurgical installations in Poland

| Installation No. | PCDD/PCDF emission [μg I-TEQ/h] | PCDD/PCDF emission [g I-TEQ/year] | PCDD/PCDF emission factor [μg/I-TEQ/Mg of product] | Total PCB emission [μg/h] | Total PCB emission [g/year] | Total PCB emission factor [μg/Mg of product] | HCB emission [μg/h] | HCB emission [g /year] | HCB emission factor [μg/Mg of product] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.414 | 0.0015 | 0.059 | 50.7 | 0.178 | 7.239 | 207 | 0.729 | 29.60 |
| 2 | 197.8 | 1.474 | 1.099 | 11698 | 87.2 | 64.99 | 232119 | 1729 | 1290 |
| 3 | 1.966 | 0.0075 | 0.007 | 71.2 | 0.271 | 0.237 | 35.3 | 0.134 | 0.118 |
| 4 | 1.577 | 0.0130 | 0.005 | 42.4 | 0.349 | 0.141 | 2690 | 22.14 | 8.966 |
| 5 | 0.358 | 0.0018 | 0.004 | 1824 | 9.122 | 22.81 | 529 | 2.644 | 6.609 |
| 6 | 0.248 | 0.0016 | 0.002 | 18.69 | 0.121 | 0.187 | 139.3 | 0.906 | 1.393 |
| 7 | 14.38 | 0.0449 | 4.109 | 11590 | 36.16 | 3312 | 1715 | 5.350 | 489.9 |
| 8 | 0.563 | 0.0018 | 0.030 | 4581 | 14.66 | 247.6 | 617 | 1.976 | 33.37 |
| 9 | 12.97 | 0.0778 | 8.649 | 9.31 | 0.056 | 6.210 | 391 | 2.346 | 260.7 |
| 10 | 0.236 | 0.0016 | 0.337 | 31.3 | 0.219 | 44.70 | 81.6 | 0.571 | 116.5 |
| 11 | 4.218 | 0.0211 | 1.687 | 338.2 | 1.691 | 135.3 | 410 | 2.051 | 164.1 |
| 12 | 0.610 | 0.0040 | 3.052 | 577.5 | 3.754 | 2888 | 116.9 | 0.760 | 584.3 |
| 13 | 0.239 | 0.0017 | 0.012 | 17.15 | 0.120 | 0.857 | 60.2 | 0.422 | 3.012 |
| 14 | 0.180 | 0.0012 | 0.018 | 1085.3 | 7.055 | 108.5 | 235 | 1.525 | 23.46 |
| 15* | 2.740 | 0.0199 | 0.020 | 945647 | 6856 | 6755 | 6123 | 44.39 | 43.74 |
| 16 | 2.086 | 0.0147 | 0.014 | 955.3 | 6.728 | 6.369 | 219 | 1.543 | 1.460 |
| 17 | 2.409 | 0.0040 | 0.016 | 722.8 | 1.196 | 4.819 | 264 | 0.437 | 1.761 |
| 18 | 0.021 | 0.0001 | 0.017 | 16.47 | 0.115 | 13.72 | 4.078 | 0.029 | 3.398 |
| 19 | 542.4 | 4.123 | 1.466 | 143519 | 1091 | 387.9 | 315537 | 2398 | 852.8 |
| 20* | 93.55 | 0.6548 | 0.624 | 188129 | 1317 | 1254 | 89516 | 626.6 | 596.8 |

Source: Laboratory of Trace Analyses, Cracow University of Technology

*measurements were performed on the secondary off-gas.

**Table 3.8.** Concentrations of metals in flue gases from 20 metallurgical installations [Values are given in mg/m$^3$ for the standard conditions and for the operational $O_2$ concentration]

| Installation No. | Concentration of individual substances in flue gases at the examined plants | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hg | Cd | Tl | Sb | As | Pb | Cr | Co | Cu | Mn | Ni | V | Sn |
| 1 | 0.000347 | 0.000680 | 0.000094 | 0.002819 | 0.000954 | 0.023928 | 0.014313 | 0.000549 | 0.060289 | 0.860241 | 0.007229 | 0.003108 | 0.009976 |
| 2 | 0.012647 | 0.008090 | 0.004953 | 0.000991 | 0.000405 | 0.868459 | 0.004045 | 0.000908 | 0.052669 | 0.041772 | 0.002477 | 0.000883 | 0.000173 |
| 3 | 0.001326 | 0.002246 | 0.004926 | 0.001666 | 0.003093 | 3.458914 | 0.014705 | 0.010359 | 7.924717 | 0.121189 | 0.010648 | 0.071931 | 0.000551 |
| 4 | 0.000397 | 0.000073 | 0.000436 | 0.000823 | 0.003247 | 0.085128 | 0.000261 | 0.000223 | 0.009728 | 0.000581 | 0.000426 | 0.000082 | 0.000431 |
| 5 | 0.000055 | 0.000297 | 0.000426 | 0.000520 | 0.000624 | 0.041174 | 0.000362 | 0.000426 | 0.005500 | 0.002230 | 0.000332 | 0.000015 | 0.000198 |
| 6 | 0.000011 | 0.000106 | 0.000366 | 0.000509 | 0.000037 | 0.000175 | 0.000377 | 0.001485 | 0.001485 | 0.001114 | 0.000743 | 0.000034 | 0.000217 |
| 7 | 0.026904 | 0.011883 | 0.012417 | 0.176779 | 0.002443 | 1.608903 | 0.035383 | 0.003872 | 0.080111 | 4.551660 | 0.011349 | 0.008946 | 0.118031 |
| 8 | 0.000061 | 0.000061 | 0.000121 | 0.000594 | 0.000938 | 0.001417 | 0.000405 | 0.000108 | 0.002361 | 0.001889 | 0.000209 | 0.000061 | 0.000067 |
| 9 | 0.000404 | 0.000063 | 0.000005 | 0.000231 | 0.000086 | 0.003854 | 0.000349 | 0.000008 | 0.000998 | 0.000907 | 0.000172 | 0.000077 | 0.000091 |
| 10 | 0.000584 | 0.000079 | 0.000009 | 0.000262 | 0.000084 | 0.004394 | 0.000393 | 0.000013 | 0.001122 | 0.001215 | 0.000795 | 0.000037 | 0.000196 |
| 11 | 0.000560 | 0.000348 | 0.000010 | 0.000280 | 0.000137 | 0.004913 | 0.000373 | 0.000010 | 0.000572 | 0.000442 | 0.000205 | 0.000031 | 0.000081 |
| 12 | 0.000974 | 0.000276 | 0.000012 | 0.000515 | 0.000207 | 0.005527 | 0.000879 | 0.000088 | 0.011117 | 0.004585 | 0.000113 | 0.000170 | 0.001256 |
| 13 | 0.001767 | 0.000242 | 0.000047 | 0.001351 | 0.001351 | 0.002251 | 0.000520 | 0.000045 | 0.002598 | 0.001299 | 0.000416 | 0.000009 | 0.000260 |
| 14 | 0.000011 | 0.000179 | 0.003324 | 0.000464 | 0.000090 | 0.001055 | 0.000417 | 0.000026 | 0.000396 | 0.011607 | 0.000528 | 0.000016 | 0.000164 |
| 15* | 0.000541 | 0.004795 | 0.000024 | 0.000752 | 0.001133 | 0.030556 | 0.000799 | 0.000033 | 0.001786 | 0.004842 | 0.000259 | 0.000033 | 0.000799 |
| 16 | 0.000556 | 0.000240 | 0.000064 | 0.001054 | 0.001827 | 0.001932 | 0.000761 | 0.000059 | 0.001288 | 0.000345 | 0.000644 | 0.000088 | 0.000170 |
| 17 | 0.000056 | 0.004501 | 0.000098 | 0.001829 | 0.001013 | 0.143046 | 0.002954 | 0.000464 | 0.014487 | 0.159081 | 0.001969 | 0.000450 | 0.002110 |
| 18 | 0.001020 | 0.000189 | 0.000077 | 0.004287 | 0.002624 | 0.031555 | 0.011662 | 0.000266 | 0.006860 | 0.126050 | 0.001372 | 0.000943 | 0.005145 |
| 19 | 0.001469 | 0.036179 | 0.001535 | 0.001052 | 0.000592 | 0.628197 | 0.000482 | 0.000132 | 0.019624 | 0.004824 | 0.000395 | 0.000241 | 0.000175 |
| 20* | 0.001879 | 0.004352 | 0.000119 | 0.002571 | 0.002037 | 0.105426 | 0.003363 | 0.000119 | 0.007121 | 0.039757 | 0.000870 | 0.000138 | 0.003363 |

Source: Laboratory of Trace Analyses, Cracow University of Technology

*measurements were performed on the secondary off-gas.

**Table 3.9.** Emission factors for metals from 20 metallurgical installations

| Installation No. | Emission factors [g/Mg of product] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hg | Cd | Tl | Sb | As | Pb | Cr | Co | Cu | Mn | Ni | V | Sn |
| 1 | 0.00085 | 0.00166 | 0.00023 | 0.00690 | 0.00234 | 0.05856 | 0.03503 | 0.00134 | 0.14755 | 2.10536 | 0.01769 | 0.00761 | 0.02442 |
| 2 | 0.01365 | 0.00873 | 0.00535 | 0.00107 | 0.00044 | 0.93746 | 0.00437 | 0.00098 | 0.05685 | 0.04509 | 0.00267 | 0.00095 | 0.00019 |
| 3 | 0.00011 | 0.00019 | 0.00041 | 0.00014 | 0.00026 | 0.29097 | 0.00124 | 0.00087 | 0.66664 | 0.01019 | 0.00090 | 0.00605 | 0.00005 |
| 4 | 0.00021 | 0.00004 | 0.00023 | 0.00043 | 0.00170 | 0.04447 | 0.00014 | 0.00012 | 0.00508 | 0.00030 | 0.00022 | 0.00004 | 0.00023 |
| 5 | 0.00010 | 0.00053 | 0.00076 | 0.00092 | 0.00111 | 0.07301 | 0.00064 | 0.00076 | 0.00975 | 0.00395 | 0.00059 | 0.00003 | 0.00035 |
| 6 | 0.00001 | 0.00009 | 0.00032 | 0.00045 | 0.00003 | 0.00016 | 0.00033 | 0.00132 | 0.00132 | 0.00099 | 0.00066 | 0.00003 | 0.00019 |
| 7 | 0.09327 | 0.04120 | 0.04305 | 0.61287 | 0.00847 | 5.57786 | 0.12267 | 0.01342 | 0.27774 | 15.78001 | 0.03935 | 0.03101 | 0.40920 |
| 8 | 0.00063 | 0.00063 | 0.00125 | 0.00611 | 0.00966 | 0.01459 | 0.00417 | 0.00111 | 0.02431 | 0.01945 | 0.00215 | 0.00063 | 0.00069 |
| 9 | 0.00603 | 0.00095 | 0.00008 | 0.00346 | 0.00129 | 0.05764 | 0.00522 | 0.00012 | 0.01492 | 0.01356 | 0.00258 | 0.00115 | 0.00136 |
| 10 | 0.00622 | 0.00085 | 0.00010 | 0.00279 | 0.00090 | 0.04676 | 0.00418 | 0.00013 | 0.01194 | 0.01293 | 0.00846 | 0.00040 | 0.00209 |
| 11 | 0.00736 | 0.00458 | 0.00013 | 0.00368 | 0.00180 | 0.06458 | 0.00490 | 0.00013 | 0.00752 | 0.00580 | 0.00270 | 0.00041 | 0.00106 |
| 12 | 0.02507 | 0.00712 | 0.00031 | 0.01326 | 0.00534 | 0.14234 | 0.02265 | 0.00226 | 0.28631 | 0.11808 | 0.00291 | 0.00437 | 0.03235 |
| 13 | 0.00120 | 0.00016 | 0.00003 | 0.00092 | 0.00092 | 0.00153 | 0.00035 | 0.00003 | 0.00176 | 0.00088 | 0.00028 | 0.00001 | 0.00018 |
| 14 | 0.00003 | 0.00054 | 0.01002 | 0.00140 | 0.00027 | 0.00318 | 0.00126 | 0.00008 | 0.00119 | 0.03499 | 0.00159 | 0.00005 | 0.00049 |
| 15* | 0.00301 | 0.02671 | 0.00013 | 0.00419 | 0.00631 | 0.17023 | 0.00445 | 0.00018 | 0.00995 | 0.02698 | 0.00144 | 0.00018 | 0.00445 |
| 16 | 0.00267 | 0.00115 | 0.00031 | 0.00506 | 0.00878 | 0.00928 | 0.00366 | 0.00028 | 0.00619 | 0.00166 | 0.00309 | 0.00042 | 0.00082 |
| 17 | 0.00005 | 0.00393 | 0.00009 | 0.00160 | 0.00088 | 0.12495 | 0.00258 | 0.00041 | 0.01265 | 0.13895 | 0.00172 | 0.00039 | 0.00184 |
| 18 | 0.00712 | 0.00132 | 0.00054 | 0.02993 | 0.01832 | 0.22027 | 0.08140 | 0.00186 | 0.04788 | 0.87987 | 0.00958 | 0.00658 | 0.03591 |
| 19 | 0.00204 | 0.05022 | 0.00213 | 0.00146 | 0.00082 | 0.87205 | 0.00067 | 0.00018 | 0.02724 | 0.00670 | 0.00055 | 0.00033 | 0.00024 |
| 20* | 0.02165 | 0.05013 | 0.00137 | 0.02962 | 0.02347 | 1.21448 | 0.03874 | 0.00137 | 0.08203 | 0.45799 | 0.01003 | 0.00159 | 0.03874 |

Source: Laboratory of Trace Analyses, Cracow University of Technology

*measurements were performed on the secondary off-gas.

# 4. INVENTORY OF PCDD/PCDF EMISSIONS AND RELEASES FROM THE METALLURGICAL SECTOR

## 4.1. Sector and technology specific emission factors

In accordance with the project measurement scheme and the results obtained (see chapters 3.1 and 3.3) a verification of dioxins and furans air emission factors applied so far. Table 4.1 shows the dioxin and furan emission factors[5] subdivided into two main groups of emission sources: ferrous metal production and non-ferrous metal production. Such subdivision is compliant with the guidelines captioned "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" [39, 40], developed by UNEP Chemicals, commonly known as the Toolkit (see Chapter 4.2.1).

**Table 4.1.** Emission factors of PCDD/PCDF estimated during the measurement programme

| Type of activity | Emission factor(s)<br>µg I-TEQ/Mg of product |
|---|---|
| ***Ferrous metal production*** | |
| Iron ore sintering plant | 1.47; 1.10 |
| Primary Iron production-Blast Furnace (BF) | 0.01 |
| Primary and secondary steel production-Basic Oxygen Furnace (BOF) | 0.02 |
| Iron casting-hot air cupola (good APCS) | 0.06; 4.11 |
| Iron casting-gas rotary kiln | 0.02 |
| Secondary steel production; steel scrap melting-electric arc furnaces | 0.62*; 0.02* |
| Steel casting-electric arc furnace | 0.03 |
| ***Non-ferrous metal production*** | |
| Primary copper production from concentrate with $H_2SO_4$ production; copper slag recycling | 0.005; 0.004; 0.002 |
| Copper scrap melting | 0.007 |
| Secondary aluminium production; aluminium scrap and cans melting | 8.65; 3.05; 1.69; 0.34 |
| Primary zinc production | 0.012 |
| Zinc casting | 0.02 |

Source: National Emission Centre/ Institute of Environmental Protection
* only secondary off gas was measured in the plants

In several cases (sintering plants, iron casting, copper and aluminium production), the measurement programme covered two or more different plants emitting dioxins and furans within the same type of activity. Therefore, in those cases, multiple values of emission factors were estimated. It should be noted that even between two equal emitters, the technological processes could be different (e.g. different type of furnace used for pig iron casting) as well as different air pollution control systems (APCS) applied. That is why the multiple emission factors cannot be directly compared (Table 4.1).

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[5] The emission factors are determined in µg I-TEQ/Mg of product (product means the amount of raw material obtained in result of the technological process, for instance sinter of cast iron).

The detailed analysis of all measurements with respect to e.g. measurement conditions, APCS applied, type of technology used, treatment of scrap metal and representative of each plant, led to the selection of new emission factors (column 2 of Table 4.2), which were used in the 2002 PCDD/PCDF emission inventory (Table 4.5) in the Polish-Danish project. Factors listed in the last column of Table 4.2 were used for the development of the national emission inventory for the year 2000, *inter alia*, for the purpose of the National Implementation Plan for the Stockholm Convention [38].

**Table 4.2.** Comparison of new and formerly used emission factors in PCDD/PCDF emission inventories

| Type of activity | New emission factors | Emission factors used so far |
|---|---|---|
| | µg I-TEQ/Mg of product | |
| ***Ferrous metal production*** | | |
| Iron ore sintering plant | **1.35** | 1.45 |
| Steel production-Basic Oxygen Furnace (BOF) | **0.02** | 0.1 |
| Iron casting-hot air cupola (good APCS) | **0.06** | 0.03 |
| Iron casting-rotary drum | **0.02** | 4.3 |
| ***Non-ferrous metal production*** | | |
| Primary copper production | **0.004** | 0.01 |
| Secondary aluminium production-scrap melting (and cans melting) | **4** (for 85% of total production)<br>**150** (for 15% of total production) | 150 |
| Zinc casting from zinc cathodes | **0.02** | 0.3 |

Source: National Emission Centre/ Institute of Environmental Protection

In the iron and steel metallurgy, four new emission factors were adopted. The first one refers to iron ore sintering. The new value (1.35 µg I-TEQ/Mg) is based on measurements in the two main combined steelworks. The new value is an activity weighted average of two measurement results. The previously used value (1.45 µg I-TEQ/Mg) was determined during the measurements carried out in 2002 [41] as part of the UNIDO project funded the GEF: “Enabling activities to facilitate early action on the implementation of the Stockholm Convention on POPs” [38]. The other three emission factors that were updated refer to steel production (in a converter furnace: 0.02 µg I-TEQ/Mg) and iron casting plat (in hot air cupola gas fired rotary drum) 0.06 and 0.02 respectively. The previously used values (Table 4.2) were taken from the UNEP Chemicals Toolkit. The largest absolute and percentage difference occurred for pig iron casting in the rotary drum (0.02 against 4.3µg I-TEQ/Mg), which can be explained by fairly good APCS applied at the plant. The updated emission factors for iron casting in rotary drums does not affect the results of the national emissions, since the contribution of such foundries in the total national emission is very small.

In the non-ferrous metallurgy, three emission factors were updated. The first one refers to primary copper production (0.004 µg I-TEQ/Mg) and is based on measurements in three plants. The three different results despite various conditions are within a narrow range of values: 0.001–0.005 µg I-TEQ/Mg. The previously used emission factor (0.01 µg I-TEQ/Mg) was slightly higher and was taken from the UNEP Chemicals Toolkit. Four measurements of emission factors for aluminium production were taken in three different plants and the obtained values were within the range 0.34–8.65, depending primary on the type have installed and used APCS. Measurements were conducted in large enterprises, in which production process conditions are usually better than in the case of smaller co-existing plants. Therefore, it was decided, for purpose of the national inventory, to use the value of 4 µg I-TEQ/Mg suggested by the Toolkit for cases of good APCS (fabric filters; lime injection) and scrap treatment for 85% of secondary aluminium production. For the rest of this production (15%) the Toolkit value of 150 µg I-TEQ/Mg was applied, as recommended for cases with minimal treatment of input/scrap and simple dust removal systems. In the previous inventories, because of lack of domestic measurements, the Toolkit value of 150 µg I-TEQ/Mg was applied. The last updated emission factor refers to zinc casting (0.02 µg I-TEQ/Mg). It is lower than the previously used value (0.3 µg I-TEQ/Mg) recommended by the Toolkit for zinc melting plants.

## 4.2. Inventory of PCDD/PCDF emission for the year 2002

### *4.2.1. Introductory information*

Under the Polish-Danish project the inventory of dioxin and furan emission for 2002 was carried out [54] in accordance with recommendations and methodology of UNEP Chemicals concerning identification of releases and quantitative assessment of emissions to air and releases to other media.

UNEP Chemicals elaborated a set of emission factors in the form of so called Standardized Toolkit – a manual for identification and quantification of PCDD/PCDF emissions and releases. The first version of the Toolkit was published in January 2001 [39] and the next one in May 2003 [40]. The methodology described by the Toolkit was successfully applied in Poland. Page 208 of the Toolkit includes summary results of the Polish National Inventory for the year 2000 as an example of one of the comprehensive inventories worked out in recent years[6].

It should be stressed that most of the emission and release factors given in the Toolkit, come from measurements carried out in other countries and may refer to technological processes and dioxin formation conditions other than those found in Poland. For many source categories, several different emission factors are assumed to depend on the applied technology and on air pollution control systems APCS used. The differences between such emission factors may reach several orders of magnitude.

In this study, the results of domestic dioxin measurements carried out in 2002 and 2004 were used [41, 53]. These measurements, as well as experience gained and the results obtained during the inventory of dioxin and furan releases in Poland for the year 2000 [50] provided the basis for determination of new emission factors (Table 4.2).

Since direct emission estimates are usually carried out sporadically and merely for short periods of time (hours to days), the emission estimates are usually based upon application of the following approximating formula (4.1):

$$\text{emission (release)} = \text{activity} * \text{emission factor} \qquad (4.1)$$

Activity is usually understood as a typical value of a given technological process leading to formation and release of PCDDs/PCDFs, e.g. the annual production of sinter in sintering plants. Emission factor,

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[6] Similar results were presented by the national inventories of Uruguay, Jordan, Philippines, Brunei County, Lebanon, Thailand and the three Baltic republics: Lithuania, Latvia and Estonia.

in turn, expresses the emission/release per unit of activity e.g. one Mg of sinter. Emission factors are being determined for various processes and types of source in many countries.

In accordance with the UNEP Chemicals methodology, emissions and releases are grouped into nine main source categories:

- waste incineration,
- ferrous and non-ferrous metal production,
- power generation and heating/cooking,
- production of mineral products,
- transport,
- uncontrolled combustion processes,
- production of chemicals, consumer goods,
- miscellaneous,
- disposal/landfill.

