Lo studio della cinetica e dei meccanismi di formazione delle PCDD/PCDF

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THE PROBLEM

PolyChloroDibenzo-*p* -Dioxins (PCDD) and
PolyChloroDibenzoFurans (PCDF) formation in combustion processes

STATE OF ART

APCDs become more and more sophisticated as emission limits became more and more low.

(END OF PIPE STRATEGY)

OUR STRATEGY

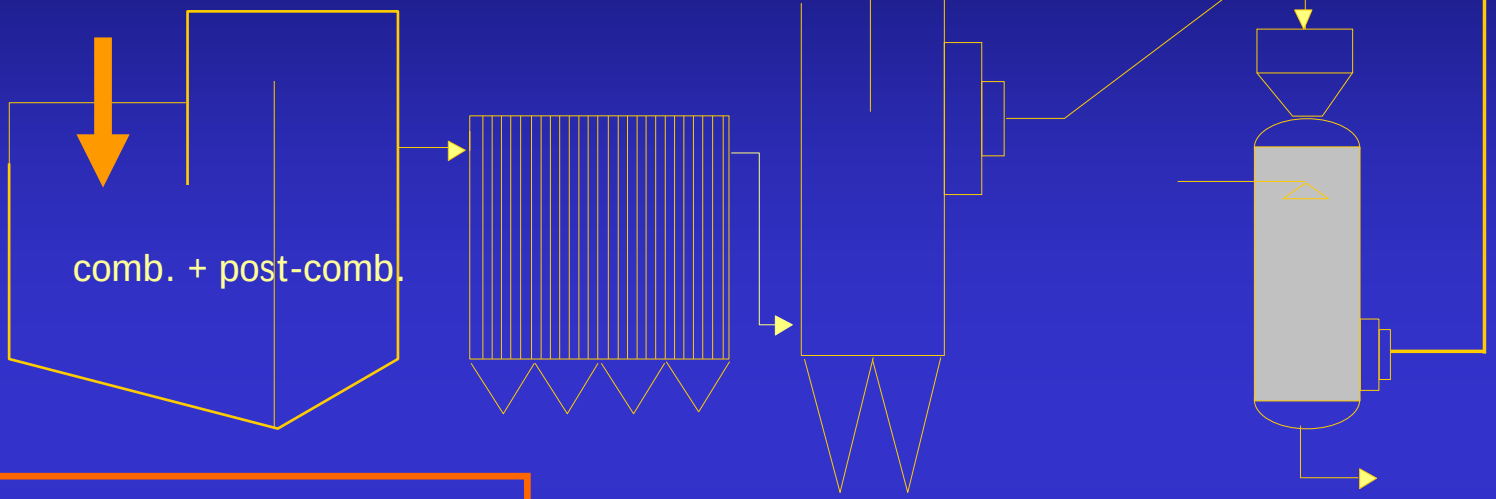
To prevent PCDD/PCDF formation.

(SUSTAINABLE TECHNOLOGY)

