

DIOXIN PREVENTION & REDUCTION

MINIMIZATION OF DIOXINS IN THERMAL AND INDUSTRIAL PROCESSES: MECHANISMS, MONITORING AND ABATEMENT (MINIDIP): MAIN ACHIEVEMENTS OF THIS EU-PROJECT

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Introduction

The Minidip Project was prepared with the aim “to develop and test a scientifically founded and technically feasible methodology to characterise the relevant major steps of formation, destruction and removal of dioxins in a variety of thermal and metallurgical processes, as a means for optimising primary and secondary measures”. The latter were to be proposed after a study of relevant mechanisms, in-plant monitoring and abatement measures. For this purpose both major pathways, the precursor and ‘de novo’ route, were to be experimentally tested at a lab scale, under conditions typical for those found in industry. Since this approach was novel, it had to be calibrated against actual plant data and experience. In parallel to the lab-scale tests, the formation of dioxins was to be investigated at an industrial scale, in close collaboration with industrial enterprise and featuring innovative methods of monitoring.

Major problems in dioxin research have been (1) the minute concentrations of dioxins and (2) the large number of possible factors influencing them. In industrial plant those factors can be varied neither in a wide range, nor independently of other variables. Moreover, memory effects and production priorities preclude a systematic in-plant testing, which was a major justification for the Minidip project. The latter proceeded methodically, by selecting suitable samples to be tested, individually identifying the precise influence of each important variable or other factor, and testing the resulting laboratory findings at a pilot or plant scale.

Materials and Methods

Monitoring and Analysis

At the start of the project Dioxins (PCDD/F) could not be monitored continuously. The Jet-REMPI (resonant multiphoton ionisation) mass spectrometric technique developed at DLR was a potential solution for this problem and was to be further developed and tested using indicator compounds such as dioxin precursors and low chlorinated PCDD/F.

Umeå University acted as service organisation to all other members for sampling and analytical techniques. Available analytical methods were optimised and new ones developed, e.g. to analyse non-to trichlorinated PCDD/F. Additionally, a long-term (1 week) sampling method, adapted from EN 1948:1, has been developed and validated.

Chemometrics

The fingerprint of PCDD/F and other chlorinated aromatics was to be compared and critically evaluated for a variety of processes by statistical and chemometric methods. The results were to be correlated with operating conditions and concentrations of indicator compounds.

Industrial samples

Numerous samples were gathered from different types of plants in various E.U.-countries and a majority of these was fully characterised and analysed for PCDD/F, PCBz, PCPh, PCB and (in part)

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PAH. De novo tests were performed under standard conditions (300 °C, 2 h) and the resulting gas/particulate distribution of chlorinated aromatics was determined. This allows a systematic comparison of (1) de novo dioxin formation from the various samples and (2) of their adsorption potential for chlorinated aromatics with a vastly different vapour pressure.

Formation and Destruction

The actual dioxin load and additional dioxin generating potential of particulate samples, collected from industrial plant, was investigated at FZ-Karlsruhe as a function of various operating parameters (temperature, time, oxygen concentration, inhibitor addition) with the aim of identifying critical parameters, studying mechanisms, developing kinetic equations, and eventually simulating the process using Computer Fluid Dynamics (CFD) and minimise dioxin output by optimising operating conditions. Similarly, at Leiden dioxin formation rates from precursors were related to operating conditions, precursor concentrations and type of particulate. With a newly designed micro-sintering set-up, experiments were performed aiming at a better understanding of dioxin formation in the sintering process, studying the effects of the nature of the ore, the form of chlorine, and the role of precursors.

Adsorption equilibriums are most important in practice, as the adsorption characteristics define the distribution of dioxins between the gas and the particulate phase and hence the dioxin removal efficiency during particulate filtration. Two methods were used for tackling this topic:

1. During de novo tests there is a spontaneous partition established for each compound between a fraction evolving and one retained. If this partition were determined by equilibrium, interesting data can be derived.