The discussion of the inventory results begins with two chapters devoted to two sectors namely: ferrous and non-ferrous metal production.

### *4.2.2. Inventory of PCDD/PCDF emission from ferrous metal production*

Table 4.3. shows the results of the inventory in the source sub-category: ferrous metal production. Most of the air emission in this sub-category originate during iron ore sintering (9.0 g I-TEQ/a) and steel production in electric arc furnaces (7.7 g I-TEQ). The contribution of the foundries is 3.5 g I-TEQ with the biggest share coming from iron casting in cold air cupolas with minimal APCS. PCDD/PCDF emissions from coke production were estimated as 2.6 g I-TEQ. The new emission factors introduced in the inventory in 2002 are shown in bold in Table 4.2. Compared to the 2000 inventory the largest difference occurred in iron ore sintering (9 vs. 40.4 g I-TEQ) mainly due to the use of domestically derived lower emission factor (1.35 vs. 5 g I-TEQ/Mg from the Toolkit).

**Table 4.3.** Annual PCDD/PCDF emission to the air from production of ferrous metals in 2002

| Cat. | Sub-cat. | Class | Source categories | Potential release route [µg I-TEQ/Mg] to: | | | | | Production | Annual PCDD/F emission |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | Water | Land | Products | Residues /Wastes | [Mg/year] | [g I-TEQ/year] |
| | **a** | | **Iron ore sintering** | | | | | | **6 591 300** | **8.898** |
| | | 2 | Low waste use, well controlled plant | **1.35** | ND | ND | ND | 0.003 | 6 591 300 | **8.898** |
| | **b** | | **Coke production** | | | | | | **8 787 900** | **2.636** |
| | | 2 | Afterburner / dust removal | 0.3 | 0.06 | ND | ND | ND | 8 787 900 | **2.636** |
| | **c** | | **Iron and steel production plants and foundries** | | | | | | **13 656 600** | **7.853** |
| | | | **Iron and steel plants** | | | | | | | |
| | | 3 | Clean scrap/virgin iron, BOS furnaces | **0.02** | ND | ND | NA | 1.5 | 5 799 000 | **0.116** |

| Cat. | Sub-cat. | Class | Source categories | Potential release route [µg I-TEQ/Mg] to: Air | Water | Land | Products | Residues /Wastes | Production [Mg/year] | Annual PCDD/F emission [g I-TEQ/year] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 | Blast furnaces with APCS | 0.01 | ND | ND | NA | ND | 5 296 400 | **0.053** |
| | | 5 | Electric Furnaces, good APCS | 3 | ND | ND | ND | 1.5 | 2 561 200 | **7.684** |
| | | | **Foundries** | | | | | | **976 900** | **3.543** |
| | | 1 | Cold air cupola or rotary drum, no APCS | 10 | ND | ND | ND | ND | 88 500 | **0.885** |
| | | 2 | Cold air cupola or rotary drum, minimal APCS | 6 | ND | ND | ND | ND | 206 500 | **1.239** |
| | | 3 | Rotary drum-fabric filter | **0.02**$^{*}$ | ND | ND | ND | 0.2 | 7 400 | **0.000** |
| | | 5 | Hot air cupola or induction furnace, fabric filter | **0.06**$^{*}$ | ND | ND | ND | 0.5 | 103 250 | **0.006** |
| | | 6 | Hot air cupola or induction furnace, minimal APCS | 0.6 | ND | ND | ND | ND | 132 750 | **0.080** |
| | | 7 | Hot air cupola or induction furnace, no APCS | 4 | ND | ND | ND | ND | 59 000 | **0.236** |
| | | 8 | Iron casting, electric arc, no APCS | 10 | ND | ND | ND | ND | 20 000 | **0.200** |
| | | 9 | Iron casting, electric arc, fabric filters | 4.3 | ND | ND | ND | ND | 80 000 | **0.344** |
| | | 10 | Iron casting, induction furnaces | 1 | ND | ND | ND | ND | 185 000 | **0.185** |
| | | 11 | Steel casting, electric arc, fabric filters | 4.3 | ND | ND | ND | ND | 83 500 | **0.359** |
| | | 12 | Steel casting, induction furnace, minimal APCS | 1 | ND | ND | ND | ND | 9 000 | **0.009** |
| | | 13 | Steel casting, basic oxygen furnace | 0.01 | ND | ND | ND | ND | 2 000 | **0.000** |

Source: National Emission Centre/ Institute of Environmental Protection
$^{*}$ new emission factors
NA - not applicable
ND - not determined/no data

### *4.2.3. Inventory of PCDD/PCDF emission from non- ferrous metal production*

Table 4.4. shows the results of the inventory in the source sub-category: non-ferrous metal production. Most of the air emission in this sub-category, originate from secondary copper production (3.5 g I-TEQ/Mg), from aluminium production and castings (3.2 g I-TEQ) and secondary zinc production in electric arc furnaces (1.3 g I-TEQ). PCDD/PCDF emission from lead production was estimated as 0.5 g I-TEQ. The emission factors introduced in inventory for 2002 are shown Table 4.2. As compared with the 2000 inventory, the biggest difference in 2002 inventory was in aluminium production (0.6 vs. 11 g I-TEQ) mainly due to the use of lower emission factor (4 vs. 150 g I-TEQ/Mg). Measurements carried out in four different plants showed emission factor values within the range from 0.34 to 8.65. This justified the application of the lower emission factor than in the previous inventory for 85% of total secondary aluminium production. The contribution of zinc production went down due to the reduced production level in the year 2002.

**Table 4.4.** Annual PCDD/PCDF emission to the air from non-ferrous metal production in 2002

| Cat. | Sub cat. | Class | Source categories | Potential release route [µg I-TEQ/Mg] to: Air | Water | Land | Products | Residues /Wastes | Production [Mg/year] | Annual PCDD/F emission [g I-TEQ/year] |
|---|---|---|---|---|---|---|---|---|---|---|
| | d | | **Copper production** | | | | | | **600 508** | **3.457** |
| | | 2 | Secondary production; Cu-well controlled | 50 | ND | ND | ND | 630 | 69 083 | **3.454** |
| | | 4 | Smelting and casting of Cu/Cu alloys | 0.03 | ND | NA | NA | ND | 20 700 | **0.001** |
| | | 5 | Primary production; Cu-including thermal steps | **0.004**$^{*}$ | ND | ND | ND | ND | 510 725 | **0.002** |
| | e | | **Aluminium production (all secondary productions)** | | | | | | **254 334** | **3.211** |
| | | 1 | Processing scrap Al, minimal treatment of inputs, simple dust removal | 150 | ND | ND | ND | 400 | 17 870 | **2.681** |
| | | 4 | Scrap treatment, well-controlled, fabric filter, lime injection | 4 | ND | ND | ND | 100 | 101 264 | **0.354** |
| | | 6 | Casting of aluminium alloys | 1.3 | ND | ND | ND | ND | 135 200 | **0.176** |
| | f | | **Lead production** | | | | | | **66 531** | **0.532** |
| | | 2 | Secondary production from scrap without PVC/$Cl_2$, filters | 8 | ND | ND | ND | ND | 66 531 | **0.532** |
| | g | | **Zinc production** | | | | | | **20 841** | **1.268** |
| | | 2 | Hot briquetting/ rotary furnaces, basic control | 100 | ND | ND | ND | ND | 12 681 | **1.268** |
| | | 4 | Casting of zinc alloys | **0.02**$^{*}$ | ND | ND | ND | ND | 8 160 | **0.000** |

Source: National Emission Centre/ Institute of Environmental Protection

$^{*}$ new emission factors

NA - not applicable

ND - not determined/no data

### *4.2.4. Inventory of PCDD/PCDF releases from other source categories and to other media*

The summary of the PCDD/PCDF emission inventory in 2002, split by sectors (recommended in Toolkit) and media (as air, water, land, products and residues/wastes) is presented in Table 4.5. The values given in the inventory reflect the mean estimates. For each mean value, a range should be attributed, in which the true value probably lies. The mean values presented in the table are regarded as best estimates.

The total air emission has been estimated at app. 348 g I-TEQ. The largest air emissions occurred in the following categories: 6. *Uncontrolled combustion processes* (app. 202 g I-TEQ), 3. *Power generation and heating* (69 g I-TEQ), 1. *Waste incineration* (app. 30 g I-TEQ) and 2. *Ferrous and non-ferrous metal production* (app. 31 g I-TEQ). The same categories with similar percentage contribution dominated in the 2000 national inventory.

The contribution of the category 2. *Production of ferrous and non-ferrous metals* decreased, mainly due to introduction of lower emission factors for iron ore sintering and aluminium production based on domestic measurements. Updated emission factors are based on national measurement results.

The main sources in category 6. *Uncontrolled combustion processes* are poorly controlled burning or co-burning of waste at households as well as uncontrolled fires of waste landfills. Co-combustion of municipal waste in household stoves and furnaces and municipal boiler houses – known as the so-called "low emission", is the source of many air pollutants (*inter alia* PM and other POPs e.g. HCB or PAHs). Low emission is especially common in Southern Poland, mainly because of easy access to hard coal. In category 3. *Power generation and heating* the largest contribution come from wood and other biomass combustion for heating and cooking purposes, and from coal fired boilers. In category 1. *Waste incineration* largest contribution comes from incineration of hazardous and industrial waste, especially in plants equipped with only simple APCS or none at all.

The shares in total emission of other main source categories are relatively lower: category 4. *Production of mineral products* 11 g I-TEQ, and the total contribution of the remaining three categories: 5. *Transport*, 7. *Production of chemicals and consumer goods* and 8. *Miscellaneous* was below 5 g I-TEQ.

**Table 4.5.** Summary of the national PCDD/PCDF emission inventory 2002 split into main sectors and media

| Cat. | | Annual releases [g I-TEQ/a] | | | | |
|---|---|---|---|---|---|---|
| | Source categories | Air | Water | Land | Products | Residues/Wastes |
| 1 | Waste incineration | 30.1 | | | | 130.5 |
| 2 | Ferrous and non-ferrous metal production | 31.4 | 0.0 | | | 73.4 |
| 3 | Power generation and heating | 68.7 | | | | |
| 4 | Production of mineral products | 11.2 | | | | 0.1 |
| 5 | Transportation | 2.8 | | | | |
| 6 | Uncontrolled combustion processes | 202.4 | | 4.8 | | 183.8 |
| 7 | Production of chemicals and consumer goods | 0.1 | 0.0 | | 11.8 | 1.0 |
| 8 | Miscellaneous | 1.7 | | | 0.1 | 0.0 |
| 9 | Disposal/landfilling | | 0.7 | | 29.8 | 42.9 |
| **Total (for the year 2002)** | | **348,4** | **0.7** | **4.8** | **41.7** | **431.7** |
| ***Total (for the year 2000)*** | | ***487.1*** | ***1.2*** | ***6.6*** | ***10.8*** | ***532.1*** |

Source: National Emission Centre/ Institute of Environmental Protection

While the potential air, emissions are fairly well represented by contributions from main categories and their sub-categories, nothing similar can be said about releases to other media in Table 4.5. For these components of the environment, only few emission factors are known and for most source categories emission factors are not known. It can be expected that the quantitative estimates in the last four columns in Table 4.5. are underestimated, especially for residues and wastes.

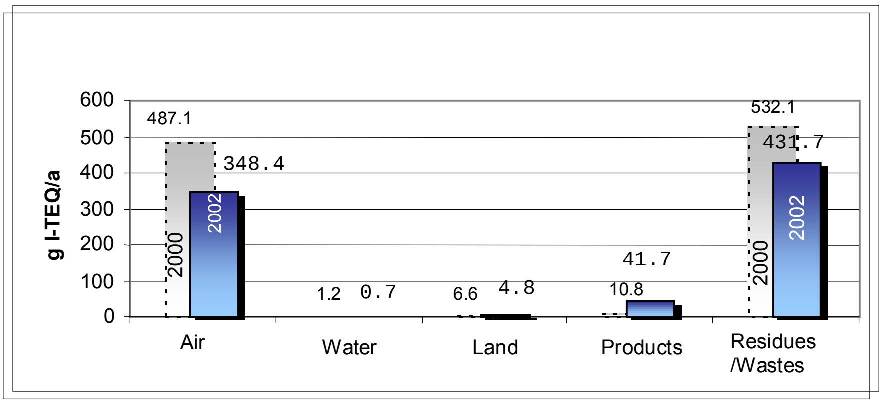
Discharge of municipal wastewater, sewage sludge and coke production contribute most to PCDD/PCDF releases into water amounting in total to about 0.7 g I-TEQ. The free chlorine is not used for paper bleaching in Poland. In other countries, this category contributes considerably to the release of PCDDs/PCDFs into water.

The only category that was estimated, responsible for direct releases into land (soil) were fires and burning of biomass in agriculture and gardening. It should be stressed that a significant part of releases into residues ultimately ends up in the land, e.g. residues from sewage sludge incineration are used in agricultural as fertilisers.

The main source of releases to products is the processing of recycled paper in paper production and production of chlorinated pesticides. In case of paper recycling dioxins may be, occur in the waste paper.

Potential releases of PCDDs/PCDFs to residues originate generally from the same processes as emissions to air. Dioxins and furans end up in residues in APC systems. Residues and wastes are disposed off on the solid waste landfills or in the ground, especially when they originate from households or wastewater treatment plants. In future solid waste landfills may constitute a significant source of PCDD/PCDF releases to the environment through washouts or leachates.

Figure 4.1 shows a comparison of inventory results for years: 2002 and 2000 carried out according to the methodology recommended by UNEP Chemicals [40].



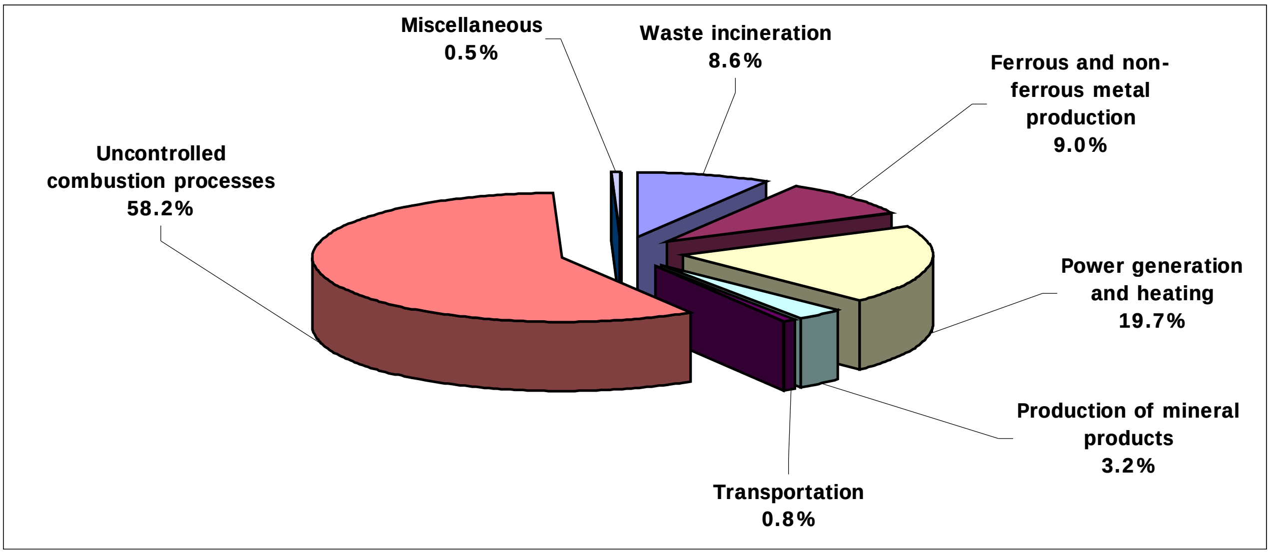
Source: National Emission Centre/ Institute of Environmental Protection

**Figure 4.1.** Summary results of dioxin inventories for 2002 and 2000 split into categories and media

In the year 2002, the air emissions and releases to residues, water and land were lower than in the year 2000, except for releases to products and residues. A quite large increase of releases into products, from app. 11 to app. 42 g I-TEQ was noted mainly due to increased composting of biomass.

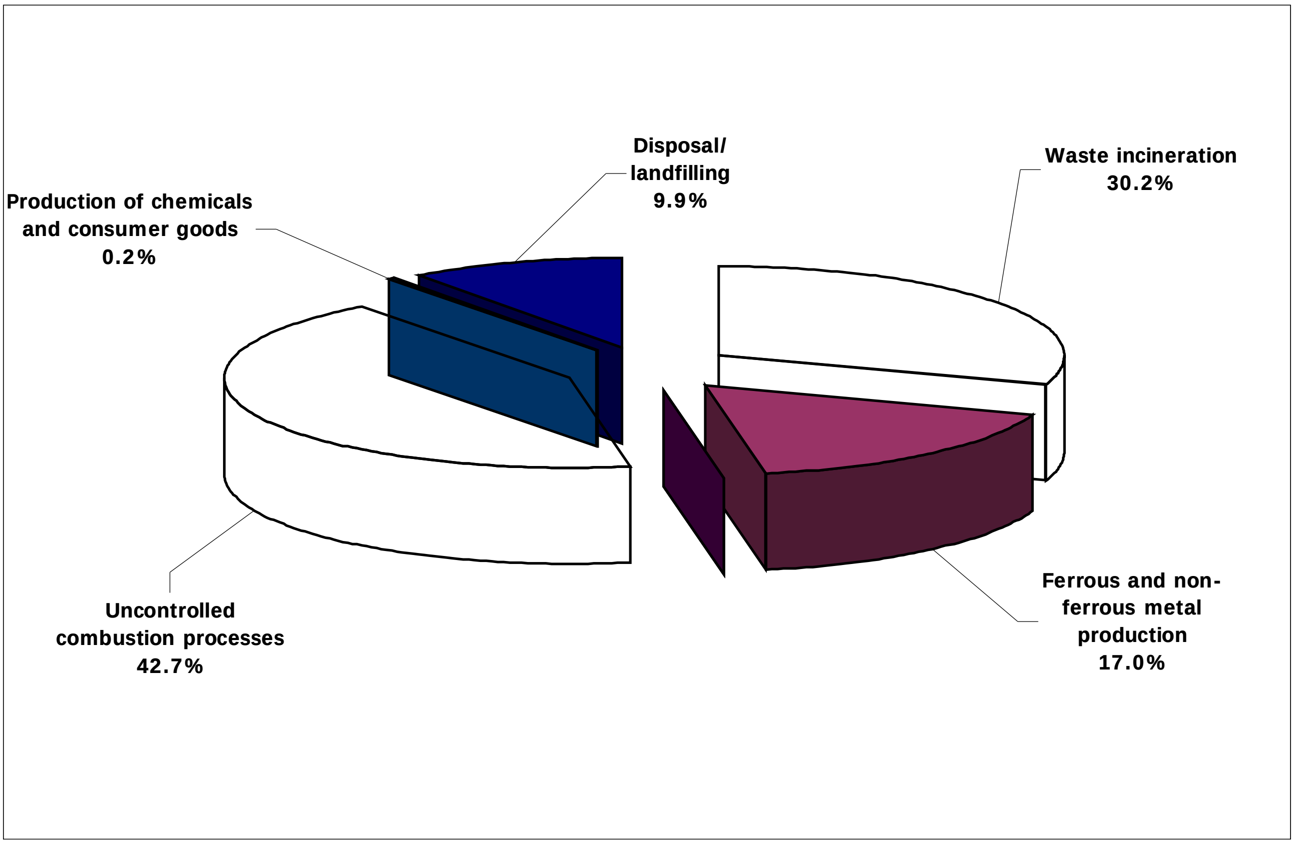
The percentage shares of individual sources in dioxin emissions to the air and dioxin releases into the residues/wastes in 2002 are shown in Figures 4.2. and 4.3.

The largest percentage contribution to air emissions (Figure 4.2) came from the following categories: 6. *Uncontrolled combustion processes* (58.2%), 3. *Power Generation and Heating* (19.7%) and 2. *Ferrous and non-ferrous metal production* (9.0%). The largest percentage contribution in case of releases into residues/wastes (Figure 4.3) came from the following categories: 6. *Uncontrolled combustion processes* (42.7%), 1. *Waste incineration* (30.2%), 2. *Ferrous and non-ferrous metal production* (17.0%) and 9. *Disposal/landfilling* (9.9%).



Source: National Emission Centre/ Institute of Environmental Protection

**Figure 4.2.** Shares of individual sectors in air emissions in 2002



Source: National Emission Centre/ Institute of Environmental Protection

**Figure 4.3.** Shares of individual sectors in release to residues/wastes in 2002

## 4.3. Summary

This chapter presents the results of the national emission and release inventory of PCDDs/PCDFs for the year 2002 (Table 4.5), obtained under the Polish-Danish project, which may only relate to the results obtained for the year 2000 [50]. Data on emission from the metallurgy sector are listed in Tables 4.3 and 4.4. The share of this sector in the PCDD/PCDF emission into the air in 2002 amounted to 9% (Figure 4.2). The inventory was carried out in line with the methodology recommended by UNEP Chemicals in its guidelines [40] taking into consideration the new emission factors on the basis of the national emission measurement results obtained from installations in the metallurgy sector [41, 53] and the analyses that were performed.

The introductory sub-chapter 2.5 presents, *inter alia*, the changes of PCDD/PCDF emissions into the air during the period of 1990-2002 (Figure 2.1), on the basis of inventory results obtained for the purpose of the Convention on Long-range Transboundary Air Pollution compliant with the EMEP recommendations. Detailed data on dioxin and furan emissions from the metallurgy sector are presented in Figure 2.3 and in Table 2.2. Reduction of production in this sector, as well as successive environmental investment have the main influence on the declining emission trend from this sector shown in Figure 2.3. A considerable emission increase in the year 2000 was determined by the change in emission source classification from SNAP97 to NFR. The metallurgy sector contributed into the national PCDD/PCDF emission to the air in 2002 by 14.5%.

