MEASUREMENTS OF ORGANOCHLORO COMPOUNDS AT A METAL RECLAMATION PLANT

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Introduction. Kuusakoski Co is a large Finnish metal reclamation company which was founded 1914 in City of Vyborg. Today

the company is operating world wide. The metals recovered are mainly aluminium, copper and different kinds of steels. Metal waste itself may contain harmful compounds, like heavy

metals and organic impurities (phenols, chlorocompounds, fike neavy plastics, paints and solvents. Chemicals, e.g. NaCl, KCl and other salts are used in different metal reclamation processes, which may cause special emission problems. A special concern has been focused to emissions of toxic PCDD and PCDF congeners¹⁻⁴.

Chlorine containing materials (PVC, salts, etc) are known to react in low and medium temperature thermal processes (250 - 350 °C) in the presence of catalytic metals (Cu, Ni, Fe, Al etc.) and different chlorinated organic compounds, e.g. polychlorobenzenes (PCBz), -phenols (PCP), PCDDs and PCDFs are formed.

Sampling and emission analysis of some organochloro compounds (PCP's, PCB's, PCDD/PCDF's) and PAH's were made from a number of different metal reclamation processes (for example aluminium, lead and zink smelting, car shredding, turnings drying, etc.) at the Heinola plant of Kuusakoski Co in 1990.

The Metal Reclamation Process at the Heinola Plant. In aluminium smelting there are two different lines: rotary-furnace-line and induction-furnace-line. In the rotary-furnace-line, sodium/potassium-chloride salt is used as flux.

Raw materials in the rotary-furnace-line are floated aluminium, dryed turnings, aluminium sheets and aluminium dross. After injection of dry calcium hydroxide the gases from smelting go to a cooler and to a baghouse filter. Gases are blown out through 42 m high stack.

In induction-holding furnace-line floated aluminium, turnings and good quality aluminium sheets are used as raw materials. The flue gases from the induction and holding furnaces are cleaned with baghouse filters. Some burning of combustible materials may occur during the process in both smelting lines.

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In car shredder old cars are chrushed with a big hammer mill. Resulting "crush" is taken to a screening system (wind screen, magnet), where the light and heavy fraction and magnetic and non-magnetic metals are separated. The dust and light material (particulates) containing gases from the crushing process are led through a cyclon and scrubber and the cleaned gases are released through a 10 m high ventilation pipe.

In "turnings dryer" wet and oily aluminium turnings are treated in a counter current dryer. Vapors from this dryer goes to an afterburner, where temperature is about 950 °C. After that, the hot gases are cooled with water and air. The gases are then cleaned with a baghouse filter.

Sampling and Emission Analysis of organochloro compounds (PCP's, PCB's, PCDD/PCDF's) and PAH's were made from aluminium-, lead- and zink-smelting, car shredder (two sampling locations), turnings drying, sink and float drying, aluminium dross-line (three sampling locations) and "ring crusher" (two sampling locations). Results from aluminium smelting, car shredder and turnings dryer are discussed and presented in more detailed in this paper. The samples were taken by a consulting company (P. Ristola Oy) and analyzed by the University of Kuopio. The sampling was made by a sampler recommended by Swedish National Protection Board (SNV-method)⁵

Results and discussion. In Figure 1A total concentrations of PCP's, PCB's, PAH's and PCDD/PCDF's are summarized in all the analyzed flue gas samples. Fig. 1 B presents total PCDD+PCDF in samples (enlarged relative to 1A). In Fig. 1C, TCDD-equivalents are presented.



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Figure 2 illustrates concentrations of toxic PCDD- and PCDF isomers at two sampling locations and Fig. 3 congener profiles of all PCDD/Fs in two other samples.



4CDD 5CDD 6CDD 7CDD 8CDD 4CDF 5CDF 6CDF 7CDF 8CDF

Figure 3.

Chlorophenol (PCP) emissions (Fig. 1A) did not correlate with concentrations of PCDDs or PCDFs (Fig. 1B) but some relation to TEQ values (Fig. 1C) can be seen. The measured emissions indicate that a large part of chlorinated organic compounds are formed due to the chlorine in PVC-plastic (PVC-plastic in cables and car components). Such processes are car shredding (IV and V) and also partly turnings drying (VI). De novo-synthesis plays an important roll in formation of organochloro compounds in the metal reclamation processes^{3,4}. The temperature profile of processes at site and the presense of oxygen and metallic catalysts favour formation of PCA-compounds in general.

4CDD 5CDD 6CDD 7CDD 8CDD

The source of PCA-compounds in metal reclamation industry can also be the exhaust pipes in cars, which contain some amount of PCA-compounds. Other car componet materials may contain as well these compounds as impurities. Chlorine, in general, must be controlled in metal reclamation processes because of its importance in the de novo-synthesis.

4CDF 5CDF 6CDF 7CDF 8CDF

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Emissions of PCBs were low and similar at each sampling site (Fig. 1A). Origin of PCB is uncertain. Most probably it comes from contamination in raw materials, while for example, MSWincinerators normally emit much lower PCB concentrations⁶. However, in our opinion, this metal reclamation plant is not a serious source of this very ecotoxic group of chemicals.

As a consequence of the present observations in this study we suggest that chlorinated benzenes (PCBz), chlorinated naphtalens (PCNs) and diphenyl ethers (PCDEs) should be measured in the emissions. On the basis of that information one could get a better knowledge on possible reaction pathways in the processes. Further, environmental importance of PCBz, PCN and PCDE compounds may be greater than that of PCPs and PCBs.

To lower the emissions of organochloro compounds in basic metal reclamation processes is difficult. Some possibilities, however, exist: Flue- and other process gases could be cleaned more efficiently. The incoming raw materials could be purified further before processing. The temperature profiles of the treatment processes could be adjusted more properly.

At present, more analyses of emissions, environmental impact studies and process retrofitting and development is under way at the Heinola plant.

References

1 Hryhorczuk OD, Withrow WA, Hesse CS, Belasy VR. A wire reclamation incinerator as a source of environmental contamination with tetrachloro dibenzo-p-dioxins and tetrachlorodibenzofurans. Arch Envir Health 1981;36:228-234.

2 Liem AKD, Hoogerbrugge R, Kootstra PR, Van der Velde EG, De Jong APJM. Occurrence of dioxins in cow's milk in the vicinity of municipal waste incinerators and a metal reclamation plant in the Netherlands. Chemosphere 1991; 23:1675-1684. 3 Van Wijnen JH, Liem AKD, Olie K, Van Zorge JA. Soil contamination with PCDDs and PCDFs of small (illegal) scrap wire and scrap car incineration sites. Chemosphere 1992;24:127-134. 4 Wuthe J, Klett M, Hagenmaier H, Päpke O, Gugel L, Siefert D. PCDD/PCDF levels in human blood of people living in a highly PCDD/PCDF contaminated area next to a metal reclamation plant. In: Hutzinger O, Fiedler H, eds. Organohalogen Compounds, Short Papers. Eco-Informa Press, Bayreuth, F.R.G. 1990;1:615-620. 5 Jansson B, Bergwall G. Recommended methodology for measurement of PCDD and PCDF in the Nordic countries. Waste Manage Res 1987;5:251-265.

6 Aittola J-P. Modernization and optimization of an old municipal solid waste (MSW) combustion plant. Paper presented in Finnish Chemical Congress 12-14.11.1991 in Helsinki.