Outline of an European Union Research Project "Minimization of Dioxins in Thermal Industrial Processes: Mechanisms, Monitoring and Abatement (MINIDIP)"

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Abstract

The European Union has recently initiated a comprehensive research project "**Mini**mization of **D**ioxins in Thermal **I**ndustrial **P**rocesses: Mechanisms, Monitoring and Abatement (MINIDIP)". The project will study industrial sources with new techniques and a novel methodology, model dioxin generation, destruction and removal, maximize prevention and minimize emissions. The project team combines skills at the highest level on dioxin analysis, in-line continuous monitoring (by the novel, emerging Jet-REMPI technique), kinetic/mechanistic investigation and modelling (lab-scale, pilot-plant scale, industrial scale) and abatement by carbon adsorption. The project starts in mid-1997 and will last for three years. In this communication the scope and activities of the project are described.

Introduction

The dioxin issue has created a world-wide societal debate hitherto unprecedented for a class of chemicals and resulting even in chemophobia with negative impact on the image of industry as a whole. On the other hand, huge research efforts have been expended and still go on in chemistry, human toxicology, and technology. As a result quite a lot on sources, environmental fate, and means to prevent further dioxin emissions are known. Great progress has especially been made in understanding waste incineration as a major dioxin-producing activity and advanced end-of-pipe technologies are available for those who can afford it.

Yet, considerable discrepancies exist between known sources and total emissions apparent from deposition or environmental burdens. It has been suggested that natural sources are too small to be significant, human activities must be responsible: in particular, thermal industrial processes with elements and conditions conducive to dioxin formation. Supported

by scattered measurements primary candidates are int. al.: metallurgy (iron ore sintering, secondary smelting of steel, copper, aluminium, etc.) and cement production.

There is clearly an urgent need for more data on dioxin emissions from these industrial sources and preventive and curative actions as indicated in the on-going U.S. EPA characterization study on dioxin as well as numerous other international studies. In this context the European Union initiates a comprehensive research project "**Mini**mization of **D**ioxins in Thermal **I**ndustrial **P**rocesses: Mechanisms, Monitoring and Abatement (MINIDIP)", in which a number of research and industrial groups from various European countries will take part.

Objectives

The main objective of MINIDIP is to develop and test a scientifically founded and technically feasible methodology to characterize the relevant major steps of formation, monitoring, destruction and removal of dioxins in a variety of industrial processes, as a means of optimizing preventive and curative measures. Answers will be provided to the key questions/issues on:

* Emission levels and dioxin patterns from different process plants. Improvement of sampling and analytical methods if/when necessary, with validation, and direct on-line monitoring.
* Pathways and levels of dioxin formation and destruction in (representative stages of) the process: via precursors, from carbonaceous material, on particulate matter, or else. The results from labscale experiments will be verified at pilot level and tested at plant scale.
* Correlations between process conditions/materials, mechanisms, and dioxin output characteristics; parameterization, statistical evaluation.
* Approaches to suppress/minimize dioxin outputs with minimal change in the process; focus on (cost-effective) measures in the primary reactors.

Results from the investigation will be utilized to formulate practical guidelines for preventive measures. The information and experience gathered in MINIDIP will be made available to the industry and research community through international seminars and publications.

Project Team

The project team consists of research groups from the following institutions:

Vrije Universiteit Brussel, Brussels, Belgium (Coordinator)
Forschungszentrum Karlsruhe, Karlsruhe, Germany
Umeå University, Umeå, Sweden
Rheinbraun AG, Köln, Germany
Leiden University, Leiden, The Netherlands
Deutsche Forschungsanstalt für Luft und Raumfahrt e.V., Stuttgart, Germany
Bayerisches Institut für Abfallforschung GmbH, Augsburg, Germany

Dioxin '97, Indianapolis, Indiana, USA

A number of industrial groups from different sectors of the industry such as iron and steel making, non-ferrous metals production, biomass burning and cement manufacturing are selected for providing representative processes plants in the dioxin measurement and reduction tests.

Project Content and Approach
The major research activity of MINIDIP includes:

Monitoring and Analysis

(1) Dioxins (polychlorinated dibenzo-p-dioxins and dibenzofurans: PCDD/PCDF) cannot at present be monitored continuously. The novel, patented Jet-REMPI (**R**esonance **E**nhanced **M**ulti **P**hoton **I**onisation) technique will be further developed and tested on industrial plants by using suitable indicator compounds including pre-dioxins. This allows for on-line monitoring of a process, yielding direct information on the effects of cyclic operation, sudden upsets in the process, occurrence of CO- or PIC-peaks, and other factors increasing PCDD/PCDF formation.
(2) Experimental data will be collected and statistically evaluated to derive PCDD/PCDF levels from other parameters that are easier to measure, such as PCPh, PCBz, or lower-chlorinated PCDDs/PCDFs.
(3) Measurements of various kinds are carried out on at least three different selected plants from at least three industrial sectors in three different countries, e.g. in Germany, Sweden, Belgium, The Netherlands, Spain and Italy. Results are related to the laboratory and pilot plant work conducted by each of the partners.
(4) The fingerprint of PCDD/PCDF will be critically evaluated for a variety of processes (int. al. all processes studied) by mathematical, statistical and chemometric methods. The results will be correlated with operating conditions, concentrations of indicator compounds, etc. for laboratory as well as large scale experiments and for industrial data. If possible, a data bank will be established for further use and gradual expansion, to screen other industrial processes for their potential to yield PCDD/PCDF.
(5) Validation of PCDD/PCDF analyses, by interlaboratory comparison of methods and results. Standardization of methods of sampling hot process gases, to yield a maximum of process information on concentration, fingerprint and distribution over the gas and particulate phase of PCDD/PCDF.