The classification of emission sources recommended by UNEP Chemicals in the Toolkit differs significantly from the classification used by EMEP (i.e. SNAP97 – used earlier, and NFR – used now a days) [11]. Therefore, the inventory results for the year 2002, also for the metallurgy sector, carried out according to different methodologies, presented in sub-chapters 4.2.4 and 2.5 are also significantly different. These differences show the range of uncertainty of estimating PCDD/PCDF emissions and releases, which according to the work plan for 2002 [51] may amount from several dozens to several hundreds of per cent.

# 5. SELECTED METHODS OF EMISSION REDUCTION

The measures proposed in this chapter are regarded as most cost effective for meeting the target value of PCDD/PCDF emission recommended by the BREFs[7].

The threshold values for PCDD/PCDF emission from the metallurgical sector have neither yet been established in the EU countries, nor in Poland. For the recommendations on PCDD/PCDF emission reduction measures in the present study, a target value of 0.1 ng I-TEQ/Nm$^3$ at operational $O_2$ has been adopted.

The measures aimed at dioxin and furan emission reduction from installations considered to the required levels has been subdivided into primary and secondary measures.

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of PCDDs/PCDFs. Possible primary measures include:

- Changes in feed material;
- Effective process control;
- Afterburners and quenching of off-gases.

Secondary measures include pollution control techniques. These methods do not eliminate the generation of PCDDs/PCDFs at source, but serve as means to contain and prevent emissions. Possible secondary measures include:

- Highly efficient dust removal equipment;
- Adsorption to activated carbon in combination with fabric filters;
- Catalytic oxidation.

All measures related to treatment of flue-gases are included under secondary measures for reasons of convenience, although some of the measures (e.g. quenching) actually reduce the formation of PCDDs/PCDFs.

## 5.1. Methodology

Basing on the results of measurements taken in 20 installations (see chapter 3), six facilities were selected for further evaluation. In fact, the measured PCDD/PCDF emission was relatively low from most facilities, and the facilities for further evaluation were selected not only on the basis of the actually measured emission, but also in their capacity of being representative of those sub-sectors in which PCDD/PCDF emission in general could be significant.

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[7] The reference document concerning BAT, developed for the purpose of obtaining the IPPC, provides a number of information concerning PCDD/Fs emissions obtained in result of BAT implementation. The level of emission possible to attain by applying such techniques for a foundry has been determined at <0.1 ng I-TEQ/Nm$^3$, and for installations of secondary aluminium processing at < 0.1-0.5 ng I-TEQ/Nm$^3$ [47,46]. For the remaining metallurgical processes application of BAT enables the achievement of similar emission levels. As long as the BREF do not present a legal standard, the information therein constitute just guidelines for the industry, governments and administration in respect of emission levels obtained through implementation of BAT. Applicable limits for specific instances will be set up by the national regulations implementing IPPC directives and by local regulations. In some EU countries, like Germany or Denmark, the binding level of permissible PCDD/PCDF emission amounts to 0.1 ng I-TEQ/Nm$^3$ (for the operational oxygen content of the process).

A set of forms for an environmental review focusing on processes of relevance for PCDD/PCDF formation and emission was developed. The structure of these forms was inspired by the US EPA Manual for Waste Minimization Opportunity Assessment, combined with the UNEP's Toolkit [39], according to Questionnaire 2 for the Category 2. *Ferrous and Non-Ferrous Metal Production*. As an example, a filled form of the questionnaire from the environmental review, of steelwork operated with the electric arc furnace, is given in Annex 3.

The filled-in forms were used as basis for a site visit including Polish and foreign experts, where specific options for PCDD/PCDF release reduction were discussed with managers of the facilities. These discussions included possible problems with emission of other pollutants and actual plans for changes of the facilities' air pollution control systems (APCS).

On the basis of the environmental review and measurements performed measures aimed PCDD/PCDF reduction, specific for particular installations as well as general measures for the sub-sector were proposed. The proposals presented in this report are mainly based on the experience with similar processes in West European. Facilities.

## 5.2. Environmental reviews of specific plants

### *5.2.1. Iron ore sintering plant*

Iron ore sintering takes place at two steel plants in Poland equipped with a total of 7 strands. Two of the strands are currently only used as backup.

The installation where the measurements have been performed consists of 4 sinter belts of 75 $m^2$ each. Two of them, that are the sinter belt No. 2 and 4 are connected to electrostatic precipitators, while the sinter belt No. 1 is currently out of service, and the sinter belt No. 3, as reserve, are connected to multi-cyclones. A system for partial (about 20%) return of the off gases to the process is in operation on the strand No. 2, where the measurement was taken.

The sinter charge consists of a fine mix of iron ores, rolling mill scale, coke breeze constituting the heat source for ignition and sintering of the sinter mix, burnt lime or carbide residue (to support micro-pellet formation process) and return sinter. Basic oxygen furnace slag is used as a lime source. The rolling mill scale used as an input material is oil contaminated and therefore its addition must be restricted.

The components are mixed in a balling drum (where a mixture of all components is dampened) to achieve the optimum air permeability of the sinter mix. The mixture from the balling drum is fed through a shuttle distributor to a hopper closed by a dosing drum, than it falls down through a chute to a sinter strand grate, forming a layer of an appropriate height (normally from 450 mm to 550 mm), depending on a position of a charging Table.

Sintering of the mixture takes place on a continuous, mobile travelling grate, called a sinter strand, consisting of many sintering pallets, their number is characteristic to a specific sinter strand.

The sintering pallets travel over a row of suction chambers (consisting of two heat resistant side walls and a heat resistant grate). Sintering starts at the moment of surface ignition of the coke breeze contained in the mixture by a flame of the ignition furnace burner. As a result of air flow through the mixture layer downwards (due to the negative pressure created by an exhaust fan), the combustion front moves gradually downwards, to the pallet grates, with the velocity depending on the mixture permeability (vertical sintering velocity is 20–25 mm/min), on the whole length of the sinter strand. In the combustion front, where the average temperature is 1250–1320ºC, fine grains of the mixture react completely, and coarser grains melt partially. Formation of sinter is a result of chemical and physical processes taking place in the mixture due to its gradually increasing temperature. There is a bin under each suction chamber, where coarser dust falling through the sinter grate is collected. After clearing the bins, this material is returned to the process.

Evaporation of moisture, partial decomposition of carbonates, reduction of higher iron oxides and synthesis reactions of newly formed mineral compounds take place at the first stage of sintering. At the second stage, the coke breeze is burnt, decomposition of carbonates ends, $Fe_3O_4$ is reduced to $FeO_x$ and part of components pass into the liquid phase. At the third stage, as a result of sinter cooling, newly formed mineral compounds crystallize from the liquid phase and originally reduced higher iron oxides partially re-oxidize.

The thickness of the layer, strand feed rate and negative pressure are controlled until the end of the process, i.e. until the combustion front reaches the grate. Usually the end of the process is set at the penultimate chamber.

Then the finished sinter, leaving the strand, goes through a sinter breaker, where it is broken up to finer pieces of grain size distribution of ca. 150–250 mm. The fragmented sinter is fed to cooling beds (or rotary sinter coolers), where it is cooled in air stream forced by fans, and next it is screened on vibration screens of 12–14 mm mesh, which ensure separation of fine sinter fraction (return sinter fines). The hot return sinter is then conveyed through bins and vibration feeders to drum cooling beds, where it is cooled by addition of a proper amount of water. The cooled return sinter is conveyed to the burdening facility. The mesh fraction of the hot sinter is cooled on a rotary sinter cooler by blowing air through the sinter bed. The sinter cooled to ca. 150°C is conveyed by conveyer strands to the burdening facility of blast furnaces. The sinter, before charging into the blast furnace is re-screened and the separated sinter screenings are returned to the sinter mix.

#### 5.2.1.1. Measurement of PCDD/PCDF releases and the main factors influencing formation and emission of PCDDs/PCDFs in the plant

The measured PCDD/PCDF concentration in the off-gas after the electrostatic precipitator was 1.3 ng I-TEQ/$Nm^3$ (at operational $O_2$) corresponding to an emission factor of 2.2 µg I-TEQ/Mg of sinters produced and a total emission from the sinter strand of 1.5 g I-TEQ/year. Besides the strand concerned, the plant employs a similar strand with an older ESP, one strand with a multicyclone and one strand for backup also with a multicyclone.

Sinter strands are well-known sources of PCDDs/PCDFs in the European Union. In general, the PCDDs/PCDFs are formed out of organic precursors like phenyl derivatives and inorganic chlorine compounds. For this reason oil containing feed material like mill scale can cause higher formation rates of PCDDs and PCDFs. In sinter plants, the *de-novo* synthesis out of solid carbon structures and inorganic chlorides predominates the formation of dioxins. This experience from several sinter plants in Western Europe is supported by the results of the PCDD/PCDF analysis at ISPAT POLSKA. The ratio between PCDFs and PCDDs in the off-gas is 3.79–0.59 ng/$m^3$. The main sources of PCDDs/PCDFs are the carbon and chloride coming with the feed material.

The formation of the PCDD/PCDF takes place inside the sinter bed probably just before the combustion zone which is moving from top to down during the sintering process. The highest emissions are expected to come from the wind boxes of the second part of the sinter strand. Diffuse emissions can also come from the surface of the sinter band.

PCDDs/PCDFs are liquids with boiling points around 200 to 300°C. For this reasons these compounds tend to adsorb on dust particles. As a consequence, high dust emissions are connected with high emissions of PCDDs/PCDFs. Conventional electric precipitators can reach dust concentrations in the clean gas of about 100 to 150 mg/Nm$^3$. The fine dust of a sinter plant contain alkali and lead chlorides which form an insulating layer on the electrodes of the electric precipitator. This is the main reason for high emissions of lead from a sinter strand. With these high dust emissions, low PCDD/PCDF emissions cannot be realised.

Emission factors for sinter strands are typically in the range of 1–10 µg I-TEQ/Mg of sinter [39]. The emission factor of investigated sinter plant of 1.4 is µg I-TEQ/Mg of sinter is therefore at the lower end of the range. Probable reasons for this are the low amount of mill scale used as feed material and the recirculation of the sinter strand off-gases via two hoods.

#### 5.2.1.2. Primary measures

Primary measures for reducing the formation of PCDDs/PCDFs from the process is use of clean charge (not contaminated with oil) or pre-burning of oil in the rolling mill scale, simultaneous reduction of other gas emissions.

#### 5.2.1.3. Secondary measures

##### *5.2.1.3.1. General secondary measures for sinter plants*

**Fabric filter.** PCDD/PCDF emissions are linked to high dust emissions. One of the most effective secondary measures is therefore a reliable dust collector like a fabric filter. With fabric filters dust emissions can be reduced to less than 5 mg/Nm$^3$. The corresponding bag-house should be equipped with high-temperature-resistant bag material (up to 200°C peak temperature). Injection of lime should be avoided since it may cause clogging of the filter bags by organic residuals (Ref.: Bremer Stahlwerke, Bremen, Germany). With fabric filters, also dust and heavy metal emissions can be reduced very effectively. The basics with references are described in the BREF notes for production of iron and steel [48, section 4.3.2].

High temperatures at the fabric filter should be avoided if possible. High off-gas temperatures require expensive bag material and causes higher emissions of PCDDs/PCDFs and mercury even when these compounds are adsorbed on activated carbon or lignite.

**Carbon injection.** By injection of lignite or activated carbon, PCDDs/PCDFs are adsorbed onto the carbon particles. These particles have to be captured by a fabric filter. An electric precipitator is not sufficient for this purpose. Since PCDDs/PCDFs are not destroyed by this method, the dust will have higher contents of these substances. The adsorption process is mainly taking place on the surface of filter bags of the fabric filter. This makes it necessary to distribute the activated carbon or lignite regularly on all filter bags. Activated carbon is more effective in adsorption of PCDDs/PCDFs than lignite but also more expensive.

With a combination of fabric filter and carbon injection PCDD/PCDF emission values of 0.1 to 0.5 ng I-TEQ/Nm$^3$ at the stack of sinter plants are possible.

**Fine wet scrubbing.** Voest Alpine Industries (Austria) developed a scrubbing system to quench the waste gas and to scrub out coarse material and gaseous components, such as $SO_2$. This technique has to be combined with effective treatment of scrubber wastewaters. The water sludge has to be disposed off on a landfill. With this method emissions concentrations of PCDDs/PCDFs of 0.2 to 0.4 ng I-TEQ/Nm$^3$ are attainable.

#### *5.2.1.3.2. Secondary measures for investigated sinter plant*

**Return of flue gases.** From the economical point of view, the most reasonable mean of PCDD/PCDF emission reduction from the discussed installation is the recirculation of the off gases to the sintering process. In case of the discussed installation, application of this process on a larger scale then it is now should ensure attainment of the required level of PCDD/PCDF emission.

**Fabric filter.** If the PCDD/PCDF emissions of investigated sinter plant should be reduced to a level of <0.1 ng I-TEQ/Nm$^3$, the installation of a fabric filter ought to be considered. By this measure, also heavy metal emissions will be minimised. Installation of a fabric filter is therefore worth to be applied, just for reduction of lead emissions, which is a well-known problem of sinter plants equipped only with electric precipitators for dust cleaning.

If the PCDD/PCDF concentrations in the gases cleaned by the bag-house would still be excessive, an additional injection of lignite would be necessary.

**Lignite injection.** The lignite injection point should be installed in the main duct just a few meters before the fabric filter. The amount of lignite has to be optimised. As a thumb rule, 40 to 100 mg of lignite per m$^3$ of flue gas to be treated is used. For the fabric filter, some safety measures should be taken. These are temperature control in the hoppers of each compartment and equipment to flood the whole system with gaseous nitrogen.

### 5.2.1.4. Cost assessment

The following cost assessment is based on prices in Western Europe for the proposed equipment only and does not include the adjustments to the local conditions, such as ductwork, foundations for the building etc. This assessment can therefore only be a rough estimate.

**Fabric filter**. For the investigated plant, in respect of the strand concerned a fabric filter with a capacity of around 400,000 m$^3$/h is required. A negative pressure jet-pulse filter seems to be the best choice. The cost estimate includes the building, all internal equipment, the filter bags (high temperature resistant, e.g. P84® (polyamide), Nomex® (arom. polyamide), Teflon® (PTFE), motor and fan, electrical installation and chimney. Not included is the electrical power supply for the main fan.

| | |
|---|---|
| Investment costs: | 2.0–2.2 million EUR. |

The maintenance costs are very much dependent on the lifetime of the filter bags. Normally a lifetime of 2 years can be assumed.

| | |
|---|---|
| Maintenance costs: | 0.1–0.12 million EUR/year. |

**Lignite injection.** The equipment for the lignite injection system includes the injection system itself, a silo for the lignite, piping and safety measures as described above.

| | |
|---|---|
| Investment costs: | 0.35 million EUR |
| Maintenance costs: | 0.05 million EUR/year |

Operating costs (lignite): 0.08 million EUR/year (approximately 50 mg/m$^3$ of lignite, 24 h, 320 days/year, 500 EUR/Mg of lignite)

**Costs.** Basing on the result of the PCDD/PCDF measurement, their total emission from the plant is estimated at 1.5 g I-TEQ/year. By reducing the emission to the target value of 0.1 ng, I-TEQ/Nm$^3$ the total emission from the strand could be reduced by approximately 1.3 g I-TEQ/year.

**Table 5.1.** Expected emission reduction and costs for one sinter strand

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €[8]] | Maintenance [million €/year] | |
| Fabric filter | 2.0–2.2 | 0.10–0.12 | lead, dust |
| Lignite injection | 0.35 | 0.05 | mercury |
| Total | 2.35–2.55 | 0.15–0.17 | |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

**Cost of equipment in Poland.** The cost of such installation (fabric filter with the control system) in Poland is comparable to the costs estimated for Western Europe presented above. According to the supplier the price of the fabric filter with control system is approximately 2.5–3.5 million PLN and the cost of the other elements (cellular radiator, cyclones, exhaust fan) approximately 5.0–6.0 million PLN. In total approximately 7.5–9.0 million PLN, corresponding to 1.8–2.2 million EUR.

### 5.2.2. *Secondary steel plant with electric arc furnace (EAF)*

Basing on results of the measurements, the steel plant with the highest measured PCDD/PCDF concentration was selected for further evaluation. The managers of the plant, however, refused to participate in the evaluation, and it was therefore decided to replace it by another steel plant.

The installation consists of 2 electric arc furnaces of 140 Mg capacity each and a ladle furnace of 130 Mg capacity. Metal scrap is charged to scrap boxes by overhead travelling cranes and lifting magnets. The boxes are transported to overhead travelling cranes above charging baskets. After loading to the charging baskets, the scrap is transported to the furnace. The scrap is melted by three-phase current in the electric arc furnaces of electric arc temperature about 3000 ºC. At this stage, burnt lime (CaO) is added in order to remove sulphur and phosphorus, which pass into the slag. Having reached the temperature about 1640 ºC the liquid metal is tapped into a ladle. Simultaneously with the tapping alloying components are supplemented according to the standard for a specific steel grade. After the electric arc furnace tapping the liquid metal is transported to a ladle treatment station (in the ladle furnace). Having reached the specific temperature and having met the quality requirements the liquid metal is transferred to a continuous caster where blooms are cast. Subsequently the blooms are directed to a rolling mill where rolled products are manufactured (merchant bars and rebars and sections).

Dioxin emission measurements were taken for one electric arc furnace of 140 Mg capacity. This furnace has the 4th holes in the ceiling for removal of off gasses forming during melting process. In

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[8] Euro symbol (in respect of Euro also the abbreviation EUR is applied).

addition, dust containing gases leaking from the EAF, are captured by hoods and transferred by collectors to spark arresters (similar to cyclones). From there, fans force the gases to a 10-chamber bag filter.

The ST-4 grade steel composed as presented in Table 5.2 is melted in the furnace. Additional details concerning the installation and process are found in the Environmental Review Report (Annex 3).

**Table 5.2.** Composition of steel grade ST-4

| Elements | Element content in % |
|---|---|
| C | 0.08–0.22 |
| Mn | 0.50–1.2 |
| Si | 0.15–0.40 |
| $P_{max}$ | 0.050 |
| $S_{max}$ | 0.050 |
| Cu | up to 0.40 |
| Cr | up to 0.20 |
| Ni | up to 0.20 |
| Mo | up to 0.02 |
| As | up to 0.007 |
| Sn | up to 0.025 |
| Sb | up to 0.003 |
| Co | up to 0.011 |
| Pb | up to 0.003 |
| Ti | up to 0.003 |
| Zn | < 0.002 |

#### 5.2.2.1. Measurement, releases and main factors influencing the formation and emission of PCDDs/PCDFs in the plant

A sample for PCDD/PCDF emission was only taken from the secondary off-gas from the hood above the furnace. During the charging of the furnace large amount of fumes (the so-called fugitive emission) is released from the heated scrap into the secondary off-gas system. However, at operational $O_2$ conditions, the concentration in the secondary off-gas after the fabric filter was only 0.004 ng I-TEQ/Nm$^3$ corresponding to an emission factor of 0.02 μg I-TEQ/Mg of steel produced and a total emission from the process by this route of 0.02 g I-TEQ/year. The result demonstrates that the PCDD/PCDF emission with the secondary off-gas is very low.

Due to the geometry of the primary off-gas system, in which the off-gases were released directly from the top of the fabric filter baghouse (the so called 4th hole) into the atmosphere, it was impossible to measure the PCDD/PCDF emission with the primary flue gas. The primary off-gas system receives the off-gas directly from the furnace and is considered the primary source of PCDD/PCDF emission from the process. In order to obtain flow conditions suitable for sampling it would be necessary to build a special installation for sampling on top of the baghouse.

Emission factors of EAF plants in Europe show values from 0.07 to 9 µg I-TEQ/Mg of produced steel. The UNEP toolkit applies an emission factor of 3 µg I-TEQ/Mg of produced steel for steel production from "Clean scrap/virgin iron, afterburner and fabric filter" and 10 µg I-TEQ/Mg from a process defined by "Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls" [39]. These emission factors are over 100 times higher than the measured emission with the secondary off-gas from the plants. Consequently, it must be expected that the current total emission of dioxins and furans from the whole plant may quite well be 100 times higher than the measured one.

The formation of PCDD/PCDF in an electric arc furnace is not totally understood yet, but there are two main formation mechanisms under discussion:

- Reaction of certain organic precursors (e.g. chlorophenols) on the surface of dust particles at a temperature exceeding 300°C. These precursors enter the process with scrap impurities like lubrication and cooling oil, paint and plastics. Also, high emissions of PCDDs and PCDFs have been measured in waste incineration processing waste containing Polyvinyl chloride (PVC).
- The *de-novo* synthesis without organic precursors, i.e. formation out of carbon, oxygen and metal chlorides (e.g. copper chloride) at a temperature of about 250–500°C in the off-gas. Copper chloride acts as a catalyst in this case. PCDDs and PCDFs are highly viscous liquids at temperatures below 300°C and can therefore be easily adsorbed at the surface of dust particles.

#### *5.2.2.1.1. PCDD/PCDF emissions from an EAF plant*

Most of existing EAF plants extracts the emissions of an electric arc furnace by the 4th hole of the furnace roof (2nd hole in case of DC-furnace). The fumes are mixed with air for post combustion of CO and unburned organic compounds. After cooling, these primary fumes are mixed with the, so-called, secondary fumes coming from the melt-shop building. The combined off-gas flux is then cleaned with fabric filters. A schematic drawing is shown in Figure 5.1.

