

SOUR I

The Role of NaCl and CaCl₂ in the Formation of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans from Carbon

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Introduction

Formation of polychlorinated dibenzo-p-dioxins/ dibenzofurans from carbon (de novo synthesis) has been advanced as an important reaction pathway in the post combustion zone of waste incinerators.¹ Laboratory experiments suggest that the DD/F structures either already exist in the carbon,² or can be formed through intermediates like chlorophenols.³ A mechanism in which chlorination of the carbon precedes the release of the PCDD/F molecules has been proposed by various authors.^{4,5}

The chlorine used in the formation mechanism could have various forms, solid inorganic and organic, and come from the gas phase (e.g. HCl) too. Stieglitz et al. have shown that both CuCl₂ and FeCl₃ assist de novo synthesis of PCDD/F on laboratory scale by catalyzing Cl transfer to carbon.⁶ Other chlorides might act as a Cl source only, i.e. no direct transfer from such a chloride to carbon is possible, unless suitable catalysts (Cu or Fe ions) are available. NaCl and CaCl₂ could be such inorganic Cl sources. Apart from the possibility that these two metal chlorides act as a Cl source, some potential catalytic activity cannot be excluded. Hinton & Lane found some correlation between PCDD formation and the presence of Na ions in laboratory experiments with pentachlorophenol as reactant;⁷ however, when present as NaOH, an inhibitory effect was seen.⁸ CaO and CaCl₂ have been advanced as chlorination catalysts for PCDD/F formation in cement kilns.⁹ In this paper, we report on preliminary results obtained with NaCl and CaCl₂ as part of a larger study on the role of inorganic and organic Cl in de novo synthesis.

Experimental

Ca. 11-17 g of fly ash from a municipal waste incinerator was sieved to a particle size < 210 μm for homogeneity and soxhlet-extracted with toluene for 63-67 h. This leaves residual carbon as reactant. In experiments where no NaCl or CaCl₂ was added to the fly ash, reaction mixtures consisted of 0.25-0.50 g fly ash and 0.50-0.75 g glass beads, mixed physically. When either NaCl or CaCl₂ were added, mixtures contained: 0.33-0.50 g fly ash, 0.03-0.17 g NaCl and 0.46-0.50 g glass beads; or 0.33-0.47 g fly ash, 0.03-0.17 g CaCl₂ and 0.50 g glass beads; all mixed physically. The total sample weight was always 1 g. We determined the amount of inorganic Cl present in a reaction mixture by splitting it prior to

the experiment, followed by aqueous extraction and titration with AgNO_3 .¹⁰

The mixture was placed in a pyrex glass or quartz tube against a glass frit. The tube was heated in a furnace (Blue M model 55035, Lindberg, Watertown, WI, USA with Eurotherm 847 digital controller, Eurotherm, Reston, VI, USA, stability $\pm 1^\circ\text{C}$) for 60 min to the desired temperature under a stream of N_2 . Once the mixture had reached the reaction temperature (251-353 $^\circ\text{C}$), a mixture of 6, 10 or 21% O_2 in N_2 was passed through the bed for 15-120 min. The flow of both N_2 and O_2/N_2 was controlled by mass flow controllers (models 202C and 202 D, Teledyne-Hastings, Hampton, VI, USA). The flow was measured using a flow meter behind the experimental apparatus. Any PCDD/F desorbing from the fly ash surface was collected in a cold trap filled with toluene (cooled with ice, 0°C).

After the experiment, the fly ash and cold trap fractions were combined, spiked with a 10 μL solution containing 9 $^{13}\text{C}_{12}$ -PCDD/F congeners (one congener for each $\text{T}_4\text{CDD-OCDD}$ and $\text{T}_4\text{CDF-H}_7\text{CDF}$ homologue, concentration 10-20 ng per spike, Cambridge Isotope Laboratories, Andover, MA, USA) and soxhlet-extracted with toluene for 24 h. Afterwards, the volume of the sample was reduced in a rotary evaporator to a few mLs. The sample was then purified using chromatographic columns containing acidified and alkaline silica (first step) and alumina (second step). Subsequently, it was dissolved in 10 μL of tetradecane and analyzed on a combined Hewlett-Packard 5890 series II Gas Chromatograph and HP 5971 Mass Selective Detector, measuring M^+ , $\text{M}+2$, $\text{M}+4$ for $\text{T}_4\text{CDD-H}_6\text{CDD}$ and $\text{T}_4\text{CDF-H}_6\text{CDF}$ and $\text{M}+2$, $\text{M}+4$ and $\text{M}+6$ for $\text{H}_7\text{CDD-OCDD}$ and $\text{H}_7\text{CDF-OCDF}$.