STACK

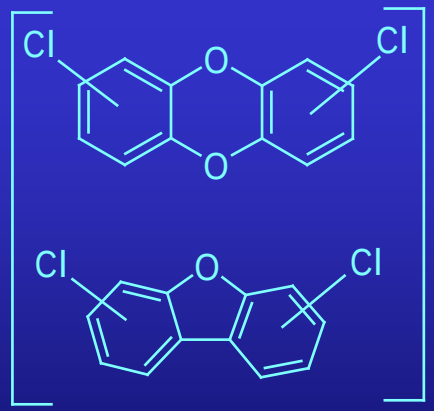
T = 950 - 1050°C

T = 250 - 400°C
COLD ZONES



BY-PRODUCTS

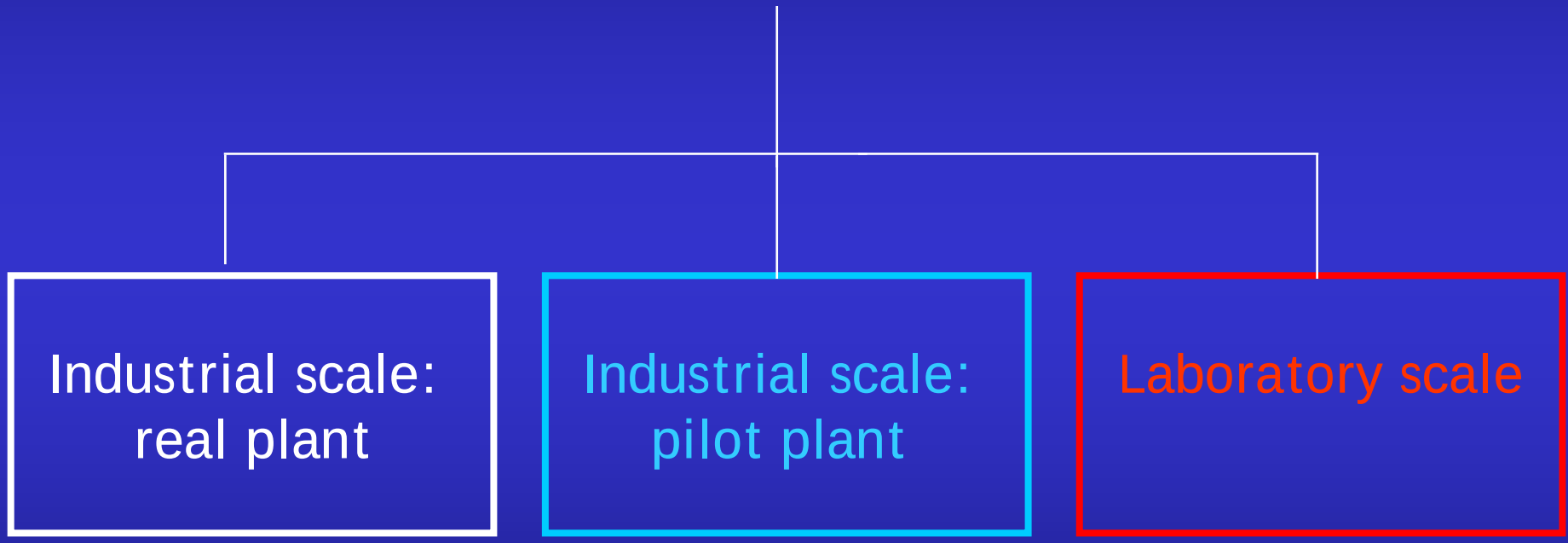
- CO, NO_X, SO_2, HCl, HF
- Inorganic micropollutants
- Organic micropollutants



PCDD/F

FLY ASH: catalyst and source of carbon

MUNICIPAL SOLID WASTE AND HAZARDOUS WASTE TREATMENT



MAIN RESULTS

PCDD/PCDF characterization in the feeding of a MSW incinerator and correlation with the possible sources.

Estimation of the environmental risk in terms of ngTEQ/Nm^3 and/or ngTEQ/g.

MAIN RESULTS

Setting-up of a methodology for *on-line* monitoring of the combustion process.

Effects of sampling procedure on qualitative and quantitative behaviour of PCDD/F fingerprints in the gaseous emissions.

MAIN RESULTS

Optimisation of process parameters in order to minimise PCDD/F formation

- ⇨ In the combustion chamber
- ⇨ In the post-combustion chamber
- ⇨ At the stack emissions

LAB SCALE STUDIES
STARTING POINTS FROM OUR AND LITERATURE STUDIES

Fly Ash collected in the "cold zone" of MSWI contains significant concentrations of PCDD/F.

PCDD/F are formed in the "cold zone" [280 < T (°C) < 350].

The observed concentrations of PCDD/F represent a balance between **degradation** and **formation** reactions.