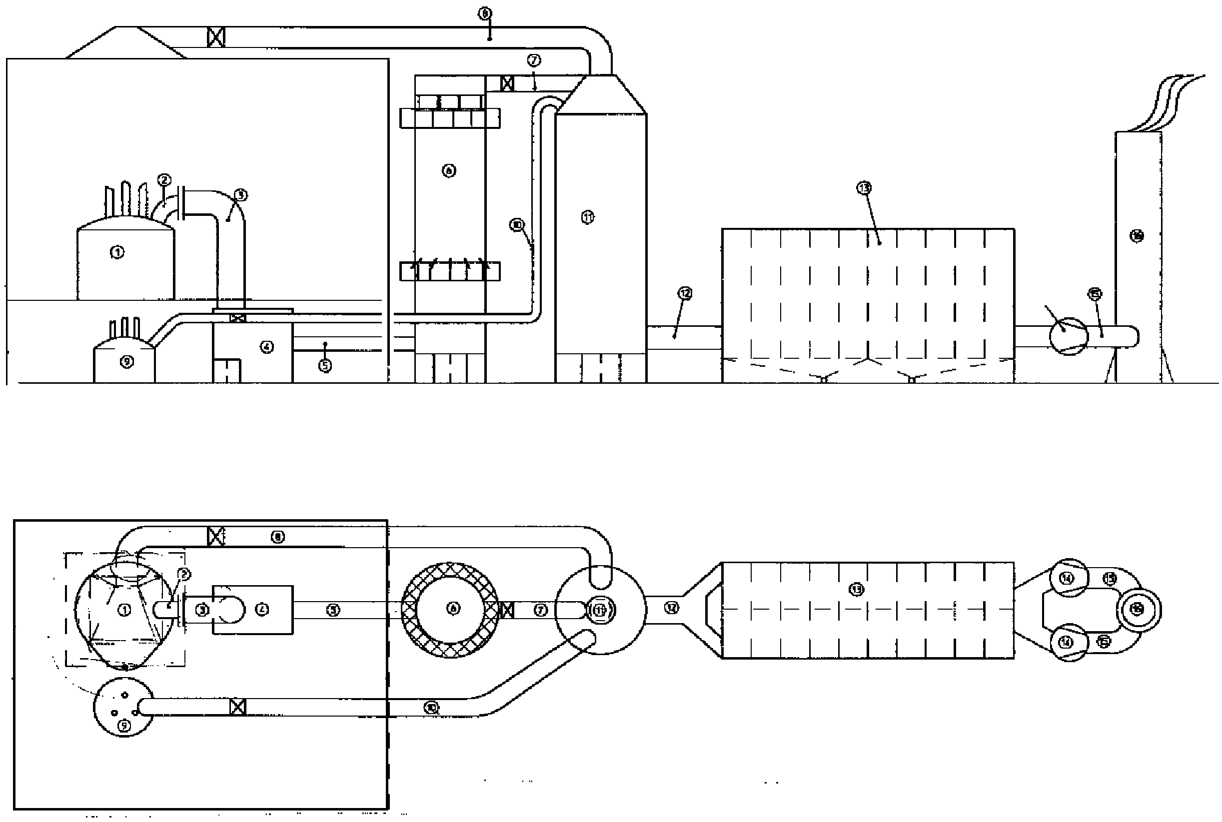
Most of the PCDDs/PCDFs take the way through the primary duct (primary off-gas). PCDD/PCDF concentrations in the secondary off-gas are normally very low (< 0.02 ng I-TEQ/Nm$^3$). At investigated EAF, the measured emission by the secondary off-gas was of the same magnitude. A measurement of the primary fumes according to the standards was not possible without an additional sampling installation.

PCDD/PCDF emissions are highest during the start of meltdown, just after charging the scrap. At this time, the required temperature profile for low PCDD/PCDF emissions cannot be met.

This installation undergoes right now revamping of its off-gas removing and cleaning system, to become similar to the one shown in Figure 5.1. Instead of a spray chamber a tubular cooler will be installed.

#### 5.2.2.2. Primary measures

Primary measures include use of less contaminated input scrap or pre-cleaning of the scrap. Based on experience from other countries such measures are only sporadically being used.



Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

1. Furnace, 2. Elbow, 3. Down leading duct, 4. P/C chamber, 5. Water-cooled duct, 6. Cooler (HTQ, 11. Mixing chamber, 13. Bag house, 14. Fans

**Figure 5.1.** State of the art EAF dedusting concept

### 5.2.2.3. Secondary measures

#### *5.2.2.3.1. General secondary measures*

**Post combustion.** Since not all of the organics can be burned in the EAF itself, a downstream post combustion chamber is needed to destroy PCDDs/PCDFs as well as their precursors. Most of the EAF plants in Western Europe are already equipped with such chambers to minimise the emission of carbon monoxide.

**Quenching chamber.** To avoid reformation of PCDDs/PCDFs a quick cooling of the waste gases is necessary. The temperature range of 600 to 200°C should be passed through in less than 2 seconds. The best way to achieve this, is a quenching chamber. A mixture of water and air is sprayed into the off-gas stream. The water amount is regulated by the outlet temperature measurement of the chamber. After the quenching, the primary fumes have to be mixed with secondary fumes to lower the moisture content on the fabric filter.

**Dust collection.** A reliable dust collection is particularly essential at low PCDD/PCDF emissions. New fabric filters can easily provide for 5 mg/Nm$^3$ dust concentration in the clean gas. Even down to less than 1 mg/Nm$^3$ of dust concentration reduction is possible. PCDDs/PCDFs either adsorb on dust particles or condense to particulate matter, which can be captured on a fabric filters when the temperature at the bag house is significantly below 100°C. Best results can be achieved when filtering temperatures are below 70°C.

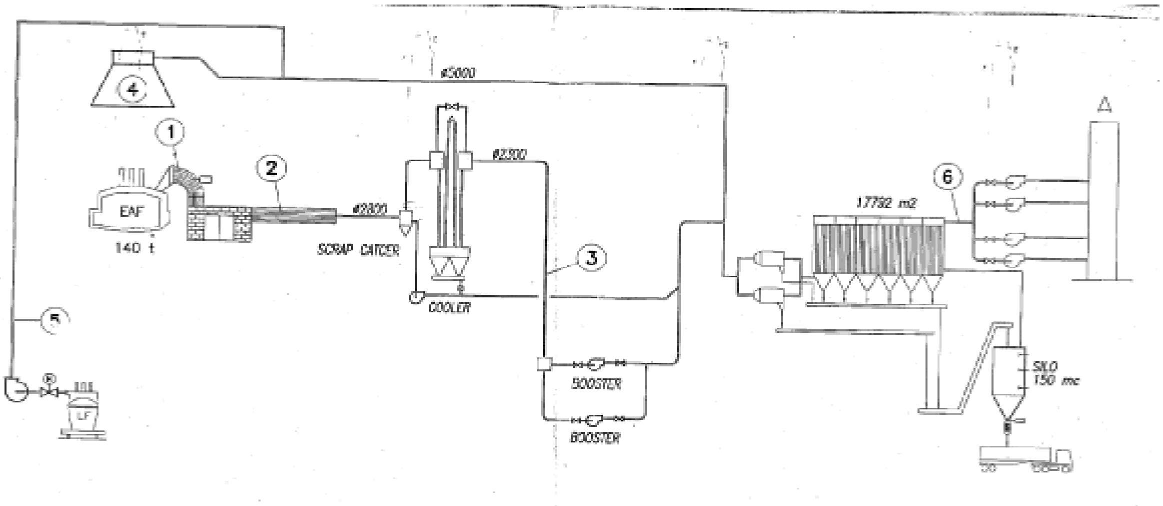
**Carbon injection.** In case when the limiting value of 0.1 ng I-TEQ/Nm$^3$ cannot be reached because of high filtering temperatures or inadequate cooling of the primary fumes, then injection of lignite or activated carbon can help to reduce the PCDD/PCDF emissions. These two carbon grades can better adsorb dioxins and furans than the EAF dust itself. Hence, higher temperatures at the filter are acceptable. On the other hand, with higher temperatures the risk of ignition increases.

Adsorption of PCDDs and PCDFs on carbon particles takes place mainly on the filter bags. The quantity of carbon injection has to be optimised to ensure even application on all bags. Together with the injection system, some safety measures should be applied to minimise the ignition risk.

EAF plants with carbon injection in the off-gas flux system show PCDD/PCDF concentrations in the clean gas of ranging between 0.02 and 0.05 ng I-TEQ/Nm$^3$. As a thumb rule, 40 to 100 mg of lignite per 1 m$^3$ of flue gas is usually applied.

#### *5.2.2.3.2. Secondary measures for the investigated EAF plant*

The flue gas system at this EAF plant is to be revamped into a system similar to the proposed system with the post combustion chamber as shown in Figure 5.2. This system will be furnished with the afterburning chamber, cooling and mixing with secondary fumes. Instead of a quenching chamber, a tubular cooler will be installed. This cooler cannot guarantee the required temperature profile with quick down cooling from 600 to 200°C. After commissioning of the new installation, new PCDD/PCDF measurement should be performed to determine the current emission values.



Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST
6 - Dioxin measurement point

**Figure 5.2.** Future off-gas system at investigated EAF

**Lignite injection.** Once the prescribed limit for PCDD/PCDF emission values are exceeded, a lignite injection system should be installed. At the investigated plant, two cyclones are installed right before the bag house. The lignite injection point should therefore be situated in front the cyclones in the main duct as indicated in Figure 5.2. Since the grain size of the injected lignite is less than 1 mm, the loss through the cyclones will be very small. Normally lignite injection is sufficient for meeting the target of 0.1 ng I-TEQ/Nm$^3$. Activated carbon has better adsorption characteristics but is more expensive.

#### 5.2.2.4. Cost assessment

The following cost assessment is based on prices in Western Europe for the proposed equipment only, and does not include the adjustments to local conditions like duct work, foundations for the building etc. This assessment can therefore only be a rough estimate.

**Lignite injection.** The equipment for the lignite injection system includes the injection system itself, a silo for the lignite, piping and safety measures as described above.

| | |
|---|---|
| Investment costs: | 0.35 million EUR |
| Maintenance costs: | 0.05 million EUR/year |

Operating costs (lignite): 0.15 million EUR/year (estimate: 1 000 000 m$^3$/h, 40 mg/m$^3$ lignite, 320 days per year)

The weight of lignite had to added to the total dust amount, which causes the rise of disposal costs. It was assumed in the estimates that about 300 Mg of lignite will be used per year. Hence, the disposal costs of 300 Mg of additional EAF dust must be added to the total of operating costs.

**Costs.** Basing on result of the PCDD/PCDF emission measurement, their total emission from the plant cannot be determined.

**Table 5.3.** Expected emission reduction and its costs for the investigated installation

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €] | Maintenance [million €/year] | |
| Lignite injection | 0.35 | 0.05 | mercury |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

**Full air pollution control systems.** With reference to, other EAF steel plants it may be necessary to built a completely new APCS installation. The cost estimate of such APCS for at steel plant of a similar capacity as the assessed one is shown in Table 5.4.

**Cost of equipment in Poland.** The cost of the lignite injection installation in Poland is close to the costs estimated for Western Europe above. According to the supplier ECO INSTAL, Poznan, the price of the lignite injection installation is approximately 1.0–1.2 million PLN, corresponding to 0.25–0.3 million EUR.

**Table 5.4.** Expected emission reduction and costs for a complete APCS for a typical EAF steel plant of a size similar to the examined one

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €] | Maintenance [million €/year] | |
| Post combustion | 0.2 | 0.01 | CO |
| Water cooled duct | 0.2–0.5 | 0.02 | |
| Spray chamber | 0.5 | 0.05 | |
| Bag house (1 million $Nm^3/h$) | 3.0–3.5 | 0.15–0.2 | |
| Lignite injection | 0.35 | 0.05 | mercury |
| Total | 4.3–5.3 | 0.28–0.33 | |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

### *5.2.3. Hot blast iron cupola*

Poland hosts about 125 iron-cast foundries and 25 steel-cast foundries. About 60–65% of the production of cast iron is produced in cupola (with hot and cold blast). Most of them have very simple installations for flue gas cleaning. Only 10 cupolas have multicyclons and bag filters.

The installation, in which the measurement to place, consists of two cupolas of a diameter ф = 700 mm with oxygen enriched blast, operating on alternative basis (each cupola every other day). The capacity of the cupolas is about 6 Mg per hour. Grey cast iron is melted in the cupola. It is a continuous furnace. The following materials are used as the charge: home cast iron scrap, purchased steel and iron scrap, cupola coke, slag forming materials (lime stone $CaCO_3$), ferroalloys. Materials are put into the furnace as alternating charges through a charge door and placed in the upper part of the furnace in the following order: metal charge, coke, lime stone. Before charging into the furnace, the scrap is subjected to fragmentation. The cupola is a shaft furnace, where the metal charge is heated by the combustion of coke, which takes place in the lower part of the furnace. Combustion air (in this case oxygen enriched) is supplied to the furnace through appropriate nozzles.

The combustion gases move upward and exchange heat with the charge before leaving the furnace. Flue gases from both cupolas are captured and carried away to a cleaning system. The gases are cleaned by a wet system by spraying with two rows of sprinklers in a star layout. Sludge remains as product of the cleaning process.

#### 5.2.3.1. PCDD/PCDF emission measurements and the main factors influencing their formation and emission in the plant

Due to the geometry of the off-gas system, in which the wet scrubbers were placed on top of the furnace and made the upper part of the stack, it was not possible to take samples for measurements downstream (beyond) the scrubbers. If such samples would need to be taken, it would be necessary to build a stack on the top of the scrubbers in order to obtain a laminar flow.

Under these circumstances, samples were taken between the furnace and the scrubbers in order to determine the level of PCDD/PCDF emission. The measured dioxin and furan concentration in the flue gas before the scrubbers was 1.2 ng I-TEQ/Nm$^3$ (at operational concentration of $O_2$), corresponding to an emission factor of 2.88 μg I-TEQ/Mg of product and a total emission of 0.05 g I-TEQ/year. The measured concentration illustrates the emission level in hot blast cupolas with no APCS.

The examined cupola has a heated blast, however, during PCDD/PCDF emission measurement the blast heating system (heat exchanger) was off and the cupola operated as a cold blast cupola. Thus, the findings may be referred to a cold blast cupola.

The efficiency of the wet scrubber in removing PCDDs/PCDFs from the flue gas is not known, but wet scrubbers are generally not very efficient in dust removal, and the actual emission could well be in the range of 3–10 times lower than the measured concentrations. There is no data in the available literature about PCDD/PCDF emissions from a hot blast cupola furnace without a fabric filter or in the raw gas of a hot blast cupola.

The main sources of PCDDs/PCDFs are the impurities of the scrap as well as the coke charged to the hot blast cupola furnace. Hot gases from coke combustion and oxygen injection rise upwards through the feed material of the cupola preheating scrap, alloy additives, coke and lime. In a certain zone of the cupola, with the temperature ranges between 250–500°C, the formation of PCDDs/PCDFs starts. PCDDs/PCDFs formed are subsequently blown out of the furnace by flue gases together with the dust. As could be concluded from tests performed, just like in sinter plants, mainly furans are formed in this process, especially the tetra- and pentachlorinated compounds. This is an indication that the *de-novo* synthesis out of coke and inorganic chlorides is predominant, compared to the formation out of organic precursors.

At the discussed foundry dust collection is performed by a two step wet scrubber. The advantage of such a system is the quick cooling of the waste gas and the very simple technique of dust trapping. On the other, hand the wastewater has to be disposed off and the de-dusting efficiency is not adequate for the requirements of European legislation. The sample for PCDD/PCDF measurement was taken in the chimney before the water injection point and is representing a measurement in the raw gas.

The dioxins and furans formation in the hot blast cupola, in which the air is preheated to a temperature of about 500–600ºC, is in general significantly lower than in cold blast cupolas. The emission factor for hot blast cupolas with fabric filters amounts to 0.03 μg I-TEQ/Mg of liquid iron.

Hot air cupolas are in Western Europe generally not considered to be a major PCDD/PCDF source if equipped with complete APCS.

### 5.2.3.2. Primary measures

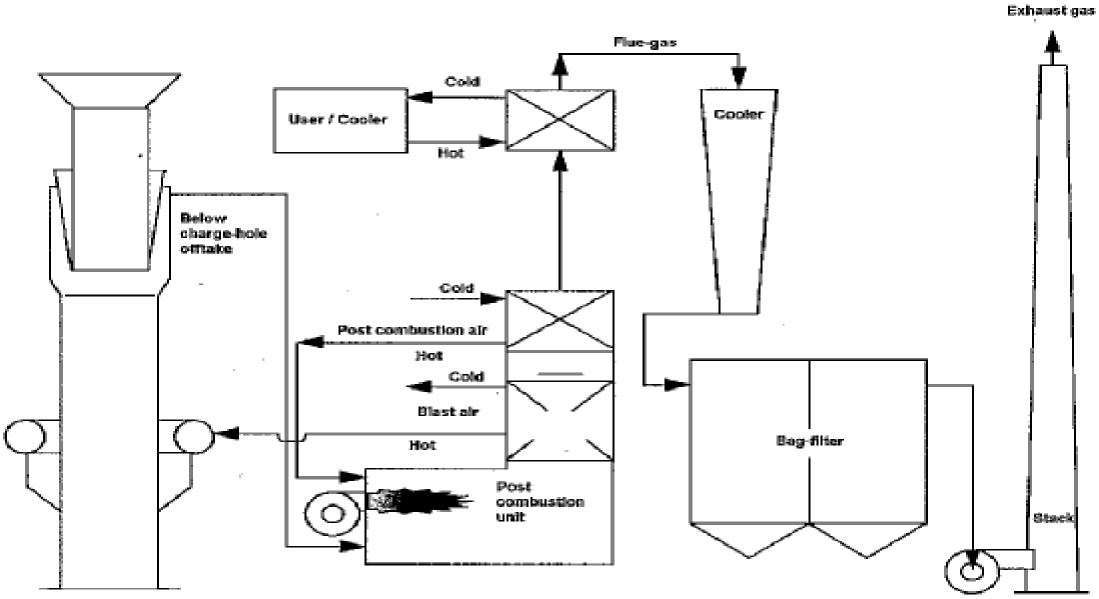
Primary measures for reduction of PCDD/PCDF formation include use of cupola off gases to heat the blast (cooling of gases and their shorter period of remaining in the adverse temperature) and scrap selection and it's pre-cleaning e.g. by preheating. The experience form other countries is that pre-cleaning of scrap is usually not used as a primary measure; instead secondary measures are used for PCDD/PCDF emission reduction.

#### 5.2.3.3. Secondary measures

##### *5.2.3.3.1. Secondary measures for a hot blast cupola furnace*

**Post combustion.** Waste gases of a hot blast cupola furnace contain carbon particles, CO and volatile organics (including PCDDs/PCDFs). These top gases are fed directly into a post combustion chamber equipped with an air-fuel burner. The environmental benefits are less CO emissions and reduction of PCDD/PCDF emissions. The heat can be recovered in a recuperator to heat the cupola furnace. After post combustion further cooling is needed for the off-gas.

**Fabric filter.** A fabric filter should perform capture of the dust. A low emission rate of less than 5 mg/Nm$^3$ can easily be attained. If the temperature at the bag house falls below 70°C a low PCDD/PCDF emissions can be expected. An installation as described in this chapter is shown in Figure 5.3. Emission factors for hot blast cupola furnaces with fabric filter shows amount to around 0.03 μg I-TEQ/Mg of liquid iron.



Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

**Figure 5.3.** Off-gas system of a hot blast cupola furnace with a bag filter

##### *5.2.3.3.2. Secondary measures for foundries*

The hot blast cupola furnaces of the investigated foundry are rather small as compared to similar installations in Western Europe. A common capacity for those furnaces is 40 to 50 Mg/h of liquid iron. That is why a complete implementation of the secondary measures described above is surely too expensive taking into account the turnover figures of such a small foundry.

**Fabric filter.** Installation of a fabric filter is necessary to reduce the dust emissions from the cupola furnaces. This filter should be installed outside the foundry building. Additional air has to be added because of the stack gases because of the moisture coming from the wet scrubbers. The amount of diluting air has to be determined by the filter supplier, based on the accurate measurement of the moisture content.

The content of volatile organic compounds (VOC) should be measured in the chimney of the cupola prior to deciding whether a fabric filter can be installed without a post combustion system.

#### 5.2.3.4. Cost assessment

The following cost assessment is based on prices in Western Europe exclusively for the proposed equipment. It does not include the adjustments to the local conditions, such as ductwork, foundations for the building etc. This assessment can therefore be regarded only as a rough estimate.

**Fabric filter.** For the investigated hot blast cupolas a fabric filter of a capacity of around 50,000 $m^3/h$ (to be checked by supplier) is required under operating conditions. A negative pressure jet-pulse filter seems to be the best choice. The estimated cost includes the building, all internal equipment, the filter bags (high temperature resistant, e.g. P84® (polyamide), Nomex® (arom. polyamide), Teflon® (PTFE), motor and fan, electrical installation and chimney. The power supply, needed to operate the main fan, is not included.

Investment costs: 0.25–0.3 million EUR.

The investment costs for a fabric filter are linked to the level flow.

Maintenance costs are very much dependent on the lifetime of filter bags. Standard lifetime of such filters is two years.

Maintenance costs: 0.02 million EUR/year.

**Complete air pollution control system with afterburner.** The size of post combustion installation with burners varies a lot with the level flow of the off-gas to be treated. Only a very rough estimate of the investment costs is therefore possible, amounting to: 0.5–2.0 million EUR.

**Costs.** The estimated costs are shown below in Table 5.5. Most probably, the installation of a fabric filter will be adequate to reduce the PCDD/PCDF emissions below 0.1 ng I-TEQ/$Nm^3$.

**Table 5.5.** Estimated costs

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €] | Maintenance [million €/year] | |
| Fabric filter | 0.3 | 0.02 | dust |
| APCS with afterburner | 0.5–2 | | dust |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

As already mentioned, the PCDD/PCDF emission will most probably fall below 0.1 ng I-TEQ/$Nm^3$ if a fabric filter, to reduce dust emission, is installed. No any specific PCDD/PCDF reduction measures will be needed. It is proposed to confirm this assumption by an actual measurement after the filter is installed.

**Equipment price in Poland.** The cost of the fabric filter with control system and installation in Poland is close the costs estimated for Western Europe shown above. According to the supplier the price of the fabric filter for ф = 700 mm cupola with a capacity of 10,000 $Nm^3/h$ and temperature of gases entering the filter ~160º C is approximately 0.37 million PLN while the cost of the other elements (cellular radiator, cyclones, exhaust fan) is approximately 0.63 million PLN. In total approximately 1 million PLN corresponding to 0.25 million EUR.

