DIOXIN EMISSION REDUCTION AT NON-FERROUS METALS PLANTS IN THE FLEMISH REGION (BELGIUM) - ENFORCEMENT APPROACH OF THE ENVIRONMENT INSPECTION SECTION

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Introduction

The Environment Inspection Section (EIS) is responsible for the enforcement of the environmental health legislation in the Flemish Region (Belgium). The EIS chooses to enforce in both a preventive and a corrective way, and aims to reach a high-level, planned and co-ordinated enforcement. In the field of air pollution, PCDD/F emissions have received particular attention during the past decade, due to high public concern for their possible health effects. After the clean up of the municipal solid waste incinerators (MSWI), the focus has shifted to industrial process plants, with a significant dioxin emission. Emission measurements showed the highest emissions to be from iron sintering plants and some non-ferrous metals plants. The enforcement approach of the EIS led to a major emission reduction at these plants within a couple of years. This paper highlights the way this clean up was reached at non-ferrous metals plants and the role the EIS has played in it.

Methods and Materials

Environmental legislation

In Flanders, the integrated environmental health legislation is covered by the Environmental Licence Decree (1985). This decree has become operational through the implementing orders Vlarem I (1991), listing the objectionable establishments by type and Vlarem II (1995), containing the general and sector-related conditions for these establishments. The legislation is based on the general principle of prevention of pollution, nuisance and damage. Its integrated approach is fully in line with the European IPPC Directive. Vlarem II contains a legally binding dioxin emission limit value (ELV) for waste incinerators, oil refineries, crematories, ferrous and non-ferrous metals plants and iron sintering plants [1].

Enforcement

The Environmental Licence Decree and Vlarem I designate the EIS as the authority being responsible for the enforcement of the environmental legislation for so-called “class 1” establishments (having the highest potential for environmental pollution). If needed, the inspectors of the EIS will take measures to obtain compliance with the environmental legislation. Within the field of criminal law, they always make an official report of the legal infringements to the Public Prosecutor. Besides this, they can take administrative measures, generally starting by giving exhortations to the operator. In a further stadium, coercive measures can be imposed, even leading to the closing-down of the plant. The findings of the inspectors in the field of air pollution control are mostly based on the results of emission measurements, performed by certified external laboratories, which are officially recognised.

Results and Discussion

Main dioxin sources in Flanders

In 1993, the EIS started organising stack emission measurement campaigns, in order to check compliance with the emission limit values. The sampling and analysis of PCDD/F received a lot of attention. The measurements clearly indicated that 3 sectors caused the bulk of the PCDD/F emission from point sources: waste incinerators, iron sintering plants and metal smelters. The thorough clean up of the municipal solid waste incinerators lowered the yearly PCDD/F emission from this sector to less than 1 g TEQ by the year 2000 [1]. At the 2 iron sintering plants, huge research, measurement and clean up efforts led to an emission reduction by over 95 % between 1998 and the end of 2000 [2]. For the non-ferrous metals industries, being a very diverse sector, the situation differed very much from plant to plant.

Non-ferrous metals industries in Flanders

In Flanders, since the 19th century, the non-ferrous metals industries have been an important economic sector. The main metals produced or processed are copper, zinc, aluminium, lead and precious metals. Most of the production is concentrated in a limited number of sites, but also a large number of small-scale smelters are being operated. Due to the absence of local ores and the increasing need to recycle materials, the input has shifted largely to secondary (recycled) metals, including the recycling of various waste streams from other metal plants.

Dioxin emission at non-ferrous metals industries and enforcement approach of the EIS

The Flemish dioxin emission inventory from the early 1990's showed that non-ferrous metals industries could be very significant sources of dioxins. Especially copper is known to be an important catalyst for the formation of PCDD/F. Measurements at the major non-ferrous metals plants were initiated by the EIS in 1995. At most of the sites monitored, little or no dioxins were found in the flue gases. At some plants, however, especially those processing recycled metals, significant amounts of dioxins were detected. It soon became clear that the input and process conditions were largely determining the dioxin output. Where needed, the EIS initiated clean up measures by giving exhortations. Generally, the injection of an adsorbent into the flue gases was chosen as an end-of-pipe abatement technique. Subsequent emission measurements proved that the emissions were substantially lowered and at nearly all plants reached a level below 0,1 ng TEQ/Nm³. At one specific site though, several plants were found to have very high and fluctuating emissions. Therefore, the clean up took some more time and effort. Two of these plants, i.e. a secondary copper smelter/casting unit and a cobalt spray-roasting oven, will be discussed as case studies in more detail.

