Remediation Methods and Control Techniques

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The Stockholm Convention on Persistent Organic Pollutants (POPs) states in Article 6 that POPs waste should be destroyed or disposed of in a way that the POPs content is destroyed or irreversibly transformed. In addition, the convention places in Article 5 the obligation to reduce the total release of POPs that are unintentional by-products from man made sources. In this context, the destruction of PCDD/F and others POPs will be discussed during the Remediation Methods and Control Techniques Session. Furthermore, control techniques and strategies that are designed to minimize the emission of PCDD/F from industrial processes will be presented. Overall, 24 short papers comprise this session. The major findings reported in these papers are briefly summarized here.

Khelifi et al. from the International Centre for Science and High Technology of the United Nations Industrial Development Organization (ICS -UNIDO) present a decision support tool (DST) which is aimed at helping decision makers assess available technologies and to preliminarily select the preferred remedial options. A new approach for building a decision support tool (based on technical, economic, environmental, and social criteria) is presented. This tool may be used to evaluate different technologies for remediation and disposal of halogenated waste. In a second paper from ICS-UNIDO, Zinovyev et al. summarize the present and former activities by ICS-UNIDO for sustainable technologies development, selection of POP disposal, and management of contaminated sites for developing or transition countries. A list of key activities and accomplishments is provided.

With respect to Article 6 of the Stockholm Convention, Weber addresses the question of the current status of the assessment of the relevance of PCDD/F formation for the evaluation of POPs destruction technologies and concludes that a detailed evaluation is lacking. The paper discusses the relevant formation pathways of PCDD/F with respect to POPs destruction technologies, describes the current status, and proposes a basic framework on how evaluations may be performed. The necessity of a more critical evaluation of POPs destruction technologies with respect to their PCDD/F formation potential is supported by a laboratory study from Weber of PCB destruction by super critical water oxidation (SCWO) (a technology listed by the United Nations Environmental Programme (UNEP) as "Commercialised Technology with Considerable Experience" and by the United Nations Industrial Development Organization (UNIDO) as "Emerging and Innovative Technologies") showing the potential to form high concentrations of PCDFs (in the % range) during PCB destruction even at temperatures of potential application (up to 450ºC).
Sako et al. show in their paper that in a hybrid SCWO pilot scale plant PCBs and PCDD/F can be completely decomposed at temperature of 500-600ºC with residence times of 80 and 250 minutes. PCDD/F on fly ashes were extracted with CO_2 in a first step (hybrid process) while solid PCB waste was directly processed.

The destruction of chlorinated aromatics by means of catalytic oxidation was investigated in two laboratory studies. Taralunga et al. evaluated the performances of a catalyst constituted of Pt deposited over a faujasite type (FAU) zeolite for catalytic oxidation of monochlorobenzene which they chose as a model molecule to represent dioxins.
Weber destroyed PCBs over a TiO_2-based V_2O_5-WO_3 catalyst and assessed the PCDD/F formation potential. The study aimed to give an example of how an assessment of PCDD/F

formation as a function of operating conditions for PCB (POPs) destruction might be performed for the evaluation of a PCB (POPs) destruction technology.

The question of the destruction of dioxins in fly ash and soil was addressed by seven papers. Mashiko et al. describes the thermal destruction of PCDD/F in various fly ashes with the addition of 2 or 5% alkanolamine in a laboratory scale experiment. The destruction efficiency varied for the different fly ashes but generally increased with the addition of alkanolamine. Ukisu et al. examined in the laboratory the detoxification of dioxin-contaminated fly ash by a combination of solvent extraction and catalytic dechlorination. Toluene was effective for the extraction. In a second step the extracted dioxins were dechlorinated in a solution of NaOH in 2-propanol in the presence of Pd/Al_2O_3 at 82ºC.
Five of these studies investigated the potential of bioremediation for PCDD/F destruction. One study performed by Souta and co-workers report results from a field test using 20 kg of bacteria and 80 kg of nutrition to decontaminate 400 kg of soil. After 5 months ca. 20% of PCDD/F (TEQ and total PCDD/F) were degraded which was lower than former results from laboratory tests.
Hoshina et al. investigated in a laboratory study the cellular membrane degradation capability of *Geobacillus midousuji* SH2B-J2 strains for 2,3,7,8-substituted tetra- to octachlorinated PCDD/F. Optimal temperature, reaction time, optimal pH, and heavy metal resistance of cellular membrane enzyme were examined. Otsuka and co-workers elucidated the degradation mechanisms of *Geobacillus midousuji.* It is proposed that the J2 strain cleaves the ether bonds of highly chlorinated dioxins in a reductive degradation step in the cellular membrane.
Ishii and co-workers studied a bioreactor system at the kg scale using a fungus (*Pseudallescheria boydii)* for the treatment of PCDD/F contaminated soils and fly ashes.. The effect of heavy metals, chlorine concentration, and pH on the total destruction efficiency was evaluated. In a second study, Ishii and colleagues attempted to purify OCDD-degrading enzymes from *Pseudallescheria boydii* using an enzyme assay.