## *5.2.4. Secondary aluminium plant with induction*

### 5.2.4.1. General consideration regarding PCDD/PCDF emission from secondary aluminium plants

#### *5.2.4.1.1. General comments*

Different techniques are used for melting secondary aluminium, which depend on the type of scrap as well as the way of further processing of the obtained metal.

The secondary aluminium plants, discussed in this report, are primarily suitable for melt relatively clean charges with a high aluminium recovery rate. "Typical" melting furnaces used in the secondary aluminium industry are mainly rotary kilns, tilting rotary kilns and multi-chamber hearth-type furnaces (with an integrated waste gases after-burning installation).

#### *5.2.4.1.2. Characteristics of emission*

Typical process steps of the secondary aluminium production are: heating up, feeding, melting, keeping warm, treatment of the melted mass and founding. Process parameters are subject to high temporary fluctuations, influencing the emission size and nature of the plant (e.g. waste gas temperature, concentration of pollutants in raw gas).

In general, releases of PCDDs/PCDFs from melting processes of the secondary aluminium industry are the result of following mechanisms:

- The feed material contains PCDD/PCDF released by thermal treatment in the process;
- PCDDs/PCDFs are formatted from chlorinated precursor compounds (e.g. chlorinated phenols, PCBs, chlorodiphenyl ether) present in the feed material (e.g. as a pollution in oils);
- PCDDs/PCDFs are formed by thermal treatment of the feed material from organic components and organic or inorganic chlorine compounds.

In formation of PCDDs/PCDFs in reaction with fly ash, the "active" carbon compounds are considered to be their source. Carbon compounds react with inorganic chlorides with participation of catalytically acting compounds (e.g. salts of metal) at the presence of oxygen and steam in a temperature range of approx. 200°C to 800°C. This process is called the *de-novo* synthesis.

#### *5.2.4.1.3. Measures to reduce PCDD/PCDF emissions*

The specific PCDD/PCDF emission factor for secondary aluminium melting plants can be achieved at 1 µg I-TEQ/Mg, or considerably less, if the best available techniques are applied in combination with measures applied to feed material, the process and the flue gas cleaning simultaneously.

**Measures concerning the charge used.** Introduction of PCDDs/PCDFs together with polluted feed materials can, with a high probability, be eliminated.

The following measures minimising PCDD/PCDF formation should be considered:

- Minimisation of organic pollutants input of (e.g. greases, oils, varnishes, plastics), by pre-treatment or processing the scrap metal (e.g. by sorting);
- Minimization of the chlorine input (e.g. by abandoning hexachloroethene, treatment of the melted mass with nitrogen/chlorine mixture);
- Avoiding use of additives containing chlorine in production and processing of aluminium (this is beyond control of the secondary aluminium industry).

**Process technical measures.** Depending on the composition of scrap different furnaces/kilns have proven to be advantageous:

- Fuel heated rotary kilns for melting polluted scrap metal covered by addition of melting salt;
- Fuel heated hearth-type furnaces for clean, fragmented or very condensed scrap metal;
- Fuel heated multi-chamber heart-type fuel fired furnaces also for organic contaminated scrap metal;
- Electrically heated induction furnaces for clean, fine-part scrap metal.

Moreover, the following general principles should be taken into account:

- Raw gas from processes must be treated by the APCS and the flux of polluted gases should be kept as low as possible (consider complete collection of the waste gas);
- Optimise burning of the organic substances (good intermixing, sufficient dwelling time and sufficiently high combustion temperatures);
- Minimise chlorine releases during treatment of the melted mass, e.g. by optimal technique of gassing.

**Secondary measures.** The retrofitting of existing plants with optimised furnaces/kilns can often be implemented partly only or at high costs. Therefore, in many cases only secondary measures, i.e. appropriate purification of waste gases is considered for minimisation of PCDD/PCDF emissions.

The major objective of the flue gas cleaning is to minimize the amount of pollutants in the waste gas and to enhance their removal, for instance in the form of dust, from the bag filters.

Cleaning of flue gases from the secondary aluminium production process is normally conducted by the dry adsorption method, with subsequent deposition on fabric filters. In some cases also scrubbers are used for waste gas treatment.

As for the dry sorption process the raw gas is admitted into a central reaction pipe where white lime hydrate as adsorbent agent is injected (in order to separate the acid components from gas). Furthermore, also salt aerosols are condensed or adsorbed at the fine-part lime hydrate. After cooling down and removal of the dusts, the waste gases are then carried out from the fabric filter. To improve dioxins and furans elimination efficiency, mixtures of lime hydrate and lignite coke, in proportion of 3–10 % are increasingly used. Also clay minerals, as additive, are applied (advantage: not combustible).

Occasionally "lime hydrate" and "lignite coke" is added as adsorbing agents, not as a mixture, but one by one into the waste gas (to reduce costs).

Using this type of flue gas cleaning technique the PCDD/PCDF concentrations of $< 0.1$ ng/Nm$^3$ can easily be achieved.

The waste gas treatment by the scrubber technique has confirmed, at least with regard to the removal of acid waste gas components, to be as efficient as the dry sorption technique. However, the degree of dust removal is lower. Concentration of PCDDs/PCDFs in the treated gases at $< 0.1$ ng/m$^3$ can be attained only under favourable conditions. Therefore, applying the scrubber systems for dioxins and furans elimination, an additional purification step (e.g. packed-bed of lignite coke) must be installed.

### 5.2.4.2. Induction furnace for secondary aluminium production

In the secondary aluminium production processes scrap, shavings and other aluminium-containing waste materials are melted and cast into ingots for further processing or final products.

Secondary aluminium production is performed by a large number of companies in Poland. The total production of secondary aluminium in the year 2000 was estimated at about 123,000 Mg.

The examined installation where measurements were taken consists of 4-channel induction furnaces designated for melting of aluminium. Tests were performed on one furnace. The furnace operates in a batch mode (the charge is 12 Mg per heat). Rolling mill process scrap (93%) and outside scrap (7%) are used as charge materials. The charge materials are thoroughly shredded in rippers and magnetically separated. Some scrap from the own rolling mill may be oil contaminated (degree of oil pollution depends on the place origin), while the scrap from outside is often heavily contaminated with oil.

During the melting process slag is formed at the top of the melt to prevent aluminium oxidation. The slag contains, among others: calcium fluorosilicate, sodium chloride and sodium sulphate. During the melting process a layer of melting loss and partially slag are removed from the metal surface and placed in a separate container.

The melt temperature is about 700ºC. The molten metal is semi-continuously cast into ingots. The ingots are intended for rolling. Off-gas from the furnace is removed only by an exhaust system (a hood over the furnace and over the melting loss container) and is carried away through a stack.

### 5.2.4.3. PCDD/PCDF emission measurements and the main factors affecting their formation and emission

The measured PCDD/PCDF concentration in off-gases from the electric arc furnace was 0.6 ng I-TEQ/Nm$^3$ (at operational $O_2$) corresponding to an emission factor of 8.7 μg I-TEQ/Mg of aluminium produced and a total emission from the furnace of 0.08 g I-TEQ/year. The plant has 4 furnaces of similar type.

The reason for the relatively low emission, in spite of the fact that the off-gas is not cleaned, may be that 93% of the scrap are cuttings and other wastes from the rolling mill. Only 7% of the raw materials are scrap or scrap from other production processes. As the product is low-alloyed aluminium for sheets production only relatively clean scrap must be used

The plant also employs a gas furnace equipped with a fabric filter. The input material in this furnace is mainly old scrap. The measured emission from the gas furnace after the fabric filter was 0.1 ng I-TEQ/Nm$^3$ and the process was not further evaluated. Compared to emissions reported from other plants the emission rates are extraordinary low for processes.

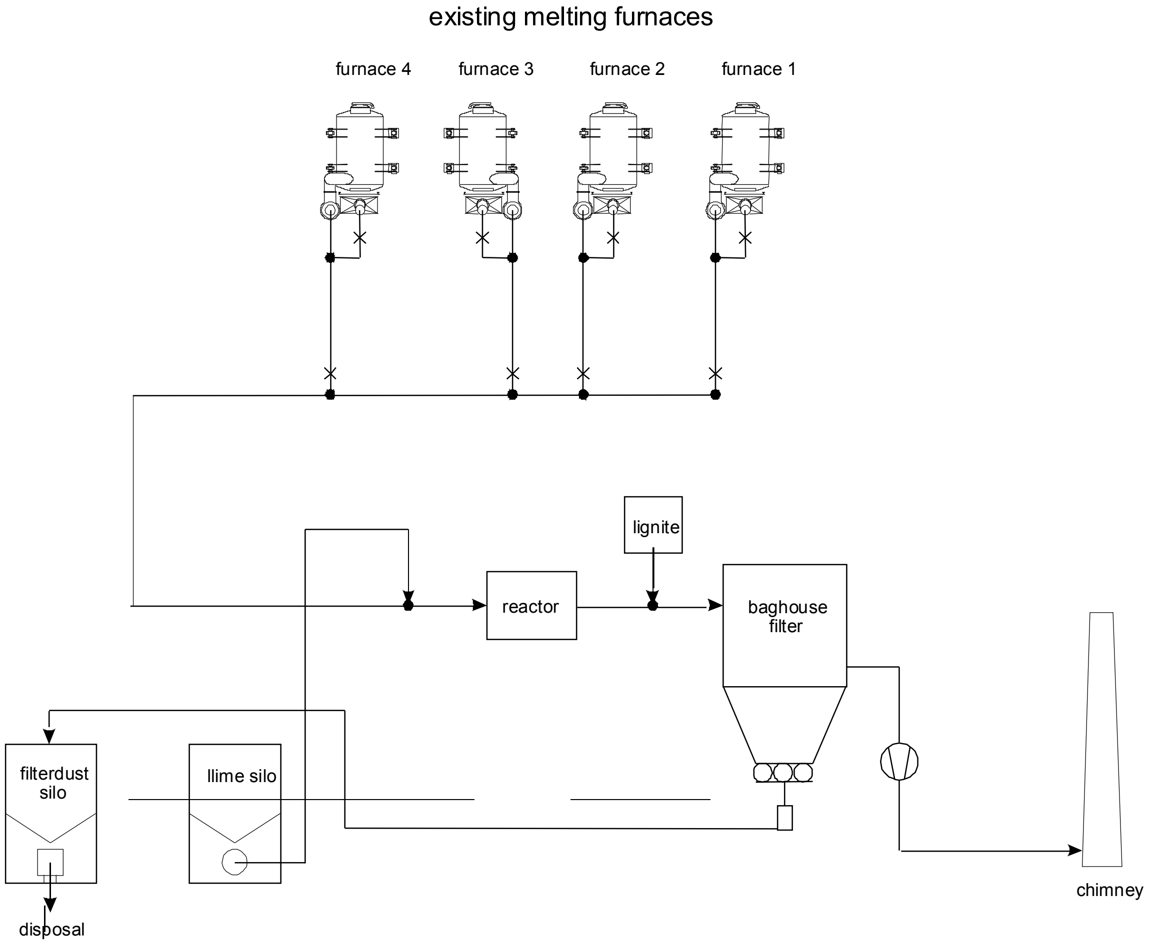
### 5.2.4.4. Primary measures

Primary measures include pre-treatment of charge materials e.g. burning of oil from rolling mill scrap. A significant part of PCDD/PCDF formed may result from use of oiled scrap (7%) and replacing this oiled scrap with clean scrap can reduce the emissions (less oiled scrap from the rolling mill, better quality scrap from outside and proper segregation of scrap).

### 5.2.4.5. Secondary measures

Basic aspects concerning emission reduction measures for melting plants of the secondary aluminium industry are described above.

PCDD/PCD emission level of < 0.1 ng/Nm³ can be obtained only with an efficient flue gas cleaning technology. For the channel-type induction furnaces the scheme presented on Figure 5.4 is suggested.



Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

**Figure 5.4.** Diagram of the APCS - concept

***Description of the air pollution control system.*** The waste gases of the four channel induction furnaces are merged into a collecting pipe. The pipe diameters were designed in a manner preventing dust depositions in the pipes.

The flue gas cleaning system consists of two lines with two filter units because of the redundancy of the system. The units are equipped with separate waste gas ventilators and the total waste gas flow amounts to 100,000 Nm$^3$/h.

The essential components of the flue gas cleaning system are:

- Dry sorption of harmful gases by means of a one-level flue gas adsorption with use of suitable powdered adsorbent agents (lime, lignite coke);
- Fabric filter for the deposition of the dusts;

For the removal of acid components upstream the reactor, lime hydrate is dosed as an additive (adsorbent agent) into the raw gas by a pneumatic feed system. The additive reacts with the acid waste gas components.

The additive is stored in an approx. 60m$^3$ silo and dosed continuously into the raw gas stream. The continuous dosage of the additive is continuously controlled. The supply of the lime hydrate is carried out with bulk transporters. The ventilation of the lime silo is directed to the raw gas pipe.

For the removal of dioxins and furans as well as other comparable high-molecular compounds, the lignite coke dust is dosed as an additive between the reactor and the filter by a pneumatic feed system. The lignite coke dust is stored in an approx. 2m$^3$ container and dosed continuously to the raw gas stream. The continuous dosage of the additive is continuously controlled.

Flue gases containing dust from the melting process, such as from the processes of charge pre-treatment, are directed into the raw gas chamber of the filter unit and after cleaning by the filter bags, sent to the purified gas chamber. The dust is arrested on external surfaces of the filter bags. Dust collected at the filter bags is removed from them automatically by continuous counter-air purging. The scavenging air blower produces the required amount of air and the scavenging air flaps the necessary impulse.

The filter bags are made of polyester needle felt with a continuous temperature resistance of max. 150° C. To guarantee maintenance of the maximum acceptable filter temperature, a ventilation flap is installed in front of the filter. This flap opens, once the maximum allowed temperature is reached.

Dust collected on the filter is conveyed pneumatically from the baghouse into an approx. 60m$^3$ baghouse dust silo. In case of system failure the baghouse dust is loaded into big bags. When required the baghouse dust is dust-freely emptied into silo vehicles and then disposed.

The baghouse dust collected in the silo is blown into the raw gas pipe. The cleaned gas is pumped into the stack by a radial fan before escaping into air.

The cleaned is forced from the pressure socket of the radial fan and blows out through a sound absorber. The manifold on the top of the sound absorber is protected against rainwater preventing interference of its function.

The main specifications concerning the discusses flue gas cleaning system are given below:

- principle: baghouse filter with fully automated bag cleaning system,
- flue gas stream: 100,000 Nm$^3$/h

- temperature before baghouse: < 100°C
- max. number of bags per filter: 2 x 864
- filter medium: polyester needle felt (oil and humidity resistant)
- heat resistance: 150°C
- filter area load: 1.0 $m^3/m^2$ x min
- negative pressure: 6500 Pa.

Comparable flue gas cleaning plants are operated at the German aluminium plants Aluminiumschmelzwerk Oetinger GmbH, Weissenhorn, and VAW-Imco GmbH, Töging and Grevenbroich.

### 5.2.4.6. Cost assessment

The following cost assessment is based on prices in Western Europe exclusively for the proposed equipment. It does not include the adjustments to the local conditions, such as ductwork, foundations for the building etc. This assessment can therefore be regarded only as a rough estimate.

For the flue gas cleaning technology described in the chapter above a capital expenditure of approx. 0.7 to 0.8 million EUR is required (see Table 5.6).

**Table 5.6.** Estimated costs

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €] | Maintenance [million €/year] | |
| Flue-gas cleaning with lime- and lignite-dosing and baghouse filter | 0.7–0.8 | 0.05 | Dust, heavy metals,<br>other organic substances |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

The annual maintenance cost (without electrical energy) include:

- Use of highly reactive lime hydrate (100 Mg/year x 140 EUR);
- Use of lignite coke (5 Mg/year x 600 EUR);
- Replacement of filter bags;
- Disposal of the filter dust (150 Mg/year x 100 EUR).

### *5.2.5. Primary zinc casting from zinc cathodes*

Zinc casting was selected for evaluation in result of misunderstanding confusing the process with secondary zinc production process, which in general is considered a significant source of PCDD/PCDF emission. The confusion was discovered during the environmental review procedure.

The installation is used for melting and casting of zinc and its aluminium containing alloys. It consists of 8 electric melting furnaces. Each of them has an individual gas and dust exhaust equipment. Captured gases and dusts from all furnaces are conveyed to a single cleaning system. The melting installation consists of the following furnaces:

- Junker furnace – medium frequency crucible induction furnace (production of alloys for sheet galvanizing),
- PIK 20 furnace – channel induction furnace (melting of cathodes),
- PIK 12 furnace – channel induction furnace (manufacturing of Zn-Al alloys),
- REMIX furnace – electric resistance furnace (manufacturing of Zn-Mn foundry alloys),
- PIK 20 furnace – channel induction furnace (melting of cathodes),
- PIK 30 furnace – channel induction furnace (melting of cathodes),
- PIK 15 furnace – channel induction furnace (melting of cathodes),
- IMR furnace – crucible resistance furnace (manufacturing of Zn based casting alloys).

The efficiency of the whole set of furnaces is 200–350 Mg per 24 hours.

Zn cathodes obtained by zinc sulphate electrolysis and some (ca. 0.5%) home zinc scrap are the charge to the furnaces used for melting cathodes. $NH_4Cl$ is used as a process additive in the cathode melting process at the rate of 1 kg per 1 Mg of pure zinc. The liquid zinc obtained is subsequently used for production of alloys for hot-dip and electrolytic galvanizing (Al-Zn alloys), Zn-Al casting alloys and Zn-Mn foundry alloys. A preparation known under the trade name Wulcanit, consisting among others of zinc chloride and zinc oxide, is used in production of alloys for hot deep galvanizing. The addition is 0.002 kg per 1 Mg of liquid metal.

The off gas cleaning system comprises of a set of fabric bag filters, consisting of 6 filtration chambers cleaned by reverse air flow. The bag dimensions are: diameter 200 mm, length 4750 mm; number of bags 312. All gases are carried away through one stack. The gas temperature at the entrance to the cleaning system is approximately equal to the ambient temperature.

#### 5.2.5.1. PCDD/PCDF emission measured and the main factors affecting their formation and emission in the plant

Samples were taken from two processes run by the plant: roasting of zinc ore and casting of zinc from the electrolytically produced cathodes.

Primary zinc production is generally not considered a significant source of PCDD/PCDF emission to the air [39] and this was confirmed by the present measurements.

The measured PCDD/PCDF concentration in the off-gas from the zinc ore roasting process was 0.045 ng I-TEQ/$Nm^3$ (at operational $O_2$) corresponding to an emission factor of 0.04 µg I-TEQ/Mg of zinc oxide produced and a total emission from the process of 0.004 g I-TEQ/year.

The measured PCDD/PCDF concentration in the off-gas from casting zinc from the electrolytically produced cathodes was 0.006 ng I-TEQ/$Nm^3$ (at operational $O_2$) corresponding to an emission factor of 0.02 µg I-TEQ/Mg of zinc produced and a total emission from the furnace of 0.001 g I-TEQ/year. The emission from the same process has in 2003 been measured at 0.02 ng I-TEQ/$Nm^3$ [49].

#### 5.2.5.2. Proposed measures

The processes are not considered a significant PCDD/PCDF emission source, and this has been confirmed also in this measurements. The measured PCDD/PCDF emission from both processes is below the target value of 0.1 ng I-TEQ/Nm$^3$ and no measures are proposed to further reduce that emission from the considered processes.

### *5.2.6. Secondary aluminium plant*

In the process of secondary aluminium production aluminium the scrap, shavings and other aluminium-containing waste materials are melted and cast into ingots for further processing or as final products.

The installation for secondary aluminium melting, in which the measurement took place, consists of two medium frequency induction furnaces of 300 kg capacity each (an additional induction furnace of 1,500 kg capacity is going to be put into operation soon).

Aluminium scrap, mainly used beverage cans and aluminium foil, is melted in these furnaces. The beverage cans are paint coated and they can contain beverage residues and sometimes also other metallic and non-metallic contaminants. The aluminium foil basically constitutes pure material, not contaminating the melt. The installed induction furnaces operate in a batch mode. The melt temperature is 800–900 ºC. Liquid metal obtained by melting is cast in a casting machine into cones, which are used for steel deoxidising.

Off gases from both furnaces (and in the future from 3 furnaces) are carried by an off-take tube to a wet scrubber, and then to the stack. The scrubber is periodically cleared of sludge.

#### 5.2.6.1. PCDD/PCDF emission measured and main factors influencing their formation and emission in the plant

The measured PCDD/PCDF concentration in the off-gas from the plant was 0.12 ng I-TEQ/Nm$^3$ (at operational $O_2$) corresponding to an emission factor of 3 µg I-TEQ/Mg of aluminium produced and a total emission from the plant of 0.004 g I-TEQ/year.

The UNEP Toolkit envisages, for the secondary aluminium processing with scrap treatment and well controlled process and use of fabric filters with lime injection, an emission factor of 35 µg I-TEQ/Mg; more than 10 times higher than the emissions determined for the examined process with less developed APCS.

The reason for the relatively low PCDD/PCDF emission compared to other reported secondary aluminium production processes may be that only beverage cans are used as input material. In the discussed process chlorine-containing salts are not applied to form a slag on top of the melted aluminium and that the melted aluminium is not fluxed with chlorine. According to producers of the beverage cans the paints on the cans (accounting for approximately 2.5% of the total weight) does not contain chlorine. Thus, the sources of chlorine for dioxins and furans formation are very limited.

However, it should be noted that changing the input material too more contaminated scrap may significantly increase the formation of PCDDs/PCDFs.

### 5.2.6.2. Primary measures

The formation of PCDDs/PCDFs from the process highly depends on the presence of contaminants in the used scrap. As PCDD/PCDF formation in the process is very low, compared to the emission levels in other secondary aluminium production processes, it is not deemed practicable to reduce the PCDD/PCDF formation further by any primary measures.

### 5.2.6.3. Secondary measures

The off-gas from the specific plant has a relatively high content of particulate matter (PM) and aromatic compounds, giving rise to complaints from neighbours and the local environmental authorities.

Considering the low emission of PCDDs/PCDFs it is estimated that their level, even with an increase in production volume, most probably will be below the target value of 0.1 ng I-TEQ/Nm$^3$, if additional APCS for reducing the PM emission is installed.