2. In numerous sampling campaigns dioxins were determined separately for the filtered and the gas phase, both in raw and cleaned gas. This partition was also studied.

Adsorption data were established for a number of well-defined mineral adsorbents using simple test substances, such as chlorobenzene, - phenol, or hexane to prepare for further study of the adsorption characteristics of particulates, sampled during the Minidip project.

Primary measures of reduction involve improved operating conditions, i.e. enhancing the burnout of gas and particles, avoiding both particle entrainment and stagnant zones, and a better control of flow patterns, temperature and oxygen concentration field. Two other potent measures are adding inhibitors, and a deep quenching of gases, avoiding the dioxin forming range from 500 to 200 °C.

Inhibition

The efficiency of various catalytically active components and their possible inhibition by urea or amines or, much more, by basic compounds was measured at a lab scale. During these inhibition tests the de novo activity was reduced, sometimes even dramatically, but the dioxin fingerprint and that of other chloroaromatics was unaffected. The positive effect from sulphur compounds was inferred from the absence of dioxin formation in the roasting of sulphide ores.

Secondary measures of reduction involve adsorption on activated carbon or lignite coke and catalytic destruction of dioxins, generally using a DeNO_x-type of catalyst.

Lignite coke Adsorption

Dioxin abatement was mainly approached by injection of lignite coke. Large-scale experiments were performed to optimise dosage, particle size and injection position. Thermal industrial plant often features the possibility of in-plant combustion of these products.

Results and Discussion

Monitoring and analysis

Jet REMPI allows an on-stream monitoring of organic compounds in a relatively clean gas by a combination of mass and laser wavelength active in selective ionisation. Hence, spectroscopic data was compiled for relevant PIC's. The original apparatus was redesigned for use under industrial conditions. The new machine³ was field-tested in 1999 and a smaller Jet-REMPI unit was also designed

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and built, but could not be completed within the timescale of Minidip. Jet REMPI was used in two series of lab experiments, in a combination with (1) the micro-sintering set-up (Univ. Leiden) and (2) the FZ-K 'de novo' reactor (VUB). Numerous PIC's could be monitored on-line, as presented in other papers proposed for DIOXIN 2002.

Chemometrics were applied to search for correlations between dioxin formation, precursors and indicator substances. Pattern analysis gave an indication regarding the degree of similarity between two samples ("similarity index"), but failed yielding conclusive discriminatory evidence regarding the predominant mechanisms of formation, indirectly indicating that common pathways of formation are prevailing. Chemometrics was also tested as a means of dioxin source allocation between various sources of emission. Cluster analysis, PCA and factor analysis were the other tools used in chemometric analysis. As a result of Minidip data collection a database was programmed to store information on dioxin homologues and congeners as well as on parameters describing operational or testing conditions.

Industrial samples were obtained without difficulty, a major factor being the large interest in Minidip work in Flanders, where allowable dioxin emission values had been reviewed and reduced rather abruptly, causing considerable consternation in industry. Moreover, Aminal, the Flemish Environmental Authority, commissioned an Inventory to be dressed by VUB of residual flows from a wide array of industrial sectors; as a consequence many more samples became available, together with precise process data. Initially main emphasis was on dioxin formation related to the iron ore sintering belt, copper smelters and other thermal or metallurgical plants^{1,2} but this selection was much extended later, e.g. to some examples of chlorine chemistry.

Formation and Destruction of Dioxins Laboratory experiments showed that:

1. For relatively long reaction times* (2 h) dioxin generation starts already at some 200 °C, becomes sizeable from 250 °C upwards, attains a maximum value between 300 and 350 °C and declines sharply above 400 °C**, when oxidation becomes too complete to further generate dioxins at a high yield. Other chlorinated aromatics are formed in parallel, and PeCBz/HxCBz are excellent surrogates. Still, compared to PCDD/F the formation of PCBz seems somewhat more favoured at higher, and that of PCPh at lower temperatures.

