PCDD/F Diffusion Velocities in Polypropylene

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Introduction

In recent years Forschungszentrum Karlsruhe developed a thermally regenerable PCDD/F removal system [1] and demonstrated the operability of the system in a pilot plant. This system is based on the property of polypropylene (PP) of absorbing PCDD/F at low temperatures (≈80°C) and releasing the absorbed PCDD/F at temperatures of ≈130°C. This absorption/desorption process is highly controlled by the diffusion velocity of PCDD/F in PP [2]. To gain a better understanding of this process, the diffusion velocities of selected PCDD/F were determined in PP at different temperatures.

Experimental

PCDD/F sampling and sample preparation for analysis were conducted in accordance with the European guideline EN 1948 [3]. All PCDD/F congeners used were obtained from Promochem (Wesel, Germany). Nearly spherical PP granules (NOVOLEN N 1100, BASF) with different diameters (PP01: 1-1.4 mm, PP02: 2-2.8 mm, PP03: 4-5 mm) were loaded homogeneously with defined amounts of the single PCDD/F.

The setup of the experiment is shown schematically in Fig.1. One layer of each of the PCDD/F-loaded PP granules was placed in a glass tube which was mounted in parallel in an oven. The glass tubes were passed by room air at a defined temperature. The desorption time was 1 hour. The desorption gas was sampled and analyzed. The experiment was carried out at temperatures of 65°C, 80°C, and 130°C.

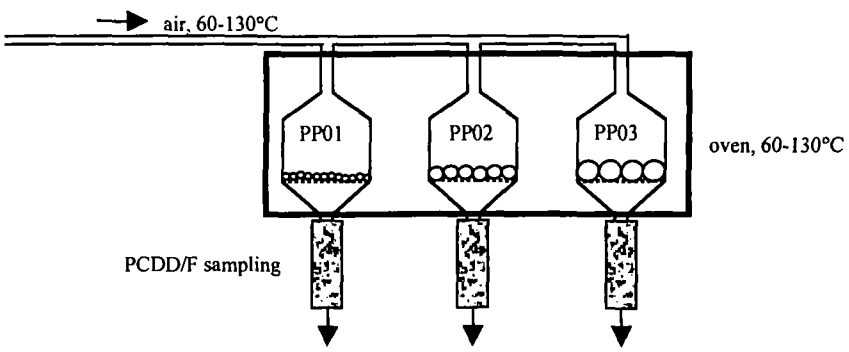

Fig.1: Schematic diagram of the experimental setup

Results

a) Diffusion Velocities of PCDD/F in PP at 130°C

From the PCDD/F concentrations in the desorption gas and the known PCDD/F concentration in PP, the desorption rates of the individual congeners were calculated for the three different grain sizes: **desorption rate = c/c_0 * 100 % per hour**
(c= PCDD/F loading of the desorption gas , c_0= PCDD/F loading of the PP)
In Table 1 the percentage of desorption/hour of each congener is listed:

Congener	PP 01 (1.0-1.4 mm)	PP 02 (2.0-2.8 mm)	PP 03 (4.0-5.0 mm)
1,2,3,4-TCDF	**35.0**	**18.3**	**8.9**
1,2,3,4-TCDD	**33.0**	**17.5**	**11.7**
1,2,3,8,9-PeCDF	**20.8**	**8.0**	**5.8**
1,2,3,4,6,8-HxCDF	**21.9**	**9.5**	**6.3**
1,2,3,4,6,7,8-HpCDF	**17.0**	**7.7**	**4.7**
OCDF	**10.5**	**4.1**	**2.5**
OCDD	**13.7**	**3.8**	**3.2**

Table 1: Desorption rates **(% per hour)** of PCDD/F at 130°C

The decrease of the desorption rate with increasing diameter of the PP particles is evident.

From these desorption rates the diffusion velocities of the PCDD/F were calculated based on the assumption of a stationary diffusion, i.e. there is no change of the PCDD/F concentration in PP during the experimental time.

In Table 2 the calculated diffusion velocities of the single congeners are listed.

Congener	PP 01 (1.0-1.4 mm)	PP 02 (2.0-2.8 mm)	PP 03 (4.0-5.0 mm)
1,2,3,4-TCDF	**80**	**78**	**70**
1,2,3,4-TCDD	**75**	**73**	**91**
1,2,3,8,9-PeCDF	**45**	**33**	**44**
1,2,3,4,6,8-HxCDF	**47**	**39**	**47**
1,2,3,4,6,7,8-HpCDF	**36**	**32**	**36**
OCDF	**22**	**18**	**20**
OCDD	**28**	**16**	**23**

Table 2: Diffusion velocity **(µm / h)** of single PCDD/F congeners at 130°C

For the three variably grained PP granules, the calculated diffusion velocities agree well within the limits of measurement accuracy. The decrease in the diffusion velocity with increasing degree of chlorination is clearly visible.

b) Temperature Dependence of Diffusion Velocities of PCDD/F in PP

The results of the experiments performed at 65°C and 80°C were computed in analogy to the results at 130°C. Also here, the results obtained for the variably sized granules are in good agreement.
To compare the temperature dependence of the diffusion velocities, the arithmetic mean was taken from the values obtained for the three different grain sizes.

In Table 3 the mean diffusion velocities are listed for the individual congeners at the three temperatures.

A strong temperature dependence of the PCDD/F diffusion velocities must be noted for all degrees of chlorination.

Congener	65°C	80°C	130°C
1,2,3,4-TCDF	**0.7**	**10**	**76**
1,2,3,4-TCDD	**0.4**	**8**	**80**
1,2,3,8,9-PeCDF	**0.2**	**4**	**41**
1,2,3,4,6,8-HxCDF	**0.1**	**1.5**	**44**
1,2,3,4,6,7,8-HpCDF	**<0.1**	**0.8**	**35**
OCDF	**<0.1**	**0.5**	**20**
OCDD	**<0.1**	**0.6**	**22**

Table 3: Temperature dependence of the PCDD/F diffusion velocities in PP (dimension:**µm / h**)

Conclusions

PCDD/F diffusion in PP was found to be strongly dependent on both the temperature and the degree of chlorination. This has the following effects on the technical process:

- Complete regeneration of PCDD/F loaded PP (grain size 4-5 mm) takes a long period of time due to the very low diffusion velocities in particular of the highly chlorinated PCDD/F.
- Use of PP granules with a smaller diameter (~1 mm) would result in a more rapid regeneration in the technical process.

References

/1/ S. Kreisz, H. Hunsinger, H. Vogg, Chemosphere, 34 (1997), 1045-52
/2/ S. Kreisz, H. Hunsinger, H. Seifert, Chemosphere, 40 (2000), 1029-31
/3/ EN 1948, Parts 1-3, draft version, 1995