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Numerical modelling of the memory effect in wet scrubbers

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) can be absorbed in and desorbed from polypropylene (PP) tower packings in wet scrubbers utilized in waste incineration lines. This behaviour, also known as the memory effect, has been modelled using a gas phase – PP surface equilibrium and a numerical solid phase diffusion model describing the transport of PCDD/Fs inside the PP. The diffusivities and gas – PP partition coefficients of TCDD/F to HxCDD/Fs in PP have been estimated using the numerical model. Two incineration lines were modelled. In the first line, the absorption and desorption in PP test rods was followed before and after installation of a fabric filter that was placed before a wet scrubber. In the second incineration line, the accumulation of PCDD/Fs in a wet scrubber during start up periods and the subsequent decline during the following three months was modelled and compared to continuous two-week gas measurements after the scrubber. The obtained diffusivities in PP range from 10^{-13} m^2/s for TCDD to 10^{-16} m^2/s for HxCDD. Lower chlorinated homologues with a distinctive change in concentrations during the desorption period (e.g. TCDF) are easier to model, and show the best agreement between the two incineration lines.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are commonly regarded as one of the most toxic classes of pollutants from incineration of waste. The sources and mechanisms behind their emissions have been intensively studied since they were first detected in flue gases and fly ash in 1977 (Olie et al., 1977). Today, emissions of PCDD/Fs are often minimized by adsorption on activated carbon or coke. The activated carbon is typically injected in the flue gas stream upstream of a fabric filter (McKay, 2002), which is sometimes followed by a wet scrubber. At several such incineration plants, elevated dioxin emissions have been found after the wet scrubber even though inlet scrubber concentrations were low (Sierhuis et al., 1996; Wevers and De Fré, 1998; Adams et al., 2000).

This phenomenon of elevated PCDD/F concentrations after wet scrubbers can be explained by the so called memory effect. The memory effect occurs when PCDDF/s are absorbed into plastic materials in a scrubber during periods with high inlet concentrations and then they are slowly desorbed when the inlet concentrations are lower. High scrubber inlet concentrations may occur during operation periods with elevated formations upstream of the scrubber, such as start up periods or combustion disturbances (Blumenstock et al., 2000; Gass et al., 2002). Concentrations up to 250 ng TEQ/m^3_N (dry gas volume normalized at 0 °C, 101.3 kPa) during a start-up period at a municipal solid waste incinerator (MSWI) have been reported (Gass et al., 2002).

Results from measurements where elevated PCDD/F emissions due to the memory effect are reported show a clear shift in the homologue pattern. Tetra and penta chlorinated homologues are found in higher ratios than otherwise found (Wilken et al., 2003; Löthgren and van Bavel, 2005). Higher vapour pressure for low chlorinated homologues (Rordorf, 1989) and shift of the pattern towards low chlorinated congeners during disturbed combustion periods (Blumenstock et al., 2000) partly explain the typical memory effect pattern. The timescale for the decline phase are in the order of weeks or months. Adams et al. (2000) reported memory effects that lasted several months.

Polypropylene (PP), which is widely used in scrubber tower packings, has shown an especially high capability to absorb dioxins (Kreisz et al., 1997). The rate and pattern of this phenomenon will be highly influenced by the diffusivity of the different PCDD/F congeners. An estimation of the diffusivities would provide an opportunity to predict the emission patterns from wet scrubbers after start-up periods or changes in the flue gas cleaning equipment e.g. the exchange of an electrostatic precipitator (ESP) to a fabric filter.

A wet MercOx scrubber for HCl, SO_2 and Hg removal was installed in 2000 after a bag house filter with carbon injection at the Swedish hazardous waste incinerator of SAKAB. The MercOx process has been described by Korell et al. (2003). The SAKAB incineration line consists of a rotary kiln, a secondary combustion

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chamber, a boiler, a semi dry absorber, a fabric filter and the MerCOx scrubber as the final flue gas cleaning stage. PCDD/F measurements made shortly after the installation showed higher concentrations downstream of the scrubber than upstream. Further measurements showed that the highest PCDD/F concentrations after the scrubber were observed during and after start-up of the plant, which normally occurs two or more times per year. After start-up, the PCDD/F concentration decreased and levelled out, which was attributed to the memory effect (Löthgren and van Bavel, 2005). During the same time period (2001-2004), PP test rods were installed in the wet scrubber at the MSWI of Thisted in Denmark. The accumulation and desorption of PCDD/Fs were followed before and after a retrofit of the flue gas cleaning where the ESP was changed to a fabric filter (Andersson et al., 2003).

In this study a numerical model for the absorption–desorption of PCDD/Fs in PP has been developed. The model has been applied to the PP test rods at the Thisted plant and to the PP tower packings at the SAKAB scrubber. The diffusivities in PP and gas/PP partition coefficients for different PCDD/F congeners were determined using the model and compared between the plants.

2. Materials and methods

In the Thisted plant, $4 \times 20 \times 165$ mm PP test rods were installed in a wet scrubber exposed to flue gases at 65 °C (Andersson et al., 2003). The average PCDD/F concentration in the gas was 8 ng TEQ/m^3_N according to method EN1948 (European Committee for Standardization, 2006) during one year. The ESP was replaced by a fabric filter after one year and the PCDD/F concentration decreased to < 0.1 ng TEQ/m^3_N. The test rods were left in this concentration for more than two years. The PCDD/F concentrations in the test rods were analysed for homologue concentrations after 1, 3, 6, 9, 12, 18, 30 and 40 months of exposure. One flue gas measurement during the operation period with the fabric filter showed that the concentration of 2,3,7,8-substituted tetra to hexa congeners were 99% lower than during the ESP operation period. This observation was used in the calculations.

