

PCCD/F EMISSIONS IN METAL MANUFACTURING PROCESSES

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Introduction

Today the situation with polychlorinated dibenzodioxin and dibenzofuran emission over the world is as follows: as far as emissions from waste incineration plants (WIP) are being regulated and reduced emissions from steelworks are coming to the first place. In the former USSR and in Russia attention to dioxin emission produced by steelworks has never been drawn. The Kirovogradsky copper-smelting plant (Sverdlovskaya Region) has been mentioned as an example of a probable PCDD/PCDF formation source where cable and radio electronics industry waste is stripped of polymer insulation including vinyl chloride polymer by direct burning of insulation on an open site.

In this paper¹ a list of Russian enterprises is given that are hazardous in terms of environmental dioxin pollution. Only several plants represent metallurgy: the Beloretsky steelworks (Bashkortostan), the Orsko-Khalilovsky steelworks (Novotroitsk), the Kirovogradsky copper smelting plant (Kirovograd). It is clear that the list of PCDD/PCDF emission hazardous objects should be much longer.

Data known from literature show that dust and gas of metallurgical processes may contain dioxin concentrations compared with waste incineration plants and steelworks may be even more considerable PCDD/PCDF emission sources than municipal waste burning plants. This contribution should be assessed by means of true dioxin measurements.

This research has been carried out for assessment of dioxin emission from the Beloretsky steelworks (BSW). The received results permit to make a rough assessment of dioxin emission in metal manufacturing processes.

Materials and methods

Sample preparation and analysis was carried out compliance with the Methods EPA USA^{2,3}. To check the sample preparation labeled standards ³⁷Cl-2,3,7,8-TCDD; ¹³C₁₂-1,2,3,4,6,7,8-HpCDD and ¹³C₁₂-OCDD were introduced into all samples. Depending on sample characteristics the labeled standards were used in the form solutions in nonane or acetone.

Water sample volume of 5 l was three times extracted by hexane simultaneously being mixed in a mechanical shaker. In case there was precipitate present the water sample was filtered through a "blue strip" filter. Precipitate and filtrate were analyzed separately.

Blast furnace dust and slag samples were analyzed by same methods in compliance with the Methods³ with modification. To a sample of ~30 g weight labeled standards were added, 250 ml of sulphuric acid diluted with water 1:1. The sample was being mixed for 5 hours at 50 °C. Precipitate was filtered, washed with twice distilled water, dried at a room temperature to the constant weight and then extracted with toluene in a Soxhlet device for 16 hours. The toluene extract was evaporated and toluene was replaced by hexane.

The hexane extracts were by one the same methods – they were washed with 20% water solution of KOH, then with 5% solution of NaCl, concentrated H₂SO₄. Washing with KOH and H₂SO₄ was continued to the moment of receiving slightly pigmented neutralizing and acid coatings. Purification of extracts was carried out on multi-layer silica gel and carbon columns. The volume of the purified extract was reduced to 10 mm³.

Results and discussion

This research presents analysis of slag, blast furnace dust and wash water samples of blast furnace production at the BSW. The blast furnace production at the BSW is processing local ore, brought pellets and metal scrap up to 50% of the total capacity. Operation mode is continuous. Blast furnace gas undergoes purification for separation of coarse and fine dust and at a temperature of 200 °C it is delivered to a power station as fuel. The blast furnace gas contains 20% of carbon oxide. Due to the absence of special equipment the blast furnace gas has not been sampled. PCDD/PCDF content in toxicity equivalent units was: in slag sampled from the surface of molten metal – 0.002 ngTEQ/g; in blast furnace dust after furnace gas purification – 0.018-0.172 ngTEQ/g and in return water after washing blast furnace gas – 2.13 ngTEQ/l. PCDD/PCDF isomer composition of samples is given in Table 1. In slag and return water the main isomers are highly chlorinated furans, in blast furnace dust samples all isomers are present except for 2,3,7,8-TCDD.

Table 1. Isomer composition of blast furnace production samples

PCDD/PCDF	Blast furnace dust 1, ng/g	Blast furnace dust 2, ng/g	Return water, ng/l	Slag from molten metal surface, ng/g
2,3,7,8-TCDD	N/D	N/D	N/D	N/D
1,2,3,7,8-PeCDD	0.12	0.024	N/D	N/D
1,2,3,6,7,8-HeCDD	0.49	N/D	N/D	N/D
1,2,3,4,6,7,8-HpCDD	0.65	N/D	10,74	N/D
OCDD	0.77	0.027	22.80	N/D
2,3,7,8-TCDF	0.11	0,024	N/D	N/D
1,2,3,7,8-PeCDF	0.38	0.071	N/D	N/D
1,2,3,4,7,8-HeCDF	0.20	N/D	11.16	N/D
1,2,3,4,6,7,8-HeCDF	0.46	N/D	58.71	0.10
OCDF	1.54	0.13	294.77	1.35
TEQ	0.172	0.018	2.130	0.002

On the basis of analyses and solid waste volumes the following approximate values of PCDD/PCDF emissions from the BSW blast furnace production were received: with blast furnace dust – 1420 mgTEQ/year, with slag – 120 mgTEQ/year.

Dioxin emission with blast furnace gas may be roughly estimated using the data on similar production. This approach was accepted by the EPA USA for inventory of PCDD/PCDF emission sources in the USA⁴. For this purpose the mean value of 4 ngTEQ/m³ received for metallurgy plants in Germany was used. On the basis of this value and blast furnace gas volume dioxin emission with blast furnace gas at the BSW will make ~470 mgTEQ/year. But this PCDD/PCDF flow together with blast furnace gas goes to the power station power as fuel.

So the received data show that in the process of high temperature cast iron melting of ore and scrap metal dioxins are being formed. Together with blast furnace dust and slag PCDD/PCDF go to a dumping place. The fate of the dioxins going together with blast furnace gas to the power station should be investigated separately.

References

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