Formation of PCDD/F on different lignites

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Abstract

The potential of formation of polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) on lignites from different opencast mines was investigated. Lignites were treated with wet air at temperatures between room temperature and 300°C to simulate possible situations in (former) opencast mines. Analysis of PCDD/F was also performed with untreated lignite. Highly chlorinated dioxins and furans were found especially after treatment at 300°C but also on some untreated lignite. Chlorine content is not the only reason for the formation of PCDD/F at 300°C. Ash content was found to have influence on amounts of PCDD/F.

Introduction

Within the scope of the BMBF project „Laborexperimente und analytische Untersuchungen über den Eintrag braunkohlebürtiger organischer Stoffe in Grundwässer und Restseegewässer bei der Flutung von Braunkohletagebauen" mobilization of organic compounds at flooding of former opencast mines is investigated. In addition to passing over of polar compounds to water formation of chlororganic compounds has to be considered. Older investigations show no uniform opinion whether lignite is a source for PCDD/F or not [1), 2), 3), 4)]. At former opencast mines conditions similar to those for a de-novo-synthesis of PCDD/F are found: the presence of carbon, chlorine and oxygen. Mineralic components may have catalytic effects. While sometimes lignites show high tendency of spontaneous selfinflammation occurence of higher temperatures has to be considered. Conditions for formation of PCDD/F on natural lignite were investigated using lignite of the opencast mines

- Berzdorf (Oberlausitzer Revier, to the east of the river Elbe)
- Scheibe (Niederlausitzer Revier, to the east of the river Elbe)
- Merseburg-Ost (Mitteldeutsches Revier, to the west of the river Elbe)

At Scheibe and Merseburg-Ost weather-beaten and unweather-beaten lignite was taken. „Weather-beaten" means atmospheric contact for several month up to years, „unweather-beaten" means only short contact (several hours) to the atmosphere before taking of samples.

In general lignites from the east of the Elbe are younger (55 million years) than those from the west of the Elbe (65-70 million years), are less conjugated, contain more oxygen and less sulphur. Following parameters are supposed to influence the formation of PCDD/F: Chlorine content, Cl/S-ratio [2)], ash content and ratio of aromatic/aliphatic groups. Characterization of the lignites was carried out using elementary analysis, ^{13}C-CP-MAS-TOS-NMR and petrography.

Experimental and clean-up

Lignite in former opencast mines is exposed to unhindered atmospheric influences which were simulated in laboratory. An apparatus as shown in fig. 1 was used. Lignite was treated with wet air at temperatures between room temperature and 300°C. Time of treatment was also varied from 2 up to 48 hours. Technical air with a flow rate about 2,5 ml/s passes throw water and flows from bottom to top throw a furnace in which lignite is located. The air stream is leaded into a cool trap filled with toluene.

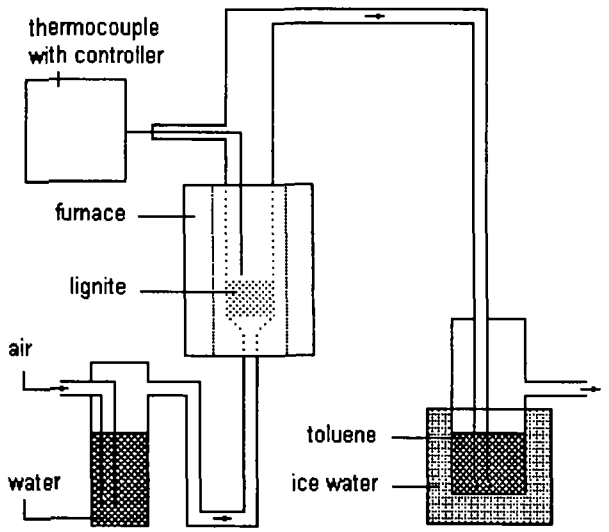

fig. 1 Apparatus for thermal treatment of lignite

After treatment the apparatus was rinsed with toluene. Then anhydrous Na_2SO_4 was added for drying. The lignite was extracted with toluene for 48 hours. The resulting extract was dried over anhydrous Na_2SO_4 again.
Large amounts of aliphatic compounds were considered to cause matrix problems therefore first clean-up step was performed using liquid/liquid extraction with dimethyl sulfoxide to separate aliphatic compounds from aromatic compounds followed by column chromatography on acid/basic silica gel and alumina.
Analyses were performed using a HP 5890 GC / HP 5971 MSD with a DB-5 ms capillary column (30m x 0.25mm x 0.25µm).