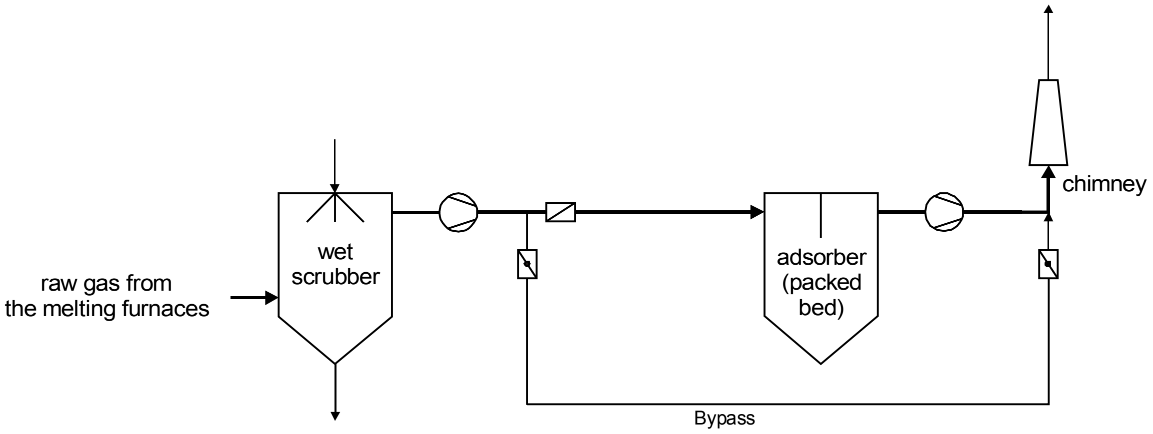
After the additional furnace together with the fabric filter is installed, a new PCDD/PCDF measurement should be made, to confirm that the emission of PCDDs/PCDFs is below 0.1 ng I-TEQ/Nm$^3$.

In principle, two options may be considered for the flue gas cleaning:

- Dry sorption method using a fabric filter;
- Lignite coke packed bed filter downstream the scrubber.

For the lower costs and the adequate performance, only cleaning by the additional packed lignite bed adsorber is hereafter considered. The packed bed adsorber is also able to bind odour substances.

The proposed flue gas cleaning system for the existing plant together with the additional, packed bed adsorber is represented by the following scheme.



Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

**Figure 5.5.** Scheme of the proposed APCS - concept (adsorption with packed bed)

***Description of the proposed gas cleaning installation.*** For a flue gas stream of approx. 10,000 $Nm^3/h$, a lignite coke packed bed adsorber is required with a volume of approx. $10m^3$.

An essential advantage of a packed bed adsorber is the stability of its concentrations. The separating power is dependent on the height of the packed bed, and for this the reduction of the emissions can be maintained without problems. In addition, other pollutants may be adsorbed and an additional cleaning is provided for these components (e.g. $SO_2$, odour substances).

Lignite coke is used as adsorbent. In result of the introduction of carbon black into the adsorbed gases a gradual growth in the pressure difference will occur. Operational experience at similar plants shows that a bed height of 1 m is sufficient to attain adequate reduction of emission.

To prevent the condensation to occur in the plant, the wet flue gases should – if necessary – be heated above the dew point by means of additional natural gas burners.

Removal of PCDDs/PCDFs takes place most rapidly in the first 20 cm of the packed bed. The absorption point for dioxins and furans lies, as is known from experience, very high and is never reached under normal conditions. Usually the presence of other pollutants, such as dust or sulphur oxides, necessitates the adsorbent to be exchanged. This has to be expected also in this case.

Experience shows, that the packed bed has to be replaced every one to two years. An external company regenerates the worn out adsorbent.

Technical specifications:

- flue gas stream: 10,000 $m^3/h$
- flue gas temperature: ca. 25–30°C
- dust concentration: 35–40 $mg/m^3$
- estimated superficial velocity: 0.3 m/s
- flow area: ca. 10 $m^2$
- typical height of the packed bed: ca. 1.0 m
- volume of the packed bed: ca. 10 $m^3$
- adsorbent: lignite coke

### 5.2.6.4. Cost assessment

The costs estimates are based on prices in Western Europe exclusively for the proposed equipment and its installation. It does not include the adjustments to the local conditions, such as ductwork, foundations for the building etc. This assessment can therefore be regarded only as a rough estimate.

For the packed bed adsorber, as described in the chapter above, a capital outlay of approx. 0.1 million EUR is required.

The annual maintenance cost is estimated, with use and disposal of 5 Mg of lignite coke/year at 700 EUR/Mg (without electrical energy).

**Table 5.7** Expected costs

| Measure | Estimated costs | | Other pollutants reduced by the measure |
|---|---|---|---|
| | Investment [million €] | Maintenance [million €/year] | |
| Flue-gas cleaning with lignite coke packed bed | 0.1 | 0.005 | sulphur dioxide<br>heavy metals<br>odour |

Source: COWI, Badische Stahl-Engineering GmbH, ProVis GmbH and AGH-UST

# 6. CONCLUSIONS AND RECOMMENDATIONS

The decline of dioxin and furan emission from the metallurgical industry noticed in Poland during 1995–2002 (Figure 2.3) was caused on one hand by the reduction in production of metallurgical produce (except for copper and silver, the output of which grew slightly – Table 2.1), and on the other in result of gradual modernisation of manufacturing processes (for instance elimination of the open hearth furnace process replaced by the oxygen converter process), implementation of environmental protection projects (for instance installation of stack gas cleaning systems) and continuous (since 1998) implementation of the iron and steel industry restructuring programme as well as the improvement of the emission assessment methods. Despite of improvement of the situation in this respect, the share of the considered sector in the total PCDD/PCDF emission is still considerably high (14,5% according to inventory carried out by the EMEP compliant method and 9% according to inventory carried out by the method compliant to the UNEP Chemicals recommendations).

Basing on dioxin and furan measurement results obtained at installations of the metallurgical industry and on the possibilities of applying modified emission factors used in the national emission inventory from the metallurgical sector in Poland the following conclusions may be drawn:

1. The results of measurements performed confirm, in most cases, the emission factors applied to date for inventory purposes. This is the case of primary copper and zinc production, melting scrap of zinc cathodes and grey iron foundries equipped with good APC systems.

2. From the remaining measurements the actual, instantaneous, considerable emission was identified in the examined installations, which – in general – differs from the emissions evaluated so far. The factors and emissions determined in result of measurements indicate that the main problem among the metallurgical industry's sub-sectors in Poland are the emissions from iron ore sintering plants, steel production in electric furnaces and the secondary copper production processes. However, consideration must be given to the fact that the emission values measured at the electric arc furnaces are related to single installations, therefore they cannot be regarded as representative for the entire emission from this sub-sector. For this reason the need for further efforts aimed at the improvement of the measuring methods to obtain values reflecting the true ones, especially when only minimum APC systems or none are used.

3. Results obtained from measurements at the secondary aluminium processing plants showing low emission levels confirm, that those plants apply BAT. For plants equipped with less sophisticated APC systems and using more outdated technologies such measurements have not been carried out.

4. Because of the fragmentary range of measurements, the results obtained cannot be applied for the development of acceptable emission standards for this sector.

5. Obtained emission factors obtained under the Polish-Danish project – the only ones available in our country - will be used for national emission inventory purposes to update the factors proposed by the Toolkit. However further development of national factors for this sector is desired.

6. It is necessary to continue the activities aiming at dioxin and furan emission reduction from the metallurgical sector, including emission measurements. This, however, depends on the possibilities for gathering sufficient financial resources.

Basing on dioxin and furan measurements results performed at installations of the metallurgical industry and the environmental reviews accomplished at several selected facilities the following recommendations, concerning reduction of formation or emission may be drawn:

1. Iron ore sintering plant:
    - *Primary measures* – use of clean (free of oil) charge or preliminary firing of oils from the rolling scale;
    - *Secondary measures* – recirculation off gases from the sinter strand to the sintering process, to the maximum extent, as allowed by technical.

2. Steel plant with electric arc furnace:
    - *Primary measures* – apply less polluted or pre-treated scrap in the charge (a measure only sporadically applied)
    - *Secondary measures* – apply the flue gas afterburning chamber, rapid cooling of off gases (for instance by application of injection a chamber), apply highly effective fabric filters to trap the dusts and possibly blow active carbon dust or lignite.

3. Hot-blast cupola furnace plant:
    - *Primary measures* – apply cupola flue gasses for blast heating and scrap preheating together with preliminary scrap cleaning, for instance by heating up;
    - *Secondary measures* – after-burn flue gases and capture dust by fabric filters.

4. Secondary aluminium production in induction furnace:
    - *Primary measures* – apply preliminary processing of charge materials, for instance firing of oils and varnish coating;
    - *Secondary measures* – include efficient methods of flue gas cleaning, such as dry sorption, for instance applying a mixture of slaked lime and lignite dust followed by fabric filter or wet scrubber cleaning, like a packed lignite bed.

5. Primary zinc production from zinc cathodes:
    - since the emission of dioxins and furans found in measurements performed was below 0.1 ng I-TEQ/Nm$^3$ no additional measures for their reduction are necessary.

The above recommendations and conclusions, significant in terms of the requirements of environmental protection, having in mind the technical and economic aspects, can also be useful for the implementation in iron and steel metallurgical industry restructuring and privatisation programme and for the preparation of a reconstruction scheme for the secondary aluminium production plants. Implementation of the latter should, among others, allow introduction of less environmentally harmful means in the process of aluminium refining as compared with the chloroorganic compounds still applied in some works.

## 6.1. Follow-up activities

The results obtained within the framework of this “Reduction of Dioxin Emission from the Metallurgical Sector in Poland” Polish-Danish joint project allowed for a preliminary recognition of the existing situation in the Polish metallurgical industry due to its limited scope and lack of the necessary data. The following indications for further activities aiming at reduction of PCDD/PCDF emissions from the subject sector could be formulated:

1. **Evaluation of opportunities for control of PCDD/PCDF emission from the casting industry (including production of pig iron, cast steel, copper alloys, aluminium, magnesium alloys).** Within this activity a systematic measurement of PCDD/PCDF emissions in the discussed industry is proposed together with the assessment of opportunities and methods for their reduction in cases of excessive releases. The BREF reference document recommends the acceptable level of PCDD/PCDF emission at 0.1 ng/ $Nm^3$ for casting houses (there are no such clear and stringent recommendations for other sub-sectors of metallurgy). Depending on the availability of funds the extension of the project scope by a capital development study, including choice of optimal methods for air protection and the construction of pilot installations for flue gas cleaning at selected plants.
   There are about 400 foundries in operation in Poland, of which 100 are obliged to obtain the Integrated Pollution Control Certificate. In general, the technical standards in the casting houses, particularly with reference to flue gas cleaning installations, are quite low. The Polish industry shows considerable delays in comparison with highly developed EU countries. Improvement of that situation requires substantial capital outlays. Most of the foundries are in Polish owners’ hands (state owned, stock companies or limited liability companies). Commonly the enterprises lack funds for new capital projects and therefore the will not be able to pay the costly PCDD/PCDF emission measurements, the results of which are indispensable for the preparation of the IPCC application.

2. **Further verification of PCDD/PCDF emission factors at the metallurgical sector, particularly in aluminium metallurgy, based on measurements performed on a larger group of installations.** Change of technologies and modernisation of production plants are causing a significant impact on the values of emission factors. Therefore, these factors must be periodically verified. This is appropriate particularly for the large emission sources. It would be useful – but very costly - to carry out regular measurements (for instance every 2–3 years) in the sub-sectors with a large share in the total national emission and to take measurements after each change of technology, which could affect the emission levels. It is advisable to give priority to measurements of dioxin and furan emission from secondary aluminium production followed by measurements at the steel production on oxygen furnaces and the production of iron ore sinters. This is justified even more by the fact that the values obtained so far from domestic investigations are considerably different from those proposed by the Toolkit. Therefore a detailed review of the technologies applied by these industries, together with the assessment of opportunities for application of compounds less burdensome to the environment in processes of aluminium refining than the chloroorganic compounds still used by some facilities, in the perspective of selecting a wider, more representative spectrum of installations to be monitored. The issue of determining installations (apart from the large factories), concerning the agreement for performance of measurements and access to reliable information on technological process as well as inconveniences arising during the measuring activities remains as usual to be solved. The results of measurements obtained will be used to specify

precisely the values of emission factors used for national inventories, the results of which are or shall be required for reporting purposes by the EU, UN ECE and UNEP.

3. **Establishment of a system of gathering information on applied metallurgical technologies** (including particularly in small and medium plants), including, *inter alia*, the following data:
    - type of installation,
    - efficiency and quality of environmental protection equipment,
    - production level.

This report on the "Opportunities for Reduction of Dioxin Emissions from the Metallurgical Sector in Poland" joint Polish-Danish project has been supplemented by comments and suggestions of the Project Steering Committee, COWI experts and recommendations and conclusions of the seminar (Warsaw, 21.03.2005). The final version of the report will be submitted to the Ministry for Economic Affairs and Labour and to the Ministry of the Environment. After its endorsement the report will be distributed to the interested production plants covered by the project activities and to the participants of the seminar. Both language versions, together with the relevant documentation, will be accessible on the website of the Institute of Environmental Protection: http://ks.ios.edu.pl.

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# EXPLANATION OF SELECTED ABBREVIATIONS USED IN THE REPORT

| **Abbreviation** | **Explanation** |
|---|---|
| APCS | Air Pollution Control Systems |
| BAT | Best Available Technique |
| BEP | Best Environmental Practice |
| BF | Blast Furnace |
| BOF | Basic Oxygen Furnace |
| DANCEE | Danish Cooperation for Environment in Eastern Europe |
| DEPA | Danish Environmental Protection Agency |
| EAF | Electric Arc Furnace |
| EMEP | Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe |
| GUS | Main Statistical Office<br>*Glowny Urzad Statystyczny* |
| IPCC | Intergovernmental Panel on Climate Change |
| IPPC | Integrated Pollution Prevention and Control |
| I-TEF | International Toxicity Equivalency Factor |
| I-TEQ | International Toxic Equivalent |
| IUPAC | International Union of Pure and Applied Chemistry |
| MoE | Ministry of the Environment |
| NFR | Nomenclature for Reporting |
| POPs | Persistent Organic Pollutants |
| SNAP97 | Selected Nomenclature for Air Pollution |
| TEF | Toxicity Equivalency Factor established by WHO/IPCS working group |
| TEQ | Toxic Equivalent |
| UNEP Chemicals | UNEP Chemicals' Programme |
| UN ECE | Economic Commission for Europe of the United Nations |
| AGH-UST | *AGH University of Science and Technology in Cracow* |
| WHO | World Health Organization |
| WHO-TEQ | Toxic Equivalent calculated from TEF |

Annex 1.

# EXAMPLE OF THE DIOXIN EMISSION MEASUREMENT REPORT

# Report on dioxin emissions measurements

according to requirements set by the European Standard EN 1948, 1-3

## Name and Type of measured plant :

**19_Sinter Plant for iron ore**

| | | |
|---|---|---|
| *Sampling No.* | *Date of sampling* | *Internal Sample Code* |
| 0608XX_288 | **August, 06 2004** | **C1/IChiTN/2004/D288** |

## Author of this report: ADAM GROCHOWALSKI

| | | | |
|---|---|---|---|
| *name* | *phone* | *fax* | *email* |
| Adam Grochowalski | 48602600878 | 48126282036 | agrochow@chemia.pk.edu.pl |

## Institute that carried out sampling: EMIPRO sp z o.o. Kraków, Poland

*responsible technician:*

| | | | |
|---|---|---|---|
| *name* | *phone* | *fax* | *email* |
| Jaroslaw Kulig | 48606229279 | 482882959 | jkulig@dioksyny.com.pl |

## Institute that carried out clean-up/analysis Cracow University of Technology

*responsible technician:*

| | | | |
|---|---|---|---|
| *name* | *phone* | *fax* | *email* |
| Malgorzata Wegiel | 48126282713 | 48126282036 | mwegiel@chemia.pk.edu.pl |

## Plant operator: CONF *if confidential please write "conf."*

*responsible technician:*

| | | | |
|---|---|---|---|
| *name* | *phone* | *fax* | *email* |
| conf | conf | conf | conf |

## Statement:

**The European Standards EN 1948, 1-3 were followed entirely**

(authors signature)

**The European Standards EN 1948, 1-3 could not be followed regarding...**

| | |
|---|---|
| **... following steps...** | **because...** |
| GC-MS was realised as GC-MS/MS method on Finnigan GCQ plus systems | |
| | |
| | |

## Plant operation conditions during measurement

### General operation conditions

|  |  |  |  |  |
|---|---|---|---|---|
| Plant was operated continuously (yes/no) | Yes |  |  |  |
| Plant was operated intermittently (yes/no) | No |  |  |  |

In case of intermittent operation:

|  |  |  |  |  |
|---|---|---|---|---|
| duration of operation cycles ranged between |  | hours:min and |  | hours:min |
| duration of plant operation interrupts ranged between |  | hours:min and |  | hours:min |

In case these conditions are untypical for the plant, please explain:

Plant operates continuously - sinter area - 312 m2

### Input materials (during measurement!)

| Number | name | Input [tons/hour] | composition | remark |
|---|---|---|---|---|
| 1 | Fe | 362,5 | mixed iron ore |  |
|  | CaCO3 | 34,3 | limestone |  |
|  | Ca,MgCO3 | 5,6 | dolomite |  |
|  | C | ca 20 | Coke |  |
|  | gas | 1710 Nm3/h | natural gas + process gas |  |
|  |  |  |  |  |
|  |  |  |  |  |

## Flue gas components and density

| **Measurement of flue gas components** | | | Remarks |
|---|---|---|---|
| $N_2$ (dry gas) | 79,06 | % (v/v) | |
| $O_2$ (dry gas) | 17,4 | % (v/v) | |
| $CO_2$ (dry gas) | 2,4 | % (v/v) | |
| Ar | | % (v/v) | |
| CO (dry gas, optional)) | 1,09 | % (v/v) | |
| $SO_2$ (dry gas, optional) | 0,05 | % (v/v) | |
| *other compounds (please fill in)* | | % (v/v) | *insert standard density in table below!* |
| *other compounds (please fill in)* | | % (v/v) | *insert standard density in table below!* |
| dust (if known) | | mg/m³ | *gravimetrically (for wet gas in measuring conditions)* |
| Moisture (absolute water content) | 0,017 | kg/m³ | |
| static pressure in stack | -0,1 | kPa | *insert differential pressure; = p(stack)-p(atmos); e.g. -0.3* |
| atmospheric pressure | 98,8 | kPa | |
| mean gas temperature | | °C | *insert here in case no temperature profile is measured* |
| *...used for t-correction:* | 110 | °C | *value is selected automatically (either mean of profile measurement or mean gas temperature given above)* |

## Calculation of gas density

| | |
|---|---|
| **T,p- correction term** | **0,694** |
| **Humidity correction term** | **1,021** |

| **compound** | **standard density kg/m³** | **volume fraction Total = 0.01** | **partial density kg/m³** |
|---|---|---|---|
| **$N_2$** | **1,251** | **0,7906** | **0,989** |
| **$O_2$** | **1,429** | **0,174** | **0,249** |
| **$CO_2$** | **1,977** | **0,024** | **0,047** |
| **Ar** | **1,78** | | |
| **CO** | **1,251** | **0,0109** | **0,014** |
| **$SO_2$** | **2,987** | **0,0005** | **0,001** |
| | | | |
| | | | |
| **density, dry, standard cond.** | | | **1,300** |
| **density, wet, standard cond.** | | | **1,290** |
| **density, wet, operation cond.** | | | **0,896** |

**End of table "Flue gas components & density"**

Note: Number and location of sampling points should be determined according to ISO 9096:1992, Annex B;
Use the values for Ki tabled therin

| | | | |
|---|---|---|---|
| Stack height | 250 | m | |
| Long side of stack $L_1$ | 4,3 | m | |
| Short side of stack $L_2$ | 4 | m | |
| Stack cross section | 17,20 | m² | |
| number of sampling points | | | |
| *recommended:* | 20 | | |
| actual: | 16 | | |
| Pitot correction factor | 1,00 | | *(=1 for standard Pitot tube = Prandtl tube)* |
| static pressure in stack | -15,90 | kPa | *differential pressure; = p(stack)-p(atmos)* |
| atmospheric pressure | 97,3 | kPa | |

| Sampling point No. | distance from...[mm] ...$L_1$ | ...$L_2$ | weight factor - | dyn. pressure kPa | gas velocity [m/s] calculated from p | directly measured | temperature [°C] measured | weighted |
|---|---|---|---|---|---|---|---|---|
| | **overwrite with actual values!** | | | | | | | |
| 1 | 540 | 500 | 1 | 0,075 | 12,9 | 12,9 | 110 | 110 |
| 2 | 1610 | 500 | 1 | 0,08 | 13,4 | 13,1 | 110 | 110 |
| 3 | 2690 | 500 | 1 | 0,08 | 13,4 | 13,8 | 110 | 110 |
| 4 | 3760 | 500 | 1 | 0,09 | 14,2 | 14,4 | 110 | 110 |
| 5 | 540 | 1500 | 1 | 0,075 | 12,9 | 12,9 | 110 | 110 |
| 6 | 1610 | 1500 | 1 | 0,08 | 13,4 | 13,2 | 110 | 110 |
| 7 | 2690 | 1500 | 1 | 0,08 | 13,4 | 13,7 | 110 | |
| 8 | 3760 | 1500 | 1 | 0,09 | 14,2 | 14,3 | 110 | |
| 9 | 540 | 2500 | 1 | 0,075 | 12,9 | 12,9 | 110 | 110 |
| 10 | 1610 | 2500 | 1 | 0,08 | 13,4 | 13,4 | 110 | 110 |
| | | | | | | | | |
| 11 | 2690 | 2500 | 1 | 0,09 | 14,2 | 14 | 110 | 110 |
| 12 | 3760 | 2500 | 1 | 0,09 | 14,2 | 14,5 | 110 | 110 |
| 13 | 540 | 3500 | 1 | 0,075 | 12,9 | 13,1 | 110 | 110 |
| 14 | 1610 | 3500 | 1 | 0,08 | 13,4 | 13,5 | 110 | 110 |
| 15 | 2690 | 3500 | 1 | 0,09 | 14,2 | 13,9 | 110 | 110 |
| 16 | 3760 | 3500 | 1 | 0,1 | 14,9 | 14,6 | 110 | 110 |
| 17 | | | | | | | | |
| 18 | | | | | | | | |
| 19 | | | | | | | | |
| 20 | | | | | | | | |
| **mean (operation conditions)** | | | | | 13,60967 | 13,6 | | 110 |
| **maximum (operation conditions)** | | | | | 14,9 | 14,6 | | 110 |
| **mean (standard conditions, dry)** | | | | | 9,3 | 9,3 | | |
| **maximum (standard conditions, dry)** | | | | | 10,2 | 9,9 | | |
| **RECTMAX value used for nozzle selection:** | | | | | 10,16 | | | |