The fly ash extracted in 11-17 g batches prior to experiments, to remove native PCDD/F and possible precursors, still contained 40-160 ng/g of PCDD and 10-30 ng/g of PCDF. These numbers were subtracted from the amounts of PCDD/F formed during the experiments. NaCl , CaCl_2 and the glass beads contained negligible amounts of PCDD/F.

Results and Discussion

In a first series of experiments, the optimum temperature for PCDD/F formation with the fly ash was determined. Results are reported in Table 1. As can be seen, the total amount of PCDD/F formed at 299 and 323 $^\circ\text{C}$ was quite similar, 2600-3000 ng/g. However, the [PCDD]:[PCDF] ratio changes from 1.0-1.1 at 299 $^\circ\text{C}$ to 0.5 at 323 $^\circ\text{C}$.

In Figure 1, the formation of PCDD/F as function of the NaCl concentration is depicted. At 0% NaCl , duplicate runs were performed with a 25% fly ash/75% glass beads mixture and with a 50%/50% mixture. The amount of formation increases from 1570 ± 110 ng/g to 2860 ± 170 ng/g. The reason of this effect is not clear. Glass beads proved to be inert in

Table 1. Temperature study of the fly ash. (Concentrations in ng/g fly ash)

Temperature, $^\circ\text{C}$	Σ PCDD	Σ PCDF	[PCDD]:[PCDF]
251	50	20	2.5
277	70	200	0.4
299	1450 ± 50	1410 ± 120	1.0-1.1
323	870	1740	0.5
353	40	540	0.1

Conditions: 0.50-0.51 g fly ash ($< 210 \mu\text{m}$, toluene extracted) and 0.48-0.49 g glass beads; reactant: residual carbon; 60 min; flow: 10% O_2 in N_2 , 93 ± 8 mL/min; single experiments, except runs at 299 $^\circ\text{C}$ (duplicate).

SOUR I

earlier studies,¹⁰ and therefore the change in the amount of fly ash (from 0.25 g to 0.50 g) probably causes the increase in formation. Since in our experiments the amount of fly ash/NaCl mixture was constant (0.5 g), at increasing NaCl concentrations less fly ash was present in the reaction mixtures. Therefore, when comparing experiments with and without NaCl, at higher NaCl concentrations this comparison should be made with the 25% fly ash/75% glass beads experiment, rather than with the 50%/50% experiment.

At 4.3% NaCl, the amount of PCDD/F formed is quite similar to that in the 50%/50% runs with no NaCl. In fact, a slight decrease is noted. At higher concentrations, there is a decrease of formation; when compared with the 25%/75% runs without NaCl, similar amounts are formed with these higher NaCl concentrations. Together, these experiments suggest that NaCl does not, at least not at 299 °C, act as a Cl source in de novo synthesis. This inhibiting effect at higher concentrations could be explained by assuming an interaction with the active sites on the fly ash, thus reducing the number of sites available for formation. However, the fly ash used already contains ca. 5% inorganic Cl and the addition of NaCl might have no effect if a zero-order dependence exists at concentrations > 5%. In fact, in the runs with 4.3% NaCl, ca. 9% inorganic Cl is present on the fly ash.

No change was seen in the homologue distribution (not shown). An increase in the average degree of chlorination, i.e. a shift towards the higher chlorinated congeners, could be expected if NaCl is a strong Cl donor. We did observe a decrease in the [PCDD]:[PCDF] ratio as a result of the increasing NaCl concentration, from 1.0-1.1 at 0% NaCl (50%/50% runs) to 0.5-0.7 in the runs with added NaCl. In the 25%/75% runs (0% NaCl), a similar decrease (0.6-0.8, compared with the 1.0-1.1 in the 50%/50% runs with no NaCl) was noted and adding NaCl or glass beads might merely have the same diluting effect.

