THE DE-NOVO-SYNTHESIS OF PCDD/PCDF AND OTHER ORGANOHALOGEN COMPOUNDS ON FLY ASH

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Basically, two completely different reactions are discussed as important pathways to PCDD/PCDF formation: a) the high temperature chemistry in the flame itself, leading to chlorobenzenes and phenols with subsequent condensation, and b) the de-novo-synthesis at low temperatures occurring by gas-solid interactions on fly ash. In detailed studies, the chemistry of the latter process and its major parameters were evaluated, with the following conclusions:

1. Preformed high molecular aromatic structures of particulate carbon in the fly ash are converted by reactions with inorganic chloride to organochloro compounds yielding a great variety of congeners and isomers of chlorobenzenes, -naphthalenes, -biphenyls, -thiophenes, -benzothiophenes, -benzonitriles, -phenols, -benzofurans, PCDD, PCDF and also non-volatile compounds.

   The formation potential for these compounds is proportional to the carbon content of the fly ash. The conversion of carbon to aromatic chlorocompounds depends on the type of carbon. The physico-chemical surface area has however, only a minor influence on the reaction yield.

2. The reaction is induced by metal ions, preferably Cu^{2+}, in the presence of oxygen, by an interaction of the metal ions with the aromatic structures, leading to the formation of organic radicals which may react with H_2O, Cl or Cl_2 to yield, finally, thermodynamically stable units. In the presence of bromide/chloride, mixed chloro-bromo compounds have been identified.

   Water vapor in the gas phase results in preferred formation of PCDD against PCDF. The end product of this degradative oxychlorination is CO_2.

3. The reaction proceeds at moderate temperatures. An optimum temperature range for the formation of PCDD/PCDF as well as for other chlorocompounds was found to be 270-350°C. A recent more detailed study shows a second maximum of formation to occur at 470°C. From this it is indicated that, depending on temperature, two different formation mechanisms must be considered.