Specify method used for direct velocity measurement:

| **Maximum flue gas flow rate [m³/h]** | | |
|---|---|---|
| **calc. with velocity based on** | **pressure data** | **direct** |
| **volume flow, wet, operation cond.** | **925161** | **904032** |
| **volume flow, wet, standard cond.** | **642523** | **627849** |
| **volume flow, dry, standard cond.** | **629219** | **614849** |

**End of table "Rectangular Stack Profile"**

# Nozzle&Sampling Rate

| | | | |
|---|---|---|---|
| Nozzle selection for... | **Rectangular stack Profile** | | |
| ...maximum flue gas velocity | **10,2** | **m/s** | standard conditions, derived from measured maximum flow rate |
| ...maximum sampling flow rate: | **2** | **$m^3/h$** | standard conditions, as given by the equipment used |

| maximum nozzle diameter [mm] | chosen nozzle [mm] | nozzle cross section [$m^2$] |
|---|---|---|
| 7,2 | 8,0 | 0,00005 |

| | | |
|---|---|---|
| Conversion factor | **0,123** | factor used to determine sampling flow rate at standard conditions<br>from measured flue gas velocity at the sampling points in stack |

Chosen sampling flow rate (at standard conditions!):

**First sampling line**

| sampling point No | flow rate [$m^3/h$] | | | remarks |
|---|---|---|---|---|
| | recommended | actually chosen *) | isokinetic? | |
| 1 | 1,592 | 1,600 | yes | |
| 2 | 1,645 | 1,600 | yes | |
| 3 | 1,698 | 1,600 | yes | |
| 4 | 1,772 | 1,600 | yes | |
| 5 | 1,592 | 1,500 | yes | |
| 6 | 1,645 | 1,500 | yes | |
| 7 | 1,686 | 1,500 | no | |
| 8 | 1,760 | 1,500 | no | |
| 9 | 1,592 | 1,500 | yes | |
| 10 | 1,649 | 1,500 | yes | |
| **Second sampling line** | | | | |
| 11 | 1,74 | 1,600 | yes | |

## Sampling Protocol

| | | | |
|---|---|---|---|
| **Sampling location at duct:** | 20,72 m length of stright canal line before sampling port of rectangular 4,3 x 4 m duct | | |
| **Sampling Train** | | | |
| Name of method | Filter/condenser method | | |
| Scheme | separately attached (see - Sampling Apparatus Scheme) | | |
| Sampling flow rate measurement with | *specify instrument, e.g. orifice/pressure or rotameter* | | |
| | value | dimension | Remarks |
| Probe diameter | 40 | mm | |
| Filter diameter | 100 | mm | |
| Filter efficiency (%, manufacturer's data) | 99,5 | % | For 0,2 micrometer p.m. particles |
| Ab/adsorbent (type) | PU foam | | Supelco Precleaned PU-Foam |
| Ab/adsorbent, amount | 10g | g | |
| *In case of flow division:* | | | |
| Mean flow rate through filter | | m$^3$/h | |
| Mean flow rate through Ab/adsorbent | | m$^3$/h | |
| **Sampling data** | value | dimension | Remarks |
| Leak check by plugged nozzle: | | | |
| Lowest pressure when pump on: | 65 | kPa | |
| Rate of pressure change when pump off | 10 | kPa/min | |
| Maximum temperature at filter | 160 | °C | |
| Maximum temperature at condenser | 24 | °C | |
| Maximum temperature at Ab/adsorbent | 24 | °C | |
| Static pressure difference at gas meter | -25,3 | kPa | |
| Mean temperature at gas meter | 32 | °C | |

| **Sampling volume...** | value | dimension | Remarks |
|---|---|---|---|
| ...at gas meter conditions (dry gas!) | 14,0440 | m$^3$ | *in case wet gas is measured please correct for moisture content* |
| ...at standard conditions (dry gas) | 9,121 | m$^3$ | |
| ...calc. from mean sample flow rate and sampling time | 9,596 | m$^3$ | |
| Reference O2 | 11 | % (v/v) | |
| ...at standard cond.& reference O2 | 3,248 | m$^3$ | |

| **Spiking** | | | | |
|---|---|---|---|---|
| Compartment spiked | yes | | | Remarks |
| Sampling standard solution | concentration | applied volume | amount | |
| C-13 congeners: | [µg/l] | [µl] | pg | |
| 1,2,3,7,8-PeCDF | 10 | 100 | 1000,0 | |
| 1,2,3,7,8,9-HxCDF | 10 | 100 | 1000,0 | |
| 1,2,3,4,7,8,9-HpCDF | 20 | 100 | 2000,0 | |

| **Actual sampling period** | Start [hh:mm] | End [hh:mm] | Period [hh:mm] | Remarks |
|---|---|---|---|---|
| overall sampling period | 12:12 | 18:19 | 06:07 | |
| Interruption period 1 | | | | |
| Interruption period 2 | | | | |
| Interruption period 3 | | | | |
| **Effective duration of sampling** | | | **06:07** | |
| **Sampling time [h]** | | | **6,12** | |

# Extraction/Clean-up

## Sample treatment after the measurement campaign

| | | | |
|---|---|---|---|
| sample storage location | Laboratory of Trace Organic Analysis Cracow University of Technology (light protected) | | |
| temperature at storage | fridge, ca 6 | °c | |
| | dd:mm:yy | hh:mm | |
| start of storage (date, time) | 9 08 2004 | 20:30 | by sampling group |
| end of storage (date, time) | 10 08 2004 | 09:45 | after delivery by sampling company |
| addition of extraction standard | 11 08 2004 | 08:15 | short description of extraction/clean-up procedure: |
| start of extraction procedure | 1 08 2004 | 09:00 | Soxhlet-toluene, sulphuric acid, carbon column, alumina |
| addition of syringe standard | 17 08 2004 | 09:30 | |
| time of injection | 17 08 2004 | 21:15 | |

## Addition of Extraction Standards to Sample Compartments:

| $^{13}C_{12}$-Congeners | Concentration | Volume added to sample compartment [µl] : | | | | | total amount |
|---|---|---|---|---|---|---|---|
| | [µg/l] | condensate | filter | adsorbent | ... | ... | [pg] |
| 2,3,7,8-TCDF | 4,8 | 50 | 50 | 50 | | | 720 |
| 2,3,7,8-TCDD | 4,8 | 50 | 50 | 50 | | | 720 |
| 2,3,4,7,8-PeCDF | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,7,8-PeCDD | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,4,7,8-HxCDF | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,6,7,8-HxCDF | 4,8 | 50 | 50 | 50 | | | 720 |
| 2,3,4,6,7,8-HxCDF | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,4,7,8-HxCDD | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,6,7,8-HxCDD | 4,8 | 50 | 50 | 50 | | | 720 |
| 1,2,3,4,6,7,8-HpCDF | 9,6 | 50 | 50 | 50 | | | 1440 |
| 1,2,3,4,6,7,8-HpCDD | 9,6 | 50 | 50 | 50 | | | 1440 |
| OCDF | | | | | | | |
| OCDD | 9,6 | 50 | 50 | 50 | | | 1440 |

## Addition of syringe standard to concentrated sample extract

volume of sample extract: 20 µl

| $^{13}C_{12}$-Congeners | Concentration | volume applied | amount |
|---|---|---|---|
| | [µg/l] | [µl] | |
| 1,2,3,4-TCDD | 200 | 2 | 400 |
| 1,2,3,7,8,9-HxCDD | 200 | 2 | 400 |

**End of table "Extraction & Clean.up"**

## Analytical Results

| | | | | | | |
|---|---|---|---|---|---|---|
| Equipment used (columns, mass spec): | DB-5MS 0,25 mm 60m, DB-17 30m 0,25mm Finnigan GCQ GC-MS/MS CID mode | | | | | |
| Flue gas sample No. | | **C1/IChiTN/2004/D288** | | | | |
| Date of sampling | | **August, 06 2004** | | | | |
| Flue gas sample volume [$m^3$] | | 9,121 | dry gas at standard t, p and operational $O_2$/$CO_2$) | | | |
| | | | | | | |
| | PCDD/PCDF in flue gas *) | | | ng I-TEQ/$m^3$ | | |
| | indicator 2) | [ng/sample] | [ng/$m^3$] | incl. DL | incl. 0.5 DL | excl. DL |
| **Dioxins:** | | | | | | |
| Sum of TCDD 1) | | | | | | |
| Sum of PeCDD 1) | | | | | | |
| Sum of HxCDD 1) | | | | | | |
| Sum of HpCDD 1) | | | | | | |
| OCDD | | 3,38 | 0,37056138 | 0,0004 | 0,0004 | 0,0004 |
| *Total PCDD* | | | 0,37056138 | | | |
| | | | | | | |
| 2,3,7,8-TCDD | | 0,21 | 0,023023044 | 0,0230 | 0,0230 | 0,0230 |
| 1,2,3,7,8-PeCDD | | 0,46 | 0,05043143 | 0,0252 | 0,0252 | 0,0252 |
| 1,2,3,4,7,8 HxCDD | | 1,73 | 0,189666032 | 0,0190 | 0,0190 | 0,0190 |
| 1,2,3,6,7,8-HxCDD | | 1,2 | 0,131560253 | 0,0132 | 0,0132 | 0,0132 |
| 1,2,3,7,8,9-HxCDD | | 1,76 | 0,192955038 | 0,0193 | 0,0193 | 0,0193 |
| 1,2,3,4,6,7,8-HpCDD | | 6,2 | 0,679727975 | 0,0068 | 0,0068 | 0,0068 |
| Sum of TCDF 1) | | | | | | |
| Sum of PeCDF 1) | | | | | | |
| Sum of HxCDF 1) | | | | | | |
| Sum of HpCDF 1) | | | | | | |
| OCDF | | 6,80 | 0,745508102 | 0,0007 | 0,0007 | 0,0007 |
| *Total PCDF* | | | 0,745508102 | | | |
| | | | | | | |
| 2,3,7,8-TCDF | | 5,79 | 0,634778222 | 0,0635 | 0,0635 | 0,0635 |
| 1,2,3,7,8-/1,2,3,4,8-PeCDF | | 4,24 | 0,464846228 | 0,0232 | 0,0232 | 0,0232 |
| 2,3,4,7,8-PeCDF | | 8,86 | 0,971353204 | 0,4857 | 0,4857 | 0,4857 |
| 1,2,3,4,7,8-/1,2,3,4,7,9- HxCDF | | 5,89 | 0,645741577 | 0,0646 | 0,0646 | 0,0646 |
| 1,2,3,6,7,8-HxCDF | | 8,23 | 0,902284071 | 0,0902 | 0,0902 | 0,0902 |
| 1,2,3,7,8,9-HxCDF | | 14,22 | 1,558989002 | 0,1559 | 0,1559 | 0,1559 |
| 2,3,4,6,7,8-HxCDF | | 0,74 | 0,081128823 | 0,0081 | 0,0081 | 0,0081 |
| 1,2,3,4,6,7,8-HpCDF | | 43,46 | 4,76467384 | 0,0476 | 0,0476 | 0,0476 |
| 1,2,3,4,7,8,9-HpCDF | | 6,82 | 0,747700773 | 0,0075 | 0,0075 | 0,0075 |
| **Dioxins and Furans:** | | | | | | |
| *Total PCDD+PCDF* | | | 1,116069482 | | | |
| International TEQ - for operational O2 | | | | **1,054** | **1,054** | **1,054** |

Annex 2.

# SUPPLEMENTARY DATA CONCERNING THE INVESTIGATED PROCESSES AND RESULTS OBTAINED AS WELL THE PREVIOUS STUDY RESULTS

Table A. Characterisation of the investigated processes

| No of installation | Source | Input material | Fuel | Process temperature [ºC] | Flue gas cleaning system | Stack height [m] | Operational time [h/year] |
|---|---|---|---|---|---|---|---|
| **Iron and Steel** | | | | | | | |
| 19 | Iron ore sintering plant | Raw iron ore, iron concentrates, dolomite, lime | Blast furnace gas and coke | 1 280-1 350 | Electrostatic precipitator | 150 | 7 600 |
| 02 | Iron ore sintering plant | Raw iron ore, iron concentrates, granulated and powdered, dolomite, lime, and other additive | Blast furnace gas, coke and coke gas | 1 250-1 400 | Electrostatic precipitator. 20% of total volume of exhaust gas is recirculated | 82 | 7 450 |
| 16 | Primary iron production - blast furnace | Iron ore, sintered iron ore, coke, limestone | Coke | 1 500-1 600 | Electrostatic precipitator | 30 | 7 043 |
| 17 | Primary and secondary steel production - basic oxygen furnace | Pig iron, steel scrap, lime, oxygen | Fed with liquid iron (1300 ºC), exothermic | 1 400-1 500 | Afterburner, wet scrubber | 80 | 1 654 |
| 18 | Secondary iron production - spheroid and grey iron - gas rotary kiln | Steel scrap, oxygen | Natural gas | 1 450-1 500 | Pulsating fabric filters in baghouse | 80 | 7 000 |
| 20 | Secondary steel production - steel scrap melting in electric arc furnace*3 | Steel scrap, CaO, coke, dolomite, recirculated dust | Electric power | 1 450-1 500 | Pulsating polypropylene fabric filters in baghouse | 35 | 7 000 |
| 15 | Secondary steel production - steel scrap melting in electric arc furnace *1 | Steel scrap, iron ore, CaO, carbon brickets | Electric power | 1 450-1 500 | Fabric filters in baghouse (primary off-gas not measured) | 33 | 7 250 |
| 01 | Hot air cupola foundry of spheroid and cast iron | Iron scrap,<br>steel scrap,<br>limestone (CaCO3)coke | Electric power | 1 550-1 550 | Fabric filter in baghouse | 16 | 3 520 |
| 07 | Hot air cupola foundry of cast iron *2 | Pig iron, iron scraps, steel scraps, phosphorous scraps, iron-phosphorous, iron-manganium, iron-silica, limestone, coke | Electric power | 1 400-1 500 | Double wet scrubbing system (samples taken upstream the scrubbing system) | 17 | 3 120 |
| 08 | Electric arc foundry of cast steel | Steel scrap, iron ore, CaO, carbon brickets | Electric power | 1 570-1 650 | Fabric filters in baghouse | 50 | 3 200 |

| No of installation | Source | Input material | Fuel | Process temperature [ºC] | Flue gas cleaning system | Stack height [m] | Operational time [h/year] |
|---|---|---|---|---|---|---|---|
| **Non-ferrous** | | | | | | | |
| 04 | Primary copper production from concentrate with $H_2SO_4$ production | Cu raw ore concentrate and "lug posulfitowy" | ? | ? | Firstly, de-dusting in fabric filter baghouses. Exhaust gases from Solinex process are cooled in cooling tower down-to 22 ºC. Cool gas is directed to absorption tower for $SO_2$ absorption followed by washing with water in washing tower. | 150 | 8 232 |
| 06 | Primary copper production from concentrate with $H_2SO_4$ production | Solid Cu concentrated ore, dust from recycling, wastes from desulphurisation plant, oil fuel, oxygen | Oil | ? | Wet electrofilters and demisters. | 150 | 6 500 |
| 05 | Primary copper production - copper slag recycling | Copper slag, coke, melted liquefied slag, limestone | Electric power | 1 350 | Fabric filter in bag-house | 120 | 5 000 |
| 03 | Copper scrap melting | Cu concentrate from raw ore and industrial copper waste, waste sulphite liquor | ? | ? | Pulsating fabric filter in baghouse | 33 | 6 000 |
| 09 | Secondary aluminium production - aluminium scrap melting | Aluminium scrap - mainly cutting from production of sheets | Electric power | 715 | No cleaning system | 20 | 6 000 |
| 10 | Secondary aluminium production - aluminium scrap and cans melting | Aluminium cans | Electric power | Preheated: 400 - 550<br>Melted: 720 - 750 | Afterburner (1100 ºC, 2 s), quenching and cooling in heat exchanger Active carbon filter | 14 | 7 000 |
| 11 | Secondary aluminium production - aluminium scrap melting | Aluminium scrap both form prod. processes and old scrap | Natural gas | 750-760 | Fabric filter in baghouse | 20 | 5 000 |
| 12 | Secondary aluminium production - aluminium scrap and cans melting | Aluminium scrap, cables, cans | Electric power | 750-800 | Wet scrubber | 21 | 6 500 |
| 13 | Primary zinc production from ZnS ore with $H_2SO_4$ production | Solid zinc ore, dusts form recycling process, | Exothermic natural gas for start up | 600-800 | Cyclones, wet scrubbers for $H_2SO_4$ production and $SO_2$ removal. Wet electrofilters and demisters | 120 | 7 000 |

| No of installation | Source | Input material | Fuel | Process temperature [ºC] | Flue gas cleaning system | Stack height [m] | Operational time [h/year] |
|---|---|---|---|---|---|---|---|
| 14 | Zinc casting from zinc cathodes | Zinc cathodes from electrolytically zinc recovery, $NH_4Cl$ as a solid crystals | Electric power | 600 | Fabric filter in baghouse of 98% de-dusting efficiency. | 30 | 6 500 |
| **Previous studies (2003)** | | | | | | | |
| 1 | Iron ore sintering plant * | Raw iron ore, iron concentrates, dolomite, lime | Blast furnace gas, coke and coke gas | 1 250-1 400 | Electrostatic precipitator | 82 | ca. 6 000 |
| 2 | Iron ore sintering plant * | | | | | | |
| 3 | Zinc oxide ore sintering* | Raw zinc oxide of different origin | Natural gas | 1 300-1 350 | Balloon chamber, cyclones, bag-house | 86 | 1 370 (sintered ZnO) 730 (zinc/lead oxide |
| 4 | Secondary Zn production - rotary kiln* | Zinc-containing wastes and scrap, coke (~40%) | | 1 100-1 250 | Precipitation chamber, cyclones, baghouse | 76 | Ca. 5 500 |
| 5 | Melting of electrolytically produced zinc (same process as 14) * | Raw zinc cathodes from electrolytically zinc recovery | | 540-560 | Baghouse (ZnO powder 98% efficiency) | 30 | Ca. 7 000 |

*1 Measurement only include off-gas from the hood above the furnace (secondary off-gas); measurement of primary off-gas from the furnace was not possible

*2 Measured upstream the APCS - measurements downstream the APCS was not possible

*3 Unclear whether the measurement include primary off-gas

* Source: Pulles, T, H. Kok, U. Quass, C. Juery and J. Matejovicova. 2004. *Dioxin emission in Candidate Countries.* TNO, IUTA, IOW and SHMU for the European Commission. http://w3.shmu.sk/sms/dioxin-BA/documents.html

Table B. PCDD/F and PCB emissions and emission factors for the investigated installations

| No of installation | Source | PCDD/F emission | | | | PCDD/F emission | PCB emission | PCB % of total |
|---|---|---|---|---|---|---|---|---|
| | | ng I-TEQ/Nm$^3$ at operational $O_2$ | µg I-TEQ/h | g I-TEQ /year | µg I-TEQ /Mg product | ng WHO-TEQ/Nm$^3$ at operational $O_2$ | | |
| | | | | **Iron and Steel** | | | | |
| 19 | Iron ore sintering plant | 1.054 | 542.4 | 4.123 | 1.47 | 1.0539 | 0.0464 | 4 |
| 02 | Iron ore sintering plant | 1.272 | 197,8 | 1.474 | 1.10 | 1.2714 | 0.0481 | 4 |
| 16 | Primary iron production - blast furnace | 0.003 | 2.1 | 0.015 | 0.01 | 0.0029 | 0.0002 | 6 |
| 17 | Primary and secondary steel production - basic oxygen furnace | 0.018 | 2.4 | 0.004 | 0.02 | 0.0177 | 0.0008 | 4 |
| 18 | Secondary iron production - spheroid and grey iron - gas rotary kiln | 0.002 | 0.02 | 0.0001 | 0.02 | 0.0024 | 0.0011 | 31 |
| 20 | Secondary steel production - steel scrap melting in electric arc furnace *3 | 0.054 | 93.6 | 0.655 | 0.62 | 0.0539 | 0.0272 | 34 |
| 15 | Secondary steel production - steel scrap melting in electric arc furnace *1 | 0.004 | 2.7 | 0.020 | 0.02 | 0.0035 | 0.0019 | 35 |
| 01 | Hot air cupola foundry of spheroid and cast iron | 0.024 | 0.4 | 0.002 | 0.06 | 0.0241 | 0.0004 | 2 |
| 07 | Hot air cupola foundry of cast iron *2 | 1.176 | 14.4 | 0.045 | 4,11 | 1.1757 | 0.1610 | 12 |
| 08 | Electric arc foundry of cast steel | 0.004 | 0.6 | 0.002 | 0.03 | 0.0042 | 0.0025 | 37 |
| | | | | **Non-ferrous** | | | | |
| 04 | Primary copper production from concentrate with $H_2SO_4$ production | 0.010 | 1.6 | 0.013 | 0.005 | 0.0101 | 0.0009 | 8 |
| 06 | Primary copper production from concentrate with $H_2SO_4$ production | 0.003 | 0.2 | 0.002 | 0.002 | 0.0028 | 0.0002 | 7 |
| 05 | Primary copper production - copper slag recycling | 0.003 | 0.4 | 0.002 | 0.004 | 0.0025 | 0.0004 | 14 |
| 03 | Copper scrap melting | 0.077 | 2.0 | 0.008 | 0.007 | 0.0774 | 0.0009 | 1 |
| 09 | Secondary aluminium production - aluminium scrap melting | 0.591 | 13.0 | 0.078 | 8.65 | 0.5809 | 0.0546 | 9 |
| 10 | Secondary aluminium production - aluminium scrap and cans melting | 0.031 | 0.2 | 0.002 | 0.34 | 0.0314 | 0.0034 | 10 |
| 11 | Secondary aluminium production - aluminium scrap melting | 0.126 | 4.2 | 0.021 | 1.69 | 0.1259 | 0.0115 | 8 |
| 12 | Secondary aluminium production - aluminium scrap and cans melting | 0.119 | 0.6 | 0.004 | 3.05 | 0.1185 | 0.0086 | 7 |
| 13 | Primary zinc production from ZnS ore with $H_2SO_4$ production | 0.018 | 0.2 | 0.001 | 0.02 | 0.0175 | 0.0002 | 1 |
| 14 | Zinc casting from zinc cathodes | 0.006 | 0.2 | 0.001 | 0.02 | 0.0060 | 0.0003 | 5 |

| No of installation | Source | PCDD/F emission | | | | PCDD/F emission | PCB emission | PCB % of total |
|---|---|---|---|---|---|---|---|---|
| | | ng I-TEQ/Nm$^3$ at operational $O_2$ | µg I-TEQ/h | g I-TEQ /year | µg I-TEQ /Mg product | ng WHO-TEQ/Nm$^3$ at operational $O_2$ | | |
| **Previous studies (2003)** | | | | | | | | |
| 1 | Iron ore sintering plant *5 | 0.363 | | | 0.43 | | | |
| 2 | Iron ore sintering plant *5 | 1.600 | | | 2.2-4.3 | | | |
| 3 | Zinc oxide ore sintering - hot briquetting*5 | 7.290 | | | 110 | | | |
| 4 | Secondary Zn Production - rotary kiln*5 | 3.660 | | | 130 | | | |
| 5 | Melting of electrolytically produced zinc (same process as 14) *5 | 0.020 | | | 0.04 | | | |

*1 Measurement only include off-gas from the hood above the furnace (secondary off-gas); measurement of primary off-gas from the furnace was not possible

*2 Measured upstream the APCS - measurements downstream the APCS was not possible

*3 Unclear whether the measurement include primary off-gas

*5 Source: Pulles, T, H. Kok, U. Quass, C. Juery and J. Matejovicova. 2004. *Dioxin emission in Candidate Countries.* TNO, IUTA, IOW and SHMU for the European Commission. http://w3.shmu.sk/sms/dioxin-BA/documents.html

Annex 3.