Figures 2 and 3 show the effect of the reaction time and [O₂] on the formation of PCDD/F. These runs were carried out with 4.3% NaCl added to the fly ash and they can be compared to runs with 50% fly ash/50% glass beads mixture (without NaCl added) under similar conditions. Increasing time or [O₂] leads to more formation of PCDD/F, but the addition of NaCl has little effect on this process: differences with runs without NaCl are small. The experiment with a reaction time of 120 min (Figure 2) suggests that addition of NaCl could have some effect at longer reaction times, but additional research is required to clarify this. In both series there was some fluctuation in the [PCDD]:[PCDF] ratio as result of the NaCl added, but without a clear trend (not shown). Again, no change was observed in either the PCDD or PCDF homologue distribution.

When 19% NaCl was added to the fly ash (299 °C, 60 min, 10% O₂/N₂), no HCl could be detected in the cold trap (filled with water). Furthermore, no change could be seen in the amount of NaCl present on the fly ash before and after the experiment. Of course, this (titration) technique does not allow for the detection of minute quantities of HCl or small (< 0.1%) changes in the NaCl concentration. Since the amount of NaCl added is some orders of magnitude higher than the amount of Cl incorporated into PCDD/F, NaCl could still play some role as a chlorinating agent on a micro scale.

When the fly ash is extracted with water prior to an experiment at 299 °C, almost no formation of PCDD/F is observed: 40 ng/g versus 2860 ± 170 ng/g with non-extracted fly ash (Table 1). Obviously, in the aqueous extraction either the catalyst, the inorganic Cl or both are removed. Redoping the fly ash with NaCl (6.4%) does not lead to a restoration of its PCDD/F formation potential: under similar conditions (60 min, 299 °C, 10% O₂/N₂), it now produces 160 ng/g PCDD/F.

In Figure 4, the influence of $[\text{CaCl}_2]$ on PCDD/F formation is shown. Again, the experiment with 3.4% should be compared with the 50%/50% runs without CaCl_2 , the higher concentrations with the 25%/75% runs. It is obvious that the addition of CaCl_2 has no effect on de novo synthesis and at higher concentrations, even acts as an inhibitor. Conversion to $\text{Ca}(\text{OH})_2$ and CaCO_3 could be an explanation, since these compounds are known to reduce PCDD/F formation.¹¹

Acknowledgement

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SOUR I

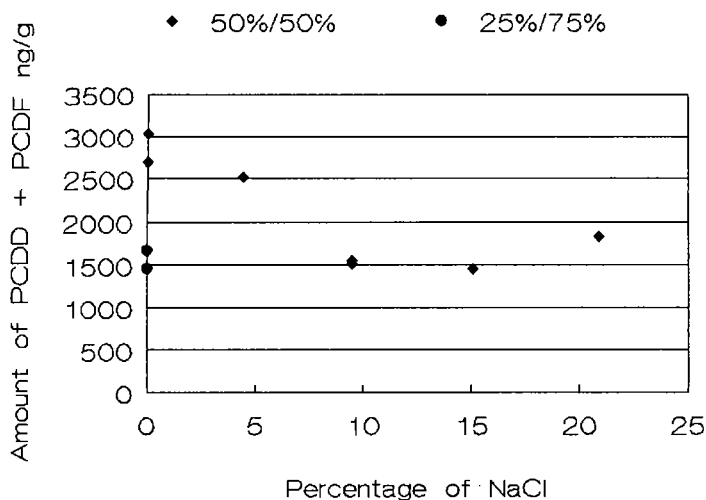


Figure 1. PCDD/F formation as function of [NaCl].

Conditions: 25%/75%: 0.25 g fly ash (<210 μm , toluene extracted) + 0.75 g glass beads; 50%/50%: 0.50 g of fly ash/NaCl and 0.50 g glass beads; reactant: residual carbon; 60 min; T=299 $^{\circ}\text{C}$; flow: 91 ± 7 mL/min of 10% O_2/N_2 .