PCDD/F are formed as traces (ppb) with respect to the organic materials in FA (very low reaction yields).

RESEARCH PROJECT AT LABORATORY SCALE

THERMAL DEGRADATION

THERMAL FORMATION

REAGENTS

OCDF in nitrogen stream with water vapor

OCDD in air stream with or without water vapor

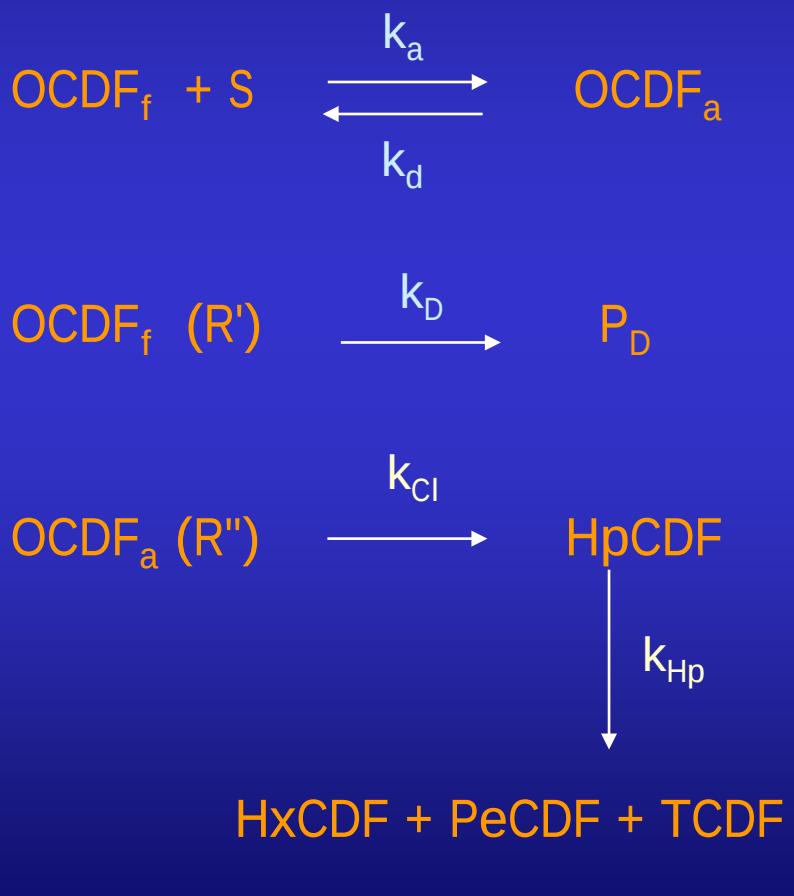
Reaction Scheme

⇨ Reactant (OCDF) partition
(**T dependent**)

⇨ Decomposition
(**pseudo-first order kinetics**)