Case study 1: reduction of the dioxin emission at a copper anode production unit

The copper anode production unit at this site consists of a copper smelter and a casting unit, with a maximum capacity of 1800 tons/day of copper. The smelter is fed with a mixture of scrap, recycled anodes and blister. The flue gases are de-dusted by a fabric filter with prior injection of lime. The first emission measurements, ordered by the EIS in 1995, revealed a rather moderate concentration of PCDD/F in the flue gases. In 1998, new measurements showed a different picture, as concentrations up to 20 ng TEQ/Nm³ were measured during several days. This meant that this plant was the second highest PCDD/F emission source in Flanders. Subsequent measurements confirmed the link between the amount of scrap input and the dioxin formation potential. Based on these findings, the EIS exhorted the plant operators to start a clean up programme, aiming at a thorough and permanent emission reduction. An emission target of 0,5 ng TEQ/Nm³ was set. The plant management decided to immediately start an extensive research and monitoring programme in order to fulfil this demand. In a first phase, process integrated measures were aimed at. Limiting the amount of scrap to less than 10% of the total input, very much lowered the PCDD/F formation. Also the quality of the scrap (lack of organic contamination) was better looked after. Secondly, the temperature profile within the unit proved to be a strong dioxin-promoting factor, causing excessive 'de novo' dioxin formation. Through modification of the internal flue gas circuit, an improved temperature window could be obtained. The third parameter influencing the dioxin emission was the dust content of the flue gases. Learning from the experience at waste incinerators, the functioning of the existing fabric filter was therefore adjusted. Optimizing these three parameters lowered the PCDD/F emission within one year to around 1 ng TEQ/Nm^3. As the determining parameters were still not sufficiently under control, the plant operators had to go for additional end-of-pipe measures. The injection of an adsorbent in front of the existing fabric filter was opted for. An optimum constitution of the adsorbent/lime mixture in order to avoid fire or explosion was soon found. Since the summer of 1999, an adsorption injection unit has been operated and, later on, been optimized. This way, an emission concentration of less than 0,5 ng TEQ/Nm^3 has been reached permanently since 2000. A further emission reduction might be even feasible by using a more active adsorbent (modified activated carbon). Due to the injection of the adsorbent, the PCDD/F loading is transferred from the flue gases to the adsorbent, yielding a highly contaminated filter dust. Dust free storage and handling of this waste is essential to avoid diffuse emissions and contamination of the surroundings. Currently, the filter dust is processed in another copper smelter from the same company. The evolution of the yearly average PCDD/F emission from this plant (expressed as µg TEQ/h) is illustrated in the following Figure.

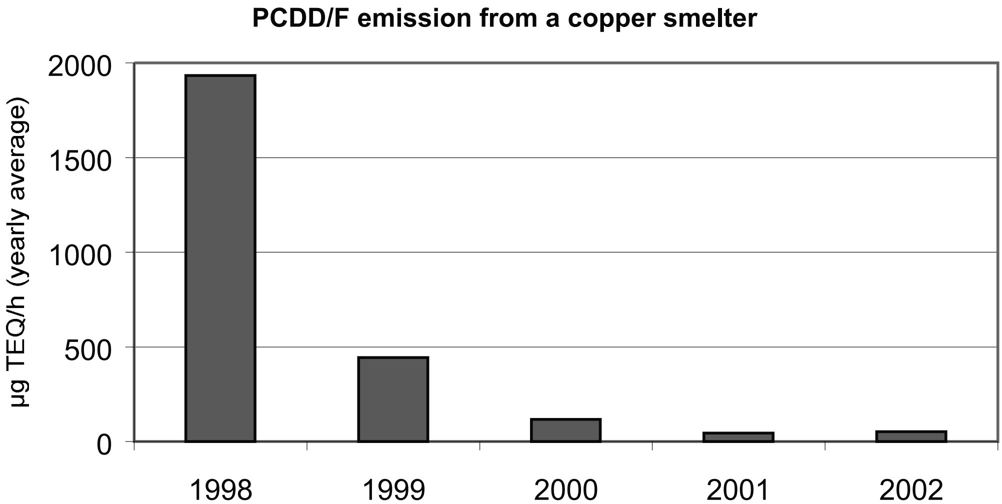
It should be noted that, at this site, also two other copper smelters (from the casting unit and rod production unit) showed very high PCDD/F emissions. These problems could be solved rather quickly, by learning from the clean up of the anode unit. In both cases, the use of an adsorbent combined with high-efficiency de-dusting, led to emission concentrations below 0,1 ng TEQ/Nm^3 by the end of 2001.