Formation and Abatement

(1) The PCDD/PCDF generating potential from carbonaceous materials in particulate matter will be studied systematically for samples collected from various industrial plants. This procedure allows to minimize PCDD/PCDF formation and eventual output by a process of operating parameters optimization.
(2) PCDDs formed from precursors may be similarly reduced or largely suppressed by relating PCDD formation rates to precursor concentrations on one hand, operating conditions on the other.
(3) The efficiency of various catalytically active components in particulate matter and their possible inhibition by sulphur or nitrogen compounds will be measured at a lab scale,

as will be the adsorption characteristics that define the distribution of PCDD/PCDF between the gas and the particulate phase.

(4) Traditional end-of-pipe technology involves the use of a final fixed, moving or fluidised bed adsorber. In this project dioxin abatement will mainly be approached by injection of lignite activated cokes. Thermal industrial processes often feature the possibility of in-plant recycling. Large scale experiments are performed to optimize dosage, particle size and injection position.

These research activities are further divided into a number of tasks, each undertaken by some of the participating institutions. The various tasks of the project are organized in a systematic, comprehensive way emphasizing an integrated and multi-disciplinary approach to the industrial dioxin problem. Project coordination will be undertaken by Vrije Universiteit Brussel.

Benefits and Impacts

A large variety of thermal industrial processes are completely indispensable, e.g. cement manufacturing, primary and secondary pyrometallurgy, thermal treatment and, of course, combustion. End-of-pipe treatment for dioxin emission control is available for thermal processes and involves chemical or catalytic oxidation or removal by adsorption on activated carbon. Preventive treatment such as those targeted in this project will be based on a reduction of the amount of precursors and on a selection of the process variables to reduce dioxin formation and/or promote its thermal oxidative or catalytic destruction. In past studies a number of preventive and curative measures have been suggested, but in practice the fundamentals of the processes are not properly understood and a comprehensive methodology of study has never been implemented and tested before.

Scientific benefits

A fundamental understanding of pathways, rates and mechanisms of dioxin formation and destruction - and revealing common factors and principles in various processes - is a major goal of MINIDIP. Furthermore, the aim is to develop a practical method for dioxin monitoring, to evaluate the relative importance of the two commonly accepted pathways, i.e. oxidation, chlorination and condensation reactions of on one hand dioxin's chemical precursors (chlorophenols and related compounds mainly) and on the other hand the carbonaceous material in particulates, responsible for *de novo* formation. Since different catalysts lead to different reaction rates and dioxin fingerprints, the effect of various catalytic materials will be studied as well as that of the major variables (temperature, oxidizing/reducing conditions, partial pressure of oxygen, water vapour, hydrogen chloride, etc.). These fundamental part of MINDIP should be of considerable guidance to further development of dioxin reduction measures for thermal processes inclusive of municipal solid waste incinerators.

The research methodology of MINIDIP is such that starting with the experience from municipal solid waste incineration a comprehensive and methodical approach of characterising the dioxin generation potential of both gas phase precursors (such as

polychlorinated phenols and benzenes) and the carbonaceous structures in particulate matter, that generate dioxins upon their gradual oxidation, is combined with an analysis of the operating conditions, of different industrial processes, that are optimized to minimize dioxin output. This structured, organized approach of tackling a series of ill-understood problems may help to diminish major dioxin problems in various large-scale industrial processes.

On the technical side a highly innovative part of MINIDIP is the further development and first ever application of the patented Jet-REMPI technique for on-line monitoring of specific dioxin isomers and precursors in an industrial plant. At present dioxin analyses imply a time lag of several weeks - or, at best, hours - between sampling and final results, which is way off for continuous monitoring and process control. As a result of the proposed research a novel instrument for the continuous, on-line analysis of a wide range of organic compounds in the gas phase is expected to become available.

Industrial

Industrial benefits from the projects are obvious. The present 0.1 ng/m^3 limit applies only to municipal solid waste incineration and in some E.U.-countries, but the industry associated with dioxin generation, involving both giant iron & steel or cement plant as well as relatively small scale smelters of secondary metals, should meet the same emission limit in the future.

Three major problems in this context are: (1) dioxin sampling and analysis are time-consuming, tedious and expensive, (2) the mechanism of dioxin generation is poorly understood, despite the considerable efforts in the field of municipal solid waste incineration, and (3) the treatment of effluent gases by means of a fixed, moving, fluidised or entrained flow of adsorbent, or in specific cases, chemical treatment with oxidants or catalytic destruction has to be applied on enormous flows of gas, which inflates investment as well as operating cost. This E.U. project MINIDIP is designed to seek solutions to these problems in an integrated, comprehensive manner as discussed in previous sections.

Economic

Given the cost of a single dioxin analysis it is more than time to coordinate efforts to inventorise data, constitute data banks and interpret all available data in a systematic way. MINIDIP will pave the way for this important activity, using the whole range of chemometric methods in classifying and interpreting the data obtained.

A most important consideration is the fact that enterprise may be forced to close its doors if no solution is found to the dioxin problem at reasonable cost and within limited time. No enterprise, however, can unite the experience and devote the means required for this project to study its own dioxin problem. In MINIDIP once the methodology is developed and tested successfully reducing and abating dioxins will become *state-of-the-art* to different sectors of the industry.