Results and discussion

After thermal treatment of lignite PCDD/F are formed especially at 300°C. Homologue profiles are very similar but great differences between various lignites were found after comparison of concentrations. Lignite from the opencast mine Berzdorf showes a higher potential of formation of PCDD/F at 300°C than lignite from Scheibe or Merseburg-Ost. PCDD/F were not detected for weather-beaten Merseburg-Ost lignite. The value for Berzdorf lignite was 29 ng/g.

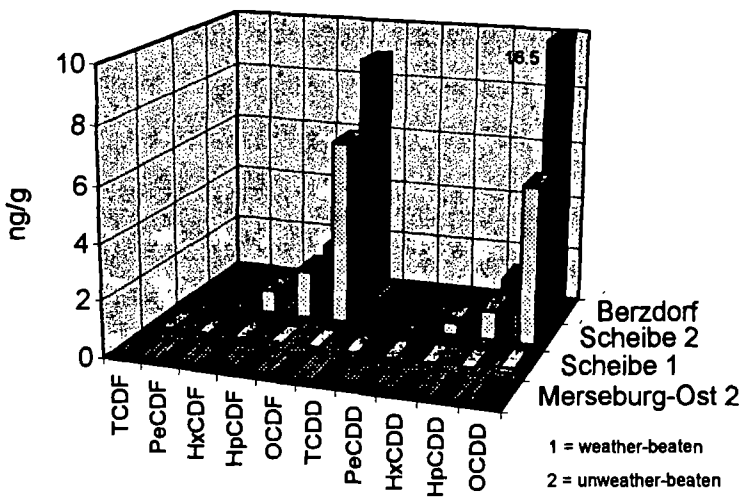

fig. 2 PCDD/F after thermal treatment of lignites (2h, 300°C)

At lower temperatures, e.g. 100°C, only OCDD/F at very low concentrations could be found for the Berzdorf and Scheibe lignite.
Unweather-beaten lignite shows higher concentrations than weather-beaten ones. This is also found for untreated lignite. The only explanation is that PCDD/F were formed during coal genesis and were reduced under atmospheric influence.
Results at higher temperatures like 300°C are astonishing because Merseburg-Ost lignite is known for high chlorine content (about 1%Cl). Investigations about combustion of salt coal in a domestic furnace show strong dependence between chlorine content and formation of PCDD/F [6]. It has to be considered that the conditions of thermal treatment as described above are different to combustion. Other parameters, e.g. ash content, were found to have great influence on PCDD/F concentrations: Berzdorf lignite with highest ash content of the investigated lignites shows highest values for PCDD/F. Ash components may have catalytic effects on PCDD/F formation.

Acknowledgments

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Literature

(1) Reissig, M. Dissertation submitted for a diploma. University of Leipzig **1991**
(2) Griffin, R.D. *Chemosphere* **1986**, 15/9-12, 1987-1990
(3) Mahle, N.H.; Whiting, L.F. *Chemosphere* **1980**, 9, 693-699
(4) Junk, G.A.; Richard, J.J. *Chemosphere* **1981**, 10/11-12, 1237-1241
(5) Orazio, C.; Meadows, J.; Kapila, S.; Palmer, C.; Yanders,A.F. *Chemosphere* **1989**, 18, 69-76
(6) Thuß, U.; Popp, P.; Ehrlich, C.; Kalkoff, W.-D. *Chemosphere* **1995**, 31, 2591-2604