Case study 2: reduction of the dioxin emission at a cobalt plant

At the same site, two cobalt spray-roasting ovens are operated for the production of cobalt oxides from a cobalt chloride solution. Before this solution is fed to the reactor, it is treated by solvent extraction, which causes some organic contamination. Measurements in early 1999 showed PCDD/F flue gas concentrations up to 20 ng TEQ/Nm^3. Model simulations indicated that the local impact of this emission was very significant. Therefore, the EIS chose to closely follow up the clean up, aiming at BAT-based measures, which permanently lower the emissions. As these ovens were equipped with a wet scrubbing system to remove and recover HCl from the flue gases, the approach that was followed at the copper plant could not simply be copied. In a first phase, attempts were made to remove the organic contaminants from the Co-solution through adsorption. Due to the potential impact on product quality, this option could not be maintained. Next, the injection of an adsorbent in the wet scrubbing system was attempted. This way, an emission concentration of 0,5-1 ng TEQ/Nm^3 could be obtained. However, the removal of the activated carbon from the wet flue gas stream caused a great deal of trouble. As plans arose to build a new Co roasting oven, which had to comply immediately with an emission limit value of 0,1 ng TEQ/Nm^3, the plant management decided to install a catalytic incinerator at one of the ovens. In 2001, a new spray-roasting reactor was built and equipped with a similar catalytic oxidation unit. Emission measurement results are currently largely below 0,1 ng TEQ/Nm^3, which means that the overall emission from this production unit has been decreased by over 99 % since 1998.

Current legal framework

Vlarem II has a PCDD/F emission limit value of 1 ng TEQ/Nm^3 for existing metals plants, which will become operational on January 1, 2003. Additionally, an emission target value of 0,4 ng TEQ/Nm^3



is mentioned. The licences of some plants have more stringent emission limit values, down to 0,1 ng TEQ/Nm³.

Conclusions

Stack emission measurements ordered by the Flemish Environment Inspection Section (EIS), revealed significant PCDD/F emissions at some non-ferrous metals plants in Flanders. By far the highest emissions appeared at a secondary copper smelter. The plant management was exhorted by the EIS to reduce the dioxin emissions. Based on measurements and model calculations, the EIS defined a middle term target of 0,5 ng TEQ/Nm³. The company reacted promptly by launching a clean up programme, aiming at process modification and evaluating possible additional end-of-pipe measures. The EIS kept a close eye on the clean up process through regular negotiations and a strict follow-up of the experiments, measures and emission measurement results. Through input and process related measures, the dioxin formation in the smelter could be largely limited. Due to the remaining process fluctuations, it was necessary to apply an end-of-pipe technique. By injecting an adsorbent in the flue gases, the emission could be reduced to below 0,5 ng TEQ/Nm³, which meant an overall emission reduction of over 95 %. A similar emission reduction was reached at a cobalt plant at the same site, leading to emission levels below 0,1 ng TEQ/Nm³. In this case, a catalytic incinerator was chosen as the end-of-pipe solution. In both cases, frequent emission monitoring was an important factor in diagnosing the causes and clean up of the dioxin emission.

References

1. François F., Bernaert P. and Baert R. (2000) Organohalogen Compounds 45, 352-355.
2. François F., Bernaert P. and Baert R. (2001) Organohalogen Compounds 54, 115-118.