Two papers are related to the remediation of PCBs associated with soils. Takigami and colleagues describe the remediation of a PCB contaminated soil (92 t) by means of a solvent extraction process. The paper describes a field case of soil contamination and evaluates the efficiency of the solvent extraction treatment by chemical analysis (GC/MS) and bioassay. Poster et al. applied radiation processing to marine sediment in the presence of food-grade surfactants for the dechlorination of PCBs. The radiolytic decay of PCBs is evident in the initial samples examined by gas chromatography/mass spectrometry.

Eight studies evaluated prevention and reduction of the formation and emission of unintended POPs in particular PCDD/F from industrial sources, namely the incineration and cement industries, in line with Article 5 of the Stockholm Convention.
Karstensen compiled data on POPs emissions from the cement industry to share state-of-the-art knowledge about PCDD/F formation mechanisms in cement production processes and how it is possible to control PCDD/F emissions from cement kilns by integrated process optimization. The report provides a comprehensive data set collected from public literature, scientific databases, and individual company measurements.
Kawamoto reports on the current status of gasification and melting plants in Japan. 70 full-scale plants in 4 different types (Shaft furnace, Fluidised bed gasification, kiln gasification and gasification/gas reforming) are presently in operation. All plants were below the 0.1 ng TEQ/ Nm^3 regulation limit. However, ca. 10 plants had target emission values of 0.01ng TEQ/m^3_N and some of these plants did not reach this ambiguous aim. The measurements of the emission of total dioxin from some facilities showed that values of around 1 µg/t-municipal

solid waste (MSW) can be reached while some facilities showed that some plants emitted more than 10 µg TEQ/t-MSW.

Grosso and co-workers present the evaluation of the total dioxin release (gaseous, liquid and solid residues) from an older full scale MSW incinerator that was built at the end of the 1970s in Italy and recently upgraded. At steady-state operation, total emissions are around 45 µg TEQ/t-MSW and in transient operation a value of 66 µg TEQ/t-MSW was measured.

Boscak and Schultz investigated in two full-scale incinerators the fate of memory effects in wet scrubbers. The results verify and deepen the fact that the memory effect in wet scrubbers containing plastic material is caused by adsorption and subsequent desorbtion of dioxin. The memory effect could be reduced or eliminated by the addition of sorbents based on active carbon to the wet scrubber. It was found that sorbent in the form of powder can cause problems in the sand filter in a wastewater treatment plant. The use of granular sorbent alleviated this problem, but the dioxin removal efficiency was reduced.

Wang et al. also observed the memory effect in a wet scrubber in their study on the formation and removal of dioxins in a Chinese MSW incinerator during start-up, shut down, and steady state operation. During start-up the emission concentrations at the stack were sometimes above the limit of 0.1 ng-TEQ/m^3_N despite high removal efficiencies of dioxins by air pollution control devices (APCD) (97% and 99%). They concluded that in addition to a proper APCD, the waste had to be processed prior to combustion (drying, shredding, or separation) and that at the start-up the temperatures of the furnace should be sufficiently high before starting the waste feed.

Chi and colleagues evaluated the PCDD/F congener distributions between the gas and particulate phases in flue gases of a Taiwanese full scale municipal waste incinerator using activated carbon spray. They concluded that the gas/particulate phase distributions and removal efficiencies of PCDD/Fs in flue gases change closely with the chlorinated level of PCDD/F congeners and can be affected by small temperature variations.

Tsuyumoto presented test results of a new wet sorbent ("foaming water glass", a sodium silicate hydrate ($l Na_2O \cdot m SiO_2 \cdot n H_2O$)) for injection in a cooling tower for HCl removal. The author reports a significant reduction of dioxin formation in two small-scale incinerators.

Palladas et al. investigated the effect of sulphur on the inhibition of PCDD/F formation during the co-combustion of coal and solid waste in a laboratory scale reactor. Their experiment confirmed former laboratory studies that demonstrated upon the addition of sulphur or sulphur containing coal, the total dioxin formation can decrease.