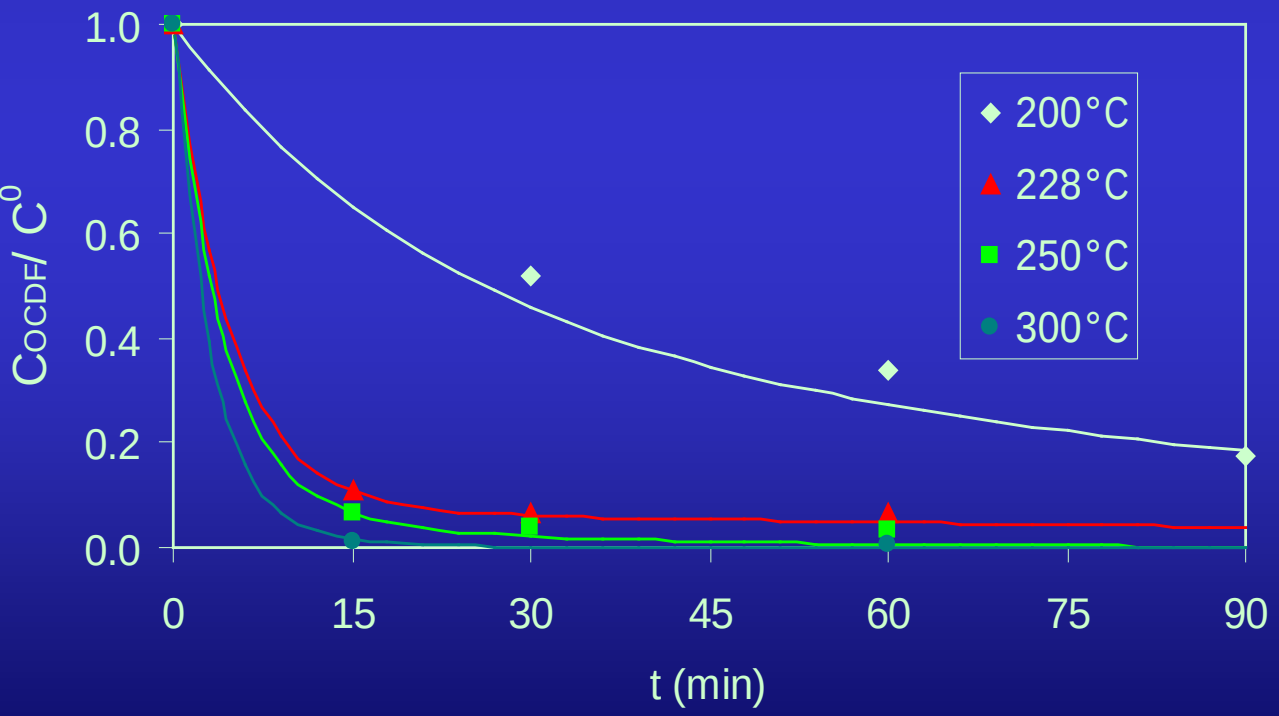
⇨ Dechlorination
(**first order series reactions**)

Reaction mechanism



REAGENT (R = OCDF in N_2) DISAPPEARANCE

$$\frac{C_R}{C^0} = \frac{C^0_{R'}}{C^0}\exp(-k_D t) + \frac{C^0_{R''}}{C^0_R}\exp(-k_{CI} t)$$



TO STUDY THE PCDD/F ***DE NOVO* SYNTHESIS** REACTIONS, IT IS NECESSARY

To characterise **Fly Ash composition and structure**

To understand the **Mechanism of Native Carbon Gasification Reaction** (complete mass balance of the reaction)

MODEL SYSTEMS

FLY ASH

MODEL SYSTEMS

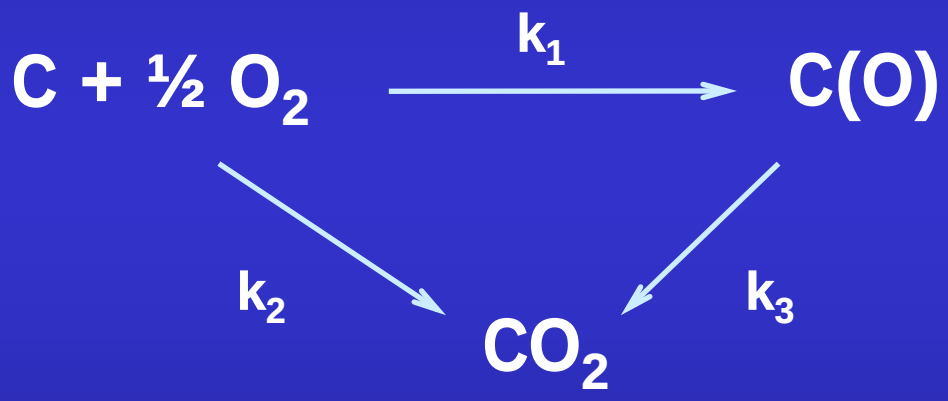
Support	Reagent	Catalyst
FA-R (Raw)	❑ DF ❑ C_{att} / C_{am} / C_{nat}	Included
FA-E (Extracted/toluene)	❑ C_{nat}	??
FA-SFE (Extracted/SFE)	❑ C_{nat} ❑ DF	??
FA-TT (Thermally Treated at 600°C)	❑ C_{att} / C_{am} / C_{nat} ❑ DF ❑ OCDD/OCDF	??
FA-W (Washed)	❑ C_{att} / C_{am} / C_{nat}	??
SiO_2	❑ C_{att} ❑ C_{att} / C_{am} / C_{nat} ❑ DF / BPh / DD	No/Cu, Fe, Zn No No