2. Fly ash from Municipal Solid Waste Incineration (MSWI) is strongly adsorptive even at 300 °C, but metallurgical filter dust barely retains chlorinated aromatics. The distribution of dioxins between the particulate and the gas phase strongly shifts towards the latter with rising temperature. Nevertheless, it is still unclear whether a delayed desorption proceeds either smoothly, or destructively. Destruction presumably follows several pathways: catalytic oxidation, as well as a stepwise dechlorination.

3. At a reference temperature of 300 °C dioxin formation is proportional to time, at least for a period of the order of 1 to 2 hours***.

4. Under combustion conditions (O₂ up to 12 vol. %) dioxin formation is proportional to the oxygen concentration in the gas stream but barely changes between 20 and 50 vol. %.

* In most industrial plant and in MSWI the retention time of dust particles is only of the order of 3 to 30 seconds, whereas a residence time of this order (2 h) implies that the particle was settled or held by a collecting electrode of an ESP, the sleeves of a baghouse filter! Hence, this data is not to be immediately extrapolated to plant conditions.

** During a few ballistic tests it was shown that also high temperature formation is possible.

*** Remarkably, recent testing at DLR showed that the formation of non- or low-chlorinated aromatics is strongly time-dependent, starting & halting after a time period rising with chlorination level. This suggests similar time constants for catalytic chlorination and gasification of carbon structures. Also desorption of aromatics, e.g. benzene, toluene, naphthalene and phenantrene prior to the de novo reaction became apparent.

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Effect of the Samples

A comparison of samples shows that the following particle parameters strongly influence upon their dioxin generating potential: copper & heavy metal content, chloride and carbon content. Obviously, the desublimation of volatile heavy metal chlorides and salts onto a particle strongly enhances its dioxin forming potential. Dr. Stieglitz and his team using DSC also studied the relation between heat effects in carbon gasification and de novo activity.

Primary measures of reduction were tested on several plants. A copper smelter was operated at much lower oxygen levels, but the effect was not very positive and operating problems were encountered. On the other hand the addition of NaOH solution gave promising results.

Secondary measures. Rheinbraun demonstrated the feasibility of the adsorption route based on lignite coke and an excellent PCDD/F-reduction was obtained in various industrial units, solving some notorious emission problems. Tests were developed for evaluating risk for spontaneous ignition, problematic in metallurgical applications.

Catalytic Destruction of dioxins was investigated using a commercial catalyst at 100 to 230 °C. Destruction efficiencies of PCDD/F of > 99.7 % (t = 130 °C) were attained at a space velocity of 8000 GHSV. Other organic compounds are also converted, particularly chlorophenols for which destruction efficiencies are almost as high as for dioxins. More recent experiments show a negative impact of HCl and SO_x on conversion efficiencies.

Computational Fluid Dynamics (CFD) modelling was made of (1) a sintering plant, (2) a Waelz rotary kiln unit (both by BifA). These CFD models allow predicting dioxin generation from simple chemical reaction models. In a third case, the vertical shaft and the melting oven of a secondary copper smelter were simulated, preparing for full-scale plant tests at reduced oxygen levels.

During the Minidip project wide experience with industrial sources and metallurgical processes was gathered. It was found that dioxin formation proceeds along similar lines, as follows from an analysis of fingerprint, namely by a low temperature gasification of carbon catalytically activated by desublimation of volatile heavy metal chlorides and salts. Precursors are formed in the same process, or as Products of Incomplete Combustion. Differences can conveniently be classified on a basis of PCDD/PCDF-ratio and the extent of chlorination of generic groups. Individual variations between processes are related to the nature of the catalytic system, carbon structures, operating conditions, amount and composition of particulate and gas. Dioxin formation was monitored in real time under laboratory conditions and computer simulated by CFD, but unfortunately it is still impossible to predict dioxin formation on actual plant.

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References

Numerous Reports were prepared during the Minidip Project. Reference is made to the various partners for a reasonably complete coverage. Minidip was first presented in:

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