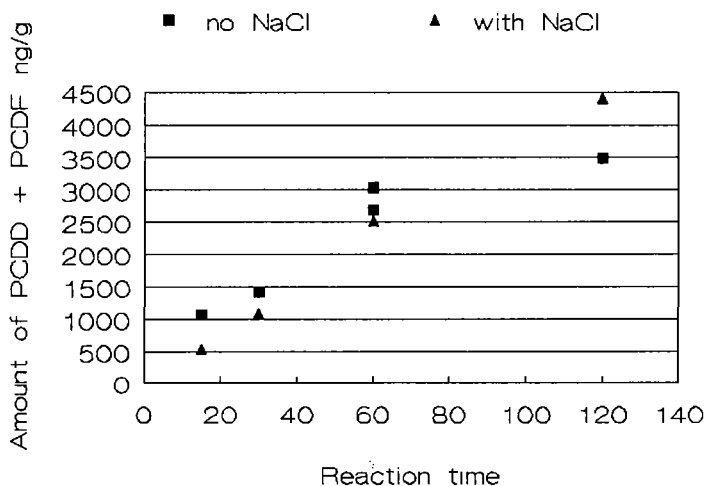


Figure 2. PCDD/F formation with/without NaCl as function of time.

Conditions: 0.46-0.50 g fly ash (<210 μm , toluene extracted), 0 or 4.3% NaCl, 0.46-0.50 g glass beads; reactant: residual carbon; 15-120 min; T=299 $^{\circ}\text{C}$; flow: 94 ± 3 mL/min of 10% O_2/N_2 .

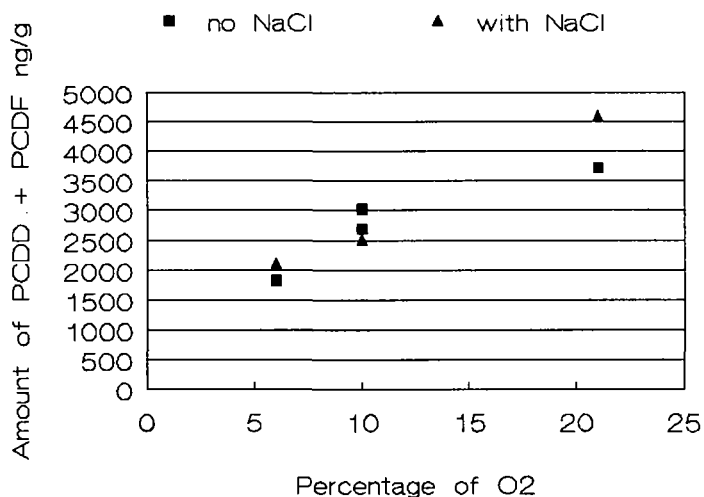


Figure 3. PCDD/F formation with/without NaCl as function of [O₂].

Conditions: 0.46-0.50 g fly ash (< 210 μm, toluene extracted), 0 or 4.3% NaCl, 0.46-0.50 g glass beads; reactant: residual carbon; 60 min; T=299 °C; flow: 93 ± 4 or 175 mL/min of 6, 10 or 21% O₂/N₂.

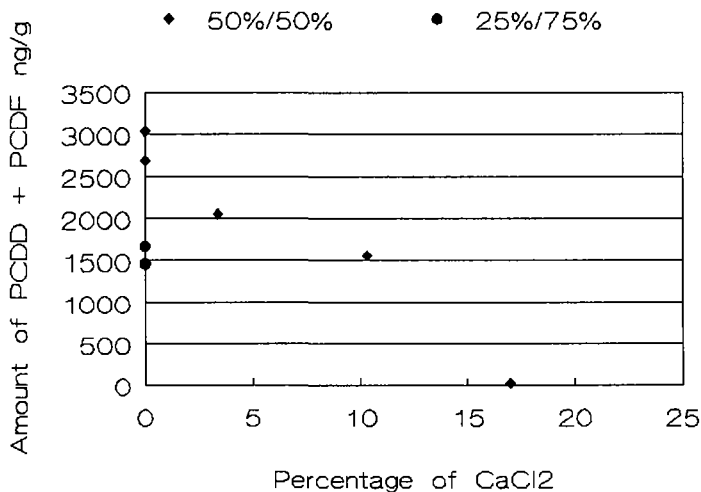


Figure 4. PCDD/F formation as function of [CaCl₂].

Conditions: 25%/75%: 0.25 g fly ash (< 210 μm, toluene extracted) + 0.75 g glass beads; 50%/50%: 0.50 g of fly ash/CaCl₂ and 0.50 g glass beads; reactant: residual carbon; 60 min; T=299 °C; flow: 91 ± 9 mL/min of 10% O₂/N₂.