Flue gases after the scrubber at the SAKAB plant have been continuously sampled for PCDD/F since July 2001 using a commercial long-term sampling equipment named AMESA. The sampling period has been two weeks for each sample. The AMESA-system has been described by Mayer et al. (2000). Flue gases from the flue gas duct after the scrubber are led through a XAD-cartridge on which the dioxins are collected. The AMESA cartridges were analyzed according to EN1948 at Eurofins GfA in Münster Roxel, Germany. Eurofins GfA is accredited according to DIN EN ISO/IEC 17025:2000 and participates in intercalibration studies on a regular basis. Three periods from 2002 showing a memory effect were chosen for the modelling of the SAKAB-scrubber. TEQ values from these periods are shown in Fig. 1.

A numerical model was developed for the absorption–desorption of PCDD/Fs in PP. It was assumed that the surface concentration of PCDD/F is proportional to the gas phase concentration as defined by the partition coefficient. The mass transport inside the PP-material (scrubber tower packings or test rods) was described by solid phase diffusion. The geometry of the test rods and of the fillings in the SAKAB scrubber suggested that a one dimensional diffusion equation could be used (Eq. (1) below). The diffusion in the shortest direction (4 mm thickness) completely dominates the mass transport in the test rods. According to Crank (1975) the partial differential equation describing one-dimensional transient diffusion is

$$\frac{\partial C}{\partial t} = D_{AB} \cdot \left[\frac{\partial^2 C}{\partial r^2} + \left(\frac{\text{geom} - 1}{r}\right) \cdot \frac{\partial C}{\partial r}\right], \quad (1)$$

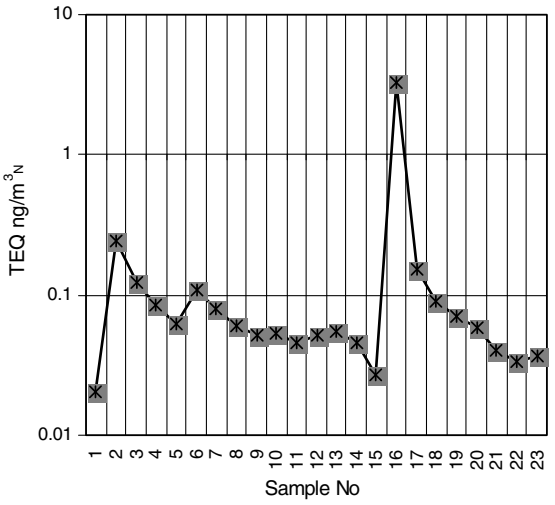

Fig. 1. TEQ-values after the SAKAB scrubber during the modelled period. The samples are consecutive samples from the AMESA system. Each sample covers two weeks of operation, except no 16 which is measured during an actual start-up period (48 h). Three decline phases can be identified, starting with point 2, 6, and 17.

where C=concentration of PCDD/F in PP with respect to time (t) and position (r). D_{AB} = the diffusivity of PCDD/F in PP. Geom = 1 for cartesian coordinates and geom = 2, for cylindrical coordinates. Discretising Eq. (1) yields

$$\frac{\Delta C}{\Delta t} = D_{AB} \cdot \left[\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta r^2} + \left(\frac{\text{geom} - 1}{r_i}\right) \frac{C_{i+1} - C_{i-1}}{2\Delta r}\right]. \quad (2)$$

A zero gradient boundary condition was applied in the middle of the material, i.e. the concentration at r_0 is equal to the concentration at r_1. The calculation points (nodes) are numbered from the centre of the PP-material to the surface. The surface node is denoted n (see list of symbols) and the surface boundary condition is given by the gas concentration and partition coefficient.

The implicit Crank–Nicolson method, where the time derivative in Eq. (2) is evaluated at time step n and $n + 1$, was used in the evaluation of Eq. (2). TriDiagonal-Matrix Algorithm (TDMA) was used to solve the resulting algebraic equations (Chapra and Canale, 2002). For the test rod model, 640 nodes and 1230 time steps were used to achieve convergence. Eq. (2) was solved for tetra, penta and hexa homologues in the test rods. The diffusivities and partition coefficients were obtained by regression, minimizing the sum of squared residuals between the measured and modelled concentrations. These results were used as input values to a numerical model of the SAKAB scrubber.

The SAKAB scrubber was modelled in a two stage model where the calculated outlet gas concentration from the first stage was the inlet gas concentration to the second stage as seen in Fig. 2. It was assumed that all absorption in the scrubber occurred in the PP tower packings since it represented the largest internal surface area. The tower packings were approximated with a long cylinder, 2.9 mm in diameter and 1.19×10^6 m long. This estimation corresponds to the surface area and volume of the packing material. For each scrubber stage, Eq. (2) was solved in cylindrical coordinates with 100 nodes in the radial direction and 6768 time steps, which correspond to 94 days of operation. The absorption was assumed to take place only during start up of the plant, which typically took 48 h. One gas measurement after the scrubber was done during start-up period (point 16 in Fig. 1). The PCDD/F concentrations after the scrubber asymptotically approached a steady state concentration at the end of each decline phase (see Fig. 1). At that point, the inlet to the scrubber was assumed to be equal to the