Formation of chlororganic compounds on different lignites

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Introduction

In the eastern part of Germany back-filling of hundreds of former opencast mines is a very important objective for the next decades. A lot of problems may occur: at flooding stability of heaps has to be considered, and after re-rising of ground waters pH values may drop below 2 leading to mobilization of heavy metals. Formation of organic lignite derived products was less investigated but has to be considered in this context.

Lignite in former opencast mines is exposed to unhindered atmospheric influences. Newly formed or released polar compounds may pass over into water and formation of chlororganic compounds has to be considered, e. g. PCDD/F are formed in a so-called de-novo-synthesis, if carbon, inorganic chloride, oxygen and catalytic metal salts are present. Since lignite may contain high amounts of chlorides and ferrous minerals these conditions were found at opencast mines. Beside copper salts ferrous salts show the highest catalytic effects on PCDD/F formation on fly ash[1]. Temperature dependence of the formation of PCDD/F and other chlororganic compounds has been described for several carbon sources, e.g. activated charcoal, soot, graphite, fullerenes and wood[2]. Maximum concentrations of PCDD/F were found at higher temperatures between 300 °C and 500 °C depending on carbon structure. So higher temperatures may be important for the formation of chlororganic compounds on lignites, too. While sometimes lignites show high tendency to spontaneous selfinflammation, occurence of higher temperatures at opencast mines has to be considered.

At the former opencast mines Scheibe (Niederlausitzer Revier, to the east of the river Elbe) and Merseburg-Ost (Mitteldeutsches Revier, to the west of the river Elbe) samples of weathered and unweathered lignite were taken in order to investigate the role of weathering in formation of chlororganic compounds. „Weathered" means atmospheric contact for several month up to years, „unweathered" means only short contact (several hours) to the atmosphere before taking of the samples.

Formation of chlororganic compounds like polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) and polychlorinated biphenyls (PCB) on different lignites was investigated. Analyses were carried out on untreated lignite and after thermal treatment of lignite. Lignites were treated with wet air at temperatures between room temperature and 300 °C in order to simulate situations possible in former opencast mines. Beside chlorine and ash contents[3]

degree of weathering was found to have an influence on whether PCDD/F and PCB are formed or not. Weathered lignites show higher potential of PCDD/F and PCB formation than unweathered ones.

Experimental and clean-up

Analyses were carried out on untreated lignite and after thermal treatment of lignite. An apparatus as shown in fig. 1 was used for thermal treatment. Lignite was treated with wet air at 300 °C. 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.

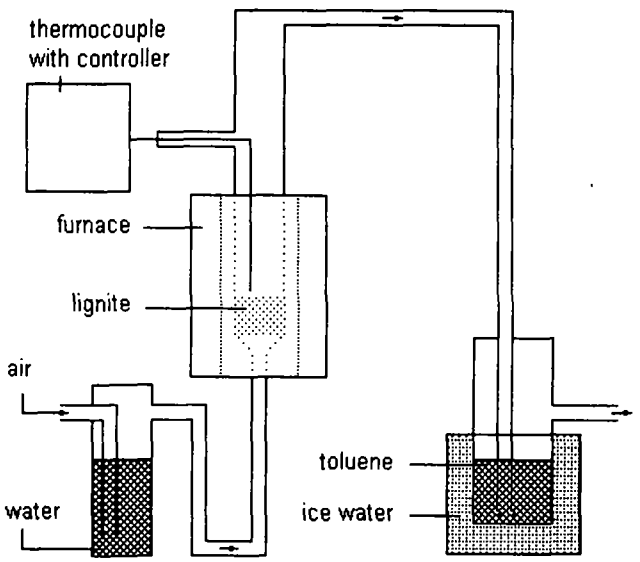

Fig. 1 Apparatus for thermal treatment of lignite

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, a 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

In untreated lignite from the former opencast mine Scheibe, PCDD/F and PCB were found at ppt level (ng/kg carbon). Higher concentrations were found in weathered than in unweathered lignite. In Merseburg-Ost lignite only PCB were found.

