

DIOXIN EMISSION IN TECHNOLOGICAL CYCLE OF BLEACHED KRAFT PULP PRODUCTION AT THE PULP AND PAPER MILLS IN THE NORTHERN REGION OF RUSSIA

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Introduction

Russia signed the Convention on POPs in 2002 and nowadays in the frame of different projects the development of equipment base for its ratification¹. Reduction and prevention of dioxin contamination of the environment through BAT (Best Available Technology) implementation in different branches of industry have some difficulties because the base for effluent limitation in Russia is still based on maximum allowed concentration. Voluntary realization of technology-based effluent limitations allowed carry out step-by-step modernization of kraft bleached pulp production for ECF bleaching technology implementation. The aim of this modernization is to minimize chlorinated compounds discharge, including dioxins, to the levels that meet the US EPA effluent limitations, at the two largest Russian pulp and paper mills^{2,3}. The results given in this paper concern reduction of dioxins formation and changes in their profile and patterns in the wastewaters of bleach plants after ECF bleaching technology implementation, as well as dioxin emission estimation in the technological cycle of bleached kraft pulp production at these mills, situated in the basin of the Arctic river the North Dvina.

Materials and methods

At the Arkhangelsk pulp and paper mill bleaching of hardwood kraft pulp is being carried out using five-stage scheme with preliminary ferment treatment. Scrubber waters from cleaning stack gases from chemical recovery furnace and the excess of acidic filtrates from the stage of chlorine dioxide treatment are used for unbleached pulp dilution. At the Syktyvkar pulp and paper mill hardwood kraft pulp is bleached using four-stage scheme with oxygen delignification, and the extraction stage is enhanced with oxygen. At the line of softwood kraft pulp production in 2007 five-stage bleaching scheme is implemented with two stages of oxygen delignification, the extraction stages are enhanced with oxygen and hydrogen peroxide. Bleach plant effluents are combined with other mill's processed wastewaters and after biological treatment with active sludge are discharged into the receiving stream.

PCDD/PCDF content was analyzed in the whole bleach plant effluents, in filtrates from the chlorination and extraction stages, as well as in the sludge from the mill effluents treatment as described in "The Guideline for pulp and paper mill effluent limitations" US EPA⁴. Samples of the effluents and the sludge were collected in monitoring system according to BAT-control scheme. PCDD/PCDF content in the samples were analyzed by GC-HRMS method (Finigan MAT 95 XL)⁵. Stack gases from bark and wood wastes combustion and from sulfate spent liquor incineration in chemical recovery furnaces were sampled according to standard EN 1948-1966A. Stack gases and scrubber water samples were analyzed in laboratory SPA «Taifun». All samples were analyzed according to national certified test method.

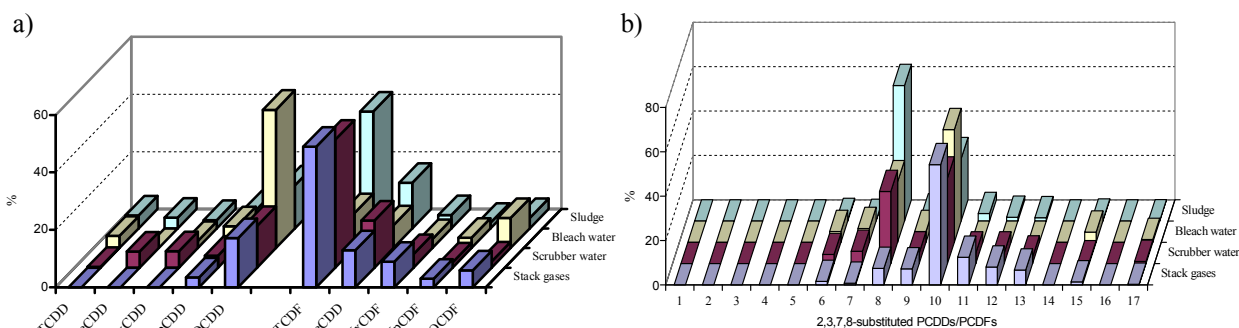
Results and discussion

At the Arkhangelsk pulp and paper mill PCDD/PCDF concentrations in the bleach plant effluents varied from 0.230 to 2.540 pg I-TEQ/l in comparison with 0.733-5.866 pg I-TEQ/l from the moment the monitoring started in 2003. In the wastewaters among 17 2,3,7,8-substituted congeners OCDD, OCDF and HpCDD dominated. The most toxic 2,3,7,8-TCDD was not found at the detection limit 0.5 pg/l. The contribution of PCDF to I-TEQ was higher than PCDD and 2,3,7,8-TCDF dominated. Normalized concentrations of 2,3,7,8-TCDF varied from 2.0 to 10.1 pg/l (BAT-limitation US EPA -31.9 pg/l). 2,3,7,8-TCDD/TCDF annual emission has reduced from 0.028 g to 0.004 g I-TEQ and nowadays the emission factor is estimated equal to 0.013 µg I-TEQ/t of pulp.