# EXAMPLE OF A FILLED QUESTIONNAIRE FORM USED FOR ENVIRONMENTAL REVIEW ON AN ELECTRIC ARC FURNACE FOR STEEL PRODUCTION

# Introduction

The following registration forms are prepared to be used in the project "Reduction of Dioxin Emission from the Metallurgical Sector in Poland"[1]. The forms are structured in the following way:

| | | |
|---|---|---|
| Form 1 | Coordinates of site and contacts | Contact addresses |
| Form 2 | Process information | Process information relevant for dioxin reduction considerations |
| Form 3 | Summary of input materials and products | Materials input/output information relevant for dioxin reduction considerations |
| Form 4 | Start-up and shutdown procedures | Procedures and durations relevant for dioxin reduction considerations |
| Form 5 | The dioxin measurements | Extracts of the measurement report giving the circumstances and result of the measurement |

*Please be free to add comments/additional data on the forms if you want to supply information that is likely to be of value to a specialist on dioxin reduction.*

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[1] The structure of the forms is inspired by the US EPA Manual for Waste Minimization Opportunity Assessment, but only few of the data fields are actually copied from this source. The contents of the forms are closer to UNEP's PCDD/PCDF Toolkit Questionnaire 2: Category 2 - Ferrous and Non-Ferrous Metal Production.

| | | |
|---|---|---|
| Firm: | **Environmental Review**<br>for reduction of dioxin emission | Prepared by: Mariusz Holtzer |
| Site: | | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 1 of 1 |

**Form**
**1**

# Coordinates of site and contacts and possibly chloride in surrounding air

Operator (firm):

Plant:

Department:

Area:

Street address:

City:

Zip code:

| | | | |
|---|---|---|---|
| Contact: | Responsible for this registration | Responsible for the measurement/analysis | Contact in plant |
| Name: | Mariusz Holtzer | Adam Grochowalski | |
| Title: | Professor | Professor | |
| Organisation: | AGH-UST in Cracow | Cracow University of Technology | |
| Telephone: | +48 12 617 27 56 | + 48 12 628 20 36 | |
| e-mail: | holtzer@agh.edu.pl | agrochow@chemia.pk.edu.pl | |
| Street address: | Reymonta 23 | Warszwska 24 | |
| City: | Cracow | Cracow | |
| Zip code: | 30-059 | 31-155 | |

| | |
|---|---|
| Are there any data on chloride in the surrounding air (e.g. HCl). Possibly from the air/IPPC permit? | if yes, please note the compound, concentration and unit (e.g. HCl, 2 mg/m$^3$): |

| | | |
|---|---|---|
| Firm: | **Environmental Review**<br>for reduction of dioxin emission | Prepared by: Mariusz Holtzer |
| Site: | | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 1 of 4 |

**Form**
**2**

## Process Information

| | | | |
|---|---|---|---|
| Type of plant<br>(make an x in one of the fields to the right) | Sinter | [ ] | |
| | Iron and/or steel | Primary: [ ] | Secondary: [X] |
| | Copper | Primary: [ ] | Secondary: [ ] |
| | Aluminium | Primary: [ ] | Secondary: [ ] |
| | Lead | Primary: [ ] | Secondary: [ ] |
| | Zinc | Primary: [ ] | Secondary: [ ] |
| | Foundry, cast iron | Primary: [ ] | Secondary: [ ] |
| | Foundry, steel iron | Primary: [ ] | Secondary: [ ] |
| | Foundry, Al alloys | Primary: [ ] | Secondary: [ ] |
| | Foundry, Cu alloys | Primary: [ ] | Secondary: [ ] |
| | Other (specify) | Primary: [ ] | Secondary: [ ] |

| | | |
|---|---|---|
| Number of furnaces | | |
| Type of operation | Batch (e.g. 140 Mg per batch) | [X] |
| | Semi-continuous (e.g. 8 hours per day) | [ ] |
| | Continuous (24 hours per day) | [ ] |

| | | |
|---|---|---|
| Type of furnace<br>(make an x in one of the fields to the right) | Blast furnace | [ ] |
| | Cupola, cold blast | [ ] |
| | Cupola, hot blast | [ ] |
| | Induction furnace | [ ] |
| | Basic oxygen furnace (BOF) | [ ] |
| | Electric arc furnace (EAF) | [X] |
| | Rotary kiln | [ ] |
| | Reverberatory | [ ] |
| | Other (please specify) | |

| Firm: | **Environmental Review**<br>for reduction of dioxin emission | Prepared by: Mariusz Holtzer |
|---|---|---|
| Site: | | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 3 of 4 |

**Form**
**2**

## Process Information

| | | |
|---|---|---|
| Type of Air Pollution Control System (APCS) (make an x in one of the fields to the right or none if no APCS) | Electrostatic precipitator | [ ] |
| | Cyclone | [X] |
| | Bag filter | [X] |
| | Wet scrubber | [ ] |
| | Dry scrubber | [ ] |
| | Lime injection | [ ] |
| | NaOH/alkali injection | [ ] |
| | Active carbon/coke injection | [ ] |
| | Active carbon filter | [ ] |
| | Catalytic converter (SCR) | [ ] |
| | Induced or forced draft fan | [ ] |
| | Water quench | [ ] |
| | Other (please specify) | |
| Heat recovery system | Yes [ ] | No [X] |

**Form**
**2**

# Process Information

| | | |
|---|---|---|
| Process diagram | Attach two sketches showing:<br>1. A situation plan with the position of furnaces, APCS etc. with main dimensions;<br>2. A system diagram of the exhaust gas system indicating:<br>• Furnace;<br>• Second chamber/afterburner (if any);<br>• Heat recovery system (if any);<br>• APCS (if any);<br>• Stack;<br>• Ducts connecting the above;<br>• All measuring points of Flow and Temperatures with indications of mean value and (possibly) variance. | |
| | Minimal requirements to measurements: | Value and (possibly) variance: |
| | Temperature in main furnace (°C): | 3 000 |
| | Temperature in second chamber/afterburner (if any, °C): | - |
| | Temperature of gases at entry to APCS (if any, °C): | Max. 60 |
| | Temperature of gases at exit from APCS (if any, °C): | 45 |
| | Stack temperature (°C): | 30 |
| | Flux of exit gases ($m^3/h$): | 1 500 000 |

| | | |
|---|---|---|
| Firm: | **Environmental Review**<br>for reduction of dioxin emission | Prepared by: Mariusz Holtzer |
| Site: | | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 1 of 2 |

**Form**
**3**

# Summary of Input Materials and Products

| Input Materials | | | | |
|---|---|---|---|---|
| Primary Metal ore | 0%: | Composition: | | |
| Secondary Metals | 100%: | Origin: | 10% own steel scrap<br>90% outside steel scrap | |
| | | Process applied to remove paint, plastics etc. | [ ] If yes, which type: | |
| Primary + Secondary | 100 % | = Metal | | |
| Auxiliary Materials e.g. flux | 1. Composition: | Alloy additions and ferroalloys | kg/Mg of Metal: | 16,7 |
| | 2. Composition: | Lime | kg/Mg of Metal: | 50,5 |
| | | Fluorite | | 1,3 |
| | | Carbide | | 0,5 |
| | | Carburise | | 22,0 |

| | | |
|---|---|---|
| Primary fuel | Type: Electric energy | 0,54 MJ/Mg<br>378 000 MJ/a |
| Secondary/alternative fuel | Type- | t/a or %:- |

| | | |
|---|---|---|
| Firm: | **Environmental Review**<br>for reduction of dioxin emission | Prepared by: Mariusz Holtzer |
| Site: | | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 2 of 2 |

**Form**
**3**

## Summary of Input Materials and Products

| | | | |
|---|---|---|---|
| Product | | | |
| Type: | | Composition: | |

| | | |
|---|---|---|
| Annual Operational/ Capacity of the unit where measurements have been performed | t/h (tons per hour) | 100 |
| | h/d (hours per day) | 24 |
| | d/w (days per week) | 6 |
| | t/d (tons per day) | 2 400 |
| | d/a (days per year) | 300 |
| | h/a (hours per year) | 7 000 |
| | t/a (tons per year) | 700 000 |
| Annual Operational/ Capacity<br>for total installation | t/h (tons per hour) | 100 |
| | h/d (hours per day) | 24 |
| | d/w (days per week) | 6 |
| | t/d (tons per day) | 2 400 |
| | d/a (days per year) | 300 |
| | h/a (hours per year) | 7 000 |
| | t/a (tons per year) | 700 000 |

| | | |
|---|---|---|
| Firm: | **Environmental Review** | Prepared by: Mariusz Holtzer |
| Site: | for reduction of dioxin emission | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 1 of 1 |

**Form**
**4**

# Start-up and Shut-down Procedures

| | | |
|---|---|---|
| Start-up | Describe start-up process – sequence of activities (only to be filled in for continuous or semi-continuous processes): | |
| | Duration of start-up (hours: minutes) | |
| | Bypass of APCS during start-up? | [ ] |
| | If yes, what is the duration of the bypass? (hours: minutes) | |

| | | |
|---|---|---|
| Shut-down | Describe shut-down process – sequence of activities (only to be filled in for continuous or semi-continuous processes): | |
| | Duration of shut-down (hours: minutes) | |
| | Bypass of APCS during shut-down? | [ ] |
| | If yes, what is the duration of the bypass? (hours: minutes) | |

**EAF working cycle:**

- Main Charging of scrap - 4 min.
- Melting - 15 min.
- Additional charging of scrap - 4 min
- Melting - 12 min.
- Additional charging of scrap - 4 min
- Melting - 7 min.
- Additional charging of scrap - 4 min
- Melting - 5 min.
- Heating and tapping - 15 min.
- Reparation - 10 min.

**Σ 80 min.**

| | | |
|---|---|---|
| Firm: | **Environmental Review** | Prepared by: Mariusz Holtzer |
| Site: | for reduction of dioxin emission | Checked by: Per Ponsaing |
| Date: 29-10-2004 | | Page 1 of 2 |

**Form**

**5**

# The Dioxin Measurement

| | | |
|---|---|---|
| The following data are extracts of Report on Dioxin Emissions Measurements | | |
| Sampling No. | Date of sampling: | File name: |
| 15-2907XX-281 | 29.07.2004 | 15-2907XX-281_Secondery_Steel_Arc_Furnace.DOC |
| File name of attached excel file | | 15-2907XX-281.XLS |

| | | | | |
|---|---|---|---|---|
| Input material during measurement | | | | |
| Primary Metal ore | % | Composition: | | |
| Secondary Metals | 100 % | Origin: | 10% own steel scrap<br>90% outside steel scrap | |
| | | Process applied to remove paint, plastics etc. | [ ] If yes, which type: | |
| Primary + Secondary | 100 % | = Metal | | |
| Auxiliary Materials e.g. flux | Composition: | Dolomite | kg/Mg of Metal: | 9,5 |
| | Composition: | Lime stone | kg/Mg of Metal: | 31,9 |
| Primary fuel | Type: Electric energy | | 378 000 MJ/a | |
| Secondary/alternative fuel | Type- | | t/a or % of primary fuel:- | |

| | |
|---|---|
| Product output during measurement | |
| Type, composition | Rate, Mg/hour |
| carbon steel ST4S; C 0,08-0,22%; Mn 0,50-1,2%; Si 0,15-0,40%; P max 0,050%, S max 0,050%, Cu up to 0,40%; Cr do 0,20%; Ni up to 0,20%; Mo up to 0,02%; As up to 0,007%, Sn up to 0,025%; Sb up to 0,003%; Co up to 0,011%, Pb up to 0,003%; Ti 0,003%, Zn < 0,002% | 100 |

**Form**
**5**

## The Dioxin Measurement

| Flue gas conditions | |
|---|---|
| $N_2$ (dry gas) | 78,8 % (v/v) |
| $O_2$ (dry gas) | 19,8 % (v/v) |
| $CO_2$ (dry gas) | 0,6 % (v/v) |
| CO (dry gas) | 0,79 % (v/v) |
| dust (if known) | 0,74 mg/m$^3$ |
| Flue gas flow rate: | 1090400 m$^3$/h |

Analytical results
Dioxins and Furans (PCDD + PCDF) in Flue Gas

| Relation to Detection Limit (DL) | Concentration in flue gas ng I-TEQ/m$^3$ | Emission factor (emission per Mg product) ng I-TEQ/Mg |
|---|---|---|
| Incl. DL | 0,003 | 20 |
| Incl. 0.5 DL | 0,003 | 20 |
| Excl. DL | 0,003 | 20 |

| Process conditions during measurement | | |
|---|---|---|
| Measurement period | 6 hours | |
| Was start-up or shut-down period included in measurement period? | Yes [X] | No [ ] |
| Did any events deviating from normal conditions take place during measurement? Please describe: | | |
| Did input material during measurement considerably deviate from average material composition from form 3 page 1? | Yes [X] | No [ ] |

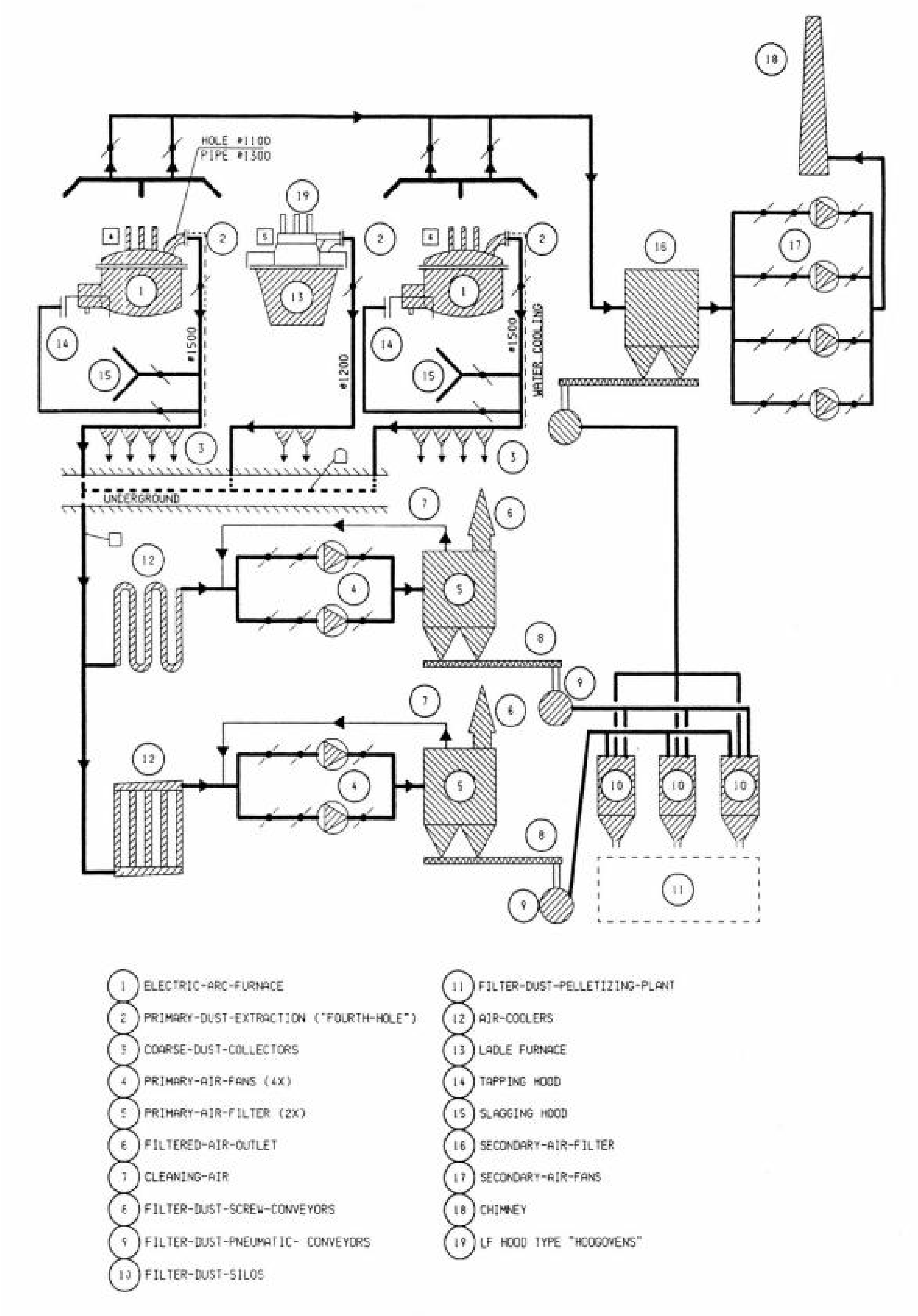

Fig. 1. A situation plan with the position of furnaces, APCS etc.

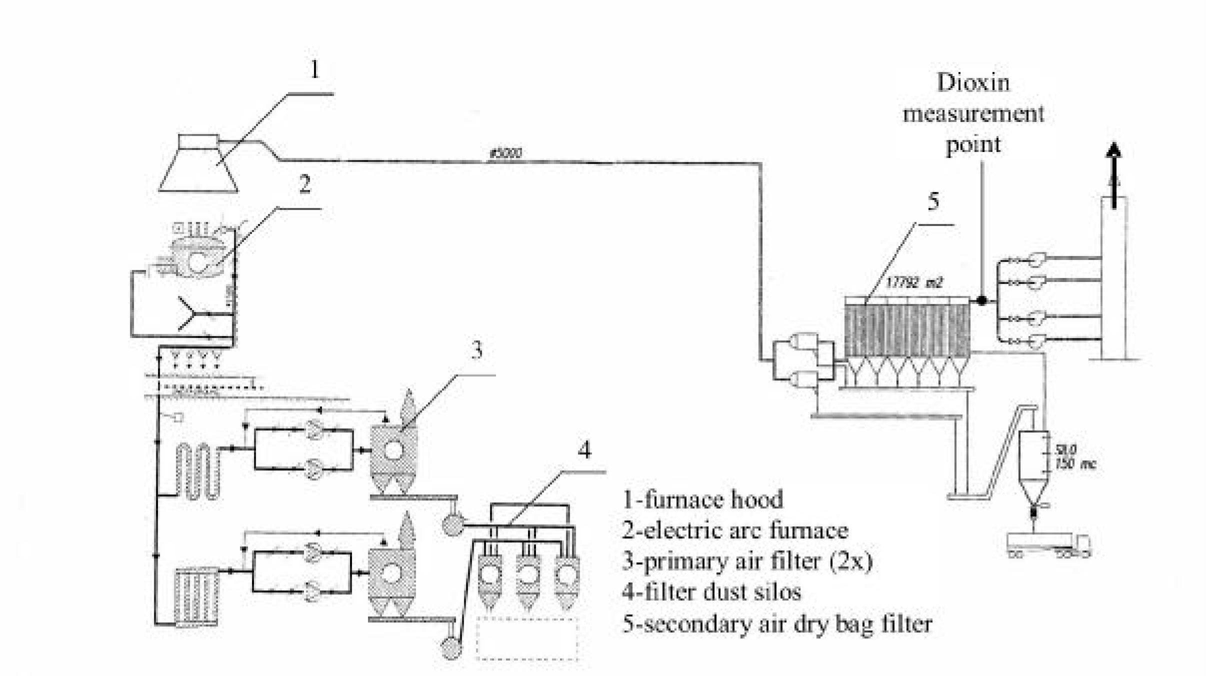

Fig. 2. A system diagram of the exhaust gas system