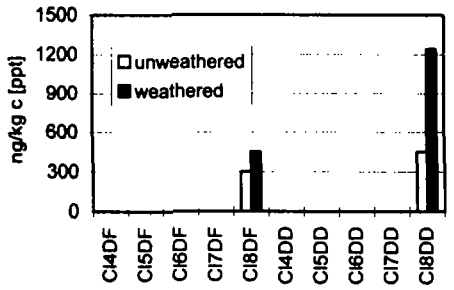

Fig. 2 PCDD/F at Scheibe

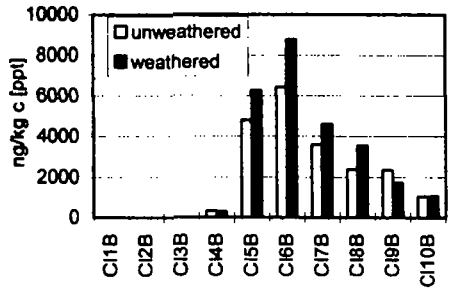

Fig. 3 PCB at Scheibe

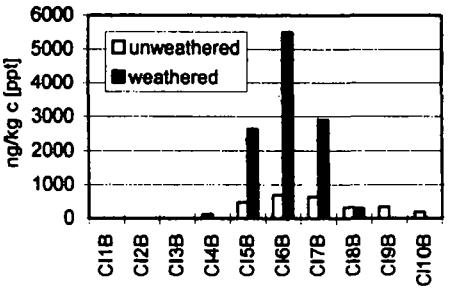

Fig. 4 PCB at Merseburg-Ost

During weathering oxidation of coal structure occurs. As described in literature[4] aromatic ethers may be formed leading to PCDD/F pre-structures. In general higher oxygen content leads to higher amounts of PCDD/F. This was found both for weathered/unweathered lignite and for relatively young/old lignite. Younger lignite contains more oxygen than older lignite; lignite from the opencast mine Scheibe is younger than from Merseburg-Ost and contains PCDD/F, but for untreated Merseburg-Ost lignite no PCDD/F were detected. Beside the formation of oxygen-containing functional groups, oxidation also means cracking of coal structure. So the effect of weathering is the same for PCB as for PCDD/F formation.

After thermal treatment of Scheibe lignite with wet air at 300 °C twice as much PCDD/F were found than in untreated lignite. PCDD/F were also found in original weathered Merseburg-Ost lignite but not in unweathered lignite. PCB concentrations decrease at higher temperatures.

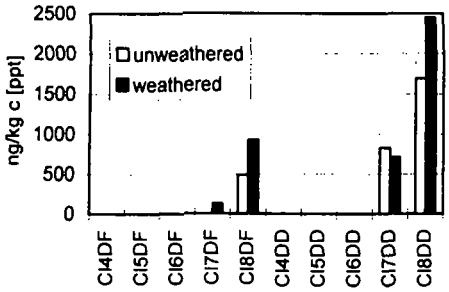

Fig. 5 PCDD/F at Scheibe after thermal treatment at 300 °C

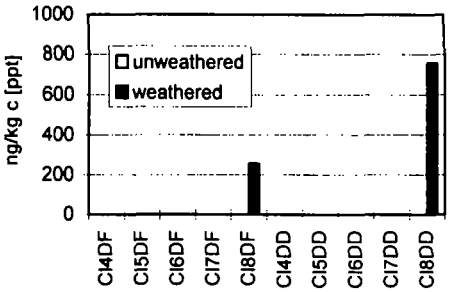

Fig. 6 PCDD/F at Merseburg-Ost after thermal treatment at 300 °C

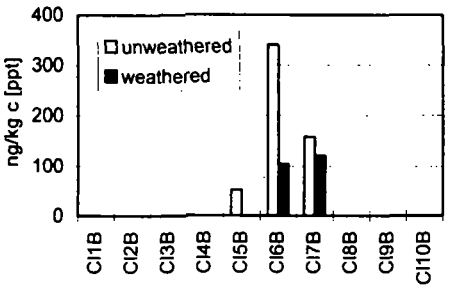

Fig. 7 PCB at Scheibe after thermal treatment at 300 °C

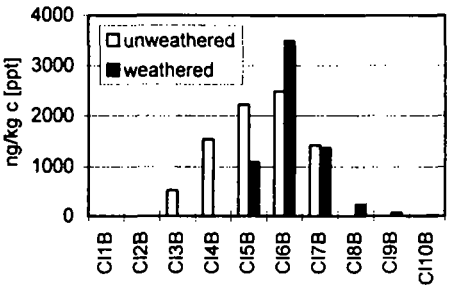

Fig. 8 PCB at Merseburg-Ost after thermal treatment at 300 °C

At higher temperatures stronger oxidative conditions were found leading to higher PCDD/F concentrations. But still the original degree of weathering plays an important role because oxygen-containing groups at coal surface are important for further oxidation. At these oxidative conditions more oxygen containing substances were formed and PCB concentrations decrease.

Acknowledgments

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