It should be pointed out that in the bleach plant effluents in some cases the PCDD/PCDF concentration reached 180 pg I-TEQ/l with the congener profile characteristic for PCDD/PCDF impurities in the Russian formulations of sodium pentachlorophenolate, where the contribution of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDD to I-TEQ value was 91.38%. It could be explained by presence of residual amounts of these PCDD/PCDF from sodium pentachlorophenolate in the surface waters. In Arkhangelsk district more than half amounts of this formulation was used as biocide by the sawmills situated in the estuary of the North Dvina where the Arkhangelsk pulp and paper mill is located too⁶. PCDD/PCDF originated from herbicide formulations, used in agriculture, were found in wastewater from pulp bleach plant where they enter with the surface water⁷.

PCDD/PCDF concentrations in the sludge from the biological treatment of the pulp and paper mill effluents varied from 2.550 to 8.194 ng I-TEQ/kg. 2,3,7,8-TCDD was not found in the investigated sludge samples at the detection limit 0.05 – 0.10 pg/g. The sludge is being combusted together with bark and wood wastes in refuse boiler that allows to utilize about 30% of PCDD/PCDF present in the sludge. PCDD/PCDF concentrations in the stack gases from bark and wood wastes combustion did not exceed the European limitation (<0.1 ng/m³) and varied in the interval 0.005 – 0.009 ng I-TEQ/m³. In the stack gases from spent sulfate liquor combustion in chemical recovery furnaces PCDD/PCDF concentrations varied in the interval 0.016-0.038 ng I-TEQ/m³. PCDD/PCDF annual emission into the ambient air is estimated equal to 0.056 g I-TEQ. PCDD/PCDF profiles in bleach plant effluents, sludge from the mill effluent treatment, scrubber water and stack gases are similar and reflect widely distributed sources of dioxins emission – combustion/incineration processes (fig. 1).

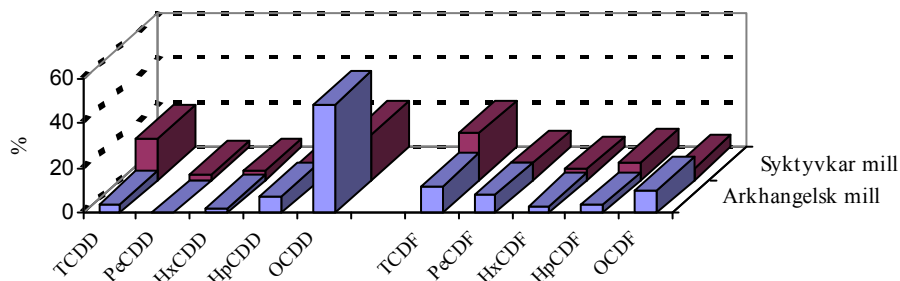
Figure 1. Homologous profiles (a) and congener-specific patterns (b) of PCDDs/PCDFs in liquid, solid and gaseous matrices.



At the Syktyvkar pulp and paper mill after ECF bleaching technology implementation for softwood kraft pulp production PCDD/PCDF load per ton of pulp in the bleach plant effluents reduced 6 times and in I-TEQ – by 70 times. PCDD/PCDF concentration in combined bleach plant effluent (softwood and hardwood lines) reduced in average from 40.60 to 1.12 pg I-TEQ/l and varied from 0.60 to 1.50 pg I-TEQ/l. 2,3,7,8-TCDD concentration before ECF bleaching technology implementation varied from 9.4 to 140,1 pg/l. In the bleach plant effluents from ECF bleaching technology 2,3,7,8-TCDD was not found at the detection limit 0.31 pg/l. Normalized 2,3,7,8-TCDF concentrations in bleach plant effluents varied from 3.3 to 11.4 pg/l which is lower than BAT limitation (31.9 pg/l).

Among 2,3,7,8-substituted PCDD/PCDF congeners in the bleach plant effluents PCDF prevailed and 2,3,7,8-TCDD/TCDF contribution was in average 29.7% at the expense of 2,3,7,8-TCDF in comparison with 92.34% for the period when molecular chlorine was used. Among PCDD/PCDF toxic congeners OCDD dominated in combined bleach plant effluents from softwood and hardwood kraft pulp production. TCDD isomers and TCDF isomers prevailed during bleaching with chlorine dioxide but as for the contribution into I-TEQ the profiles varied considerably, while 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 2,3,4,6,7,8-HxCDF prevailed. Homologous profiles of PCDD/PCDF in bleach plant effluents of the two investigated mills are rather similar to each other (fig. 2).

Figure 2. Homologous profiles of PCDD/PCDF in bleach plant effluents of the two mills.



2,3,7,8-TCDD/TCDF annual emission into bleach plant effluents reduced from 0.989 g I-TEQ to 0.012 g I-TEQ and emission factor reached the value 0.038 μg I-TEQ/t of pulp. PCDD/PCDF concentrations in stack gases from bark and wood wastes combustion in refuse boilers and are in the interval 0.003 – 0.036 ng I-TEQ/m³, from sulfate spent liquor combustion in chemical recovery furnaces 0.007 – 0.022 ng I-TEQ/m³ and did not exceed the European limitation. PCDD/PCDF annual emission into the ambient air with stack gases was 0,119 g I-TEQ. The PCDD/PCDF levels annual emission to the environment estimated on the base of actual measured concentrations allow to understand the dioxins transport through water and air to Arctic from bleached pulp production in the northern regions of Russia.

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