M. Lasagni, E. Collina, M. Tettamanti, D. Pitea (1996) *Environ. Sci. Technol.*, **30**, 1896

REAL SYSTEMS

⇨ **Raw Fly Ash from MSWI ESP hoppers: Denmark (FA1, FA2a and FA2b) and Italy (FA3)**

PROPOSED MECHANISM



$$d[C]/dt = -k_1^0[C][O_2]^{n1} - k_2^0[C][O_2]^{n2}$$

$$d[C(O)]/dt = -k_1^0[C][O_2]^{n1} - k_3^0[C(O)][O_2]^{n3}$$

$$k_i = k_i^0 [O_2]^{ni}$$

$$d[C]/dt = -(k_1+k_2)[C]$$

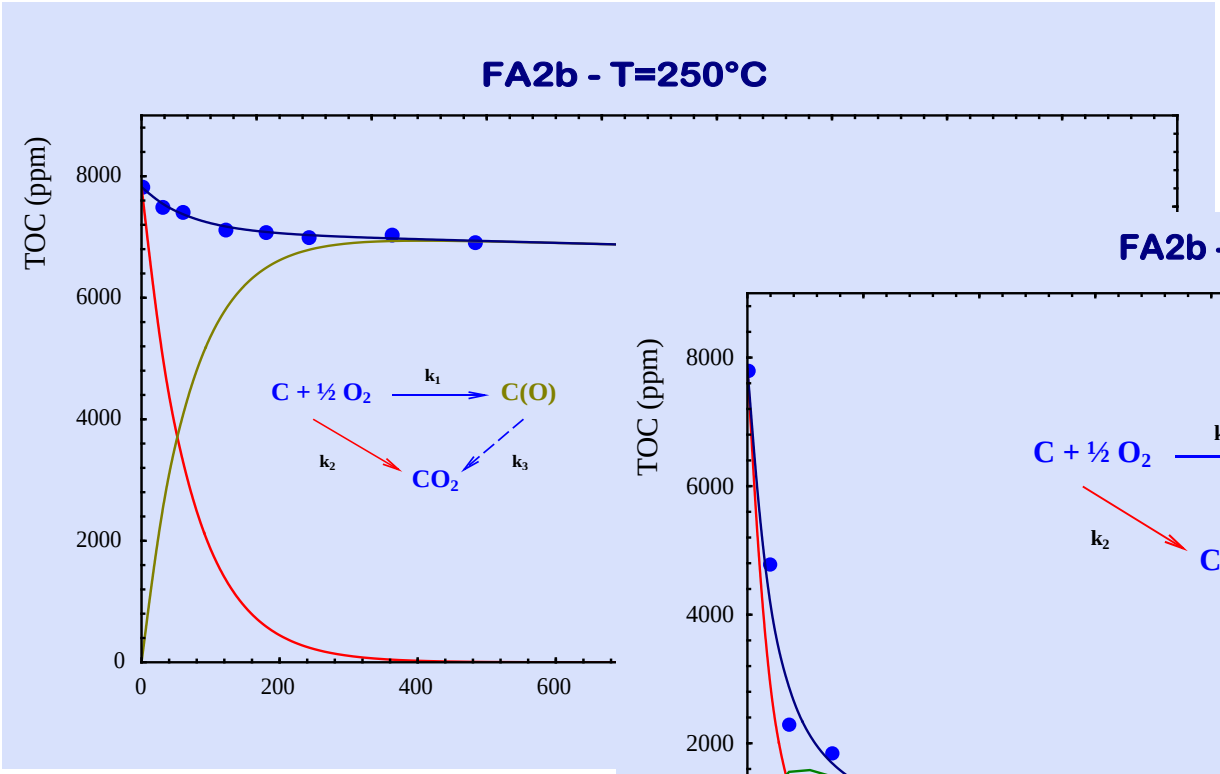
$$d[C(O)]/dt = k_1[C] - k_3[C(O)]$$

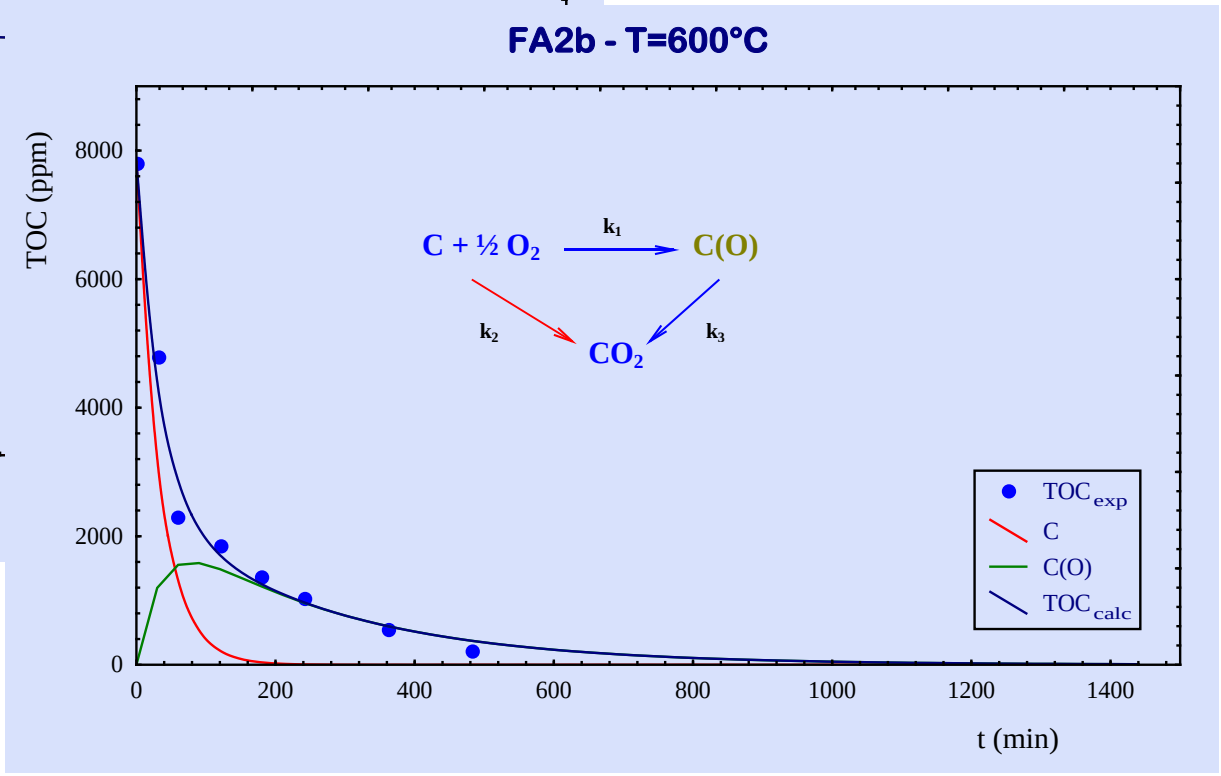
Boundary condition:
$[C(O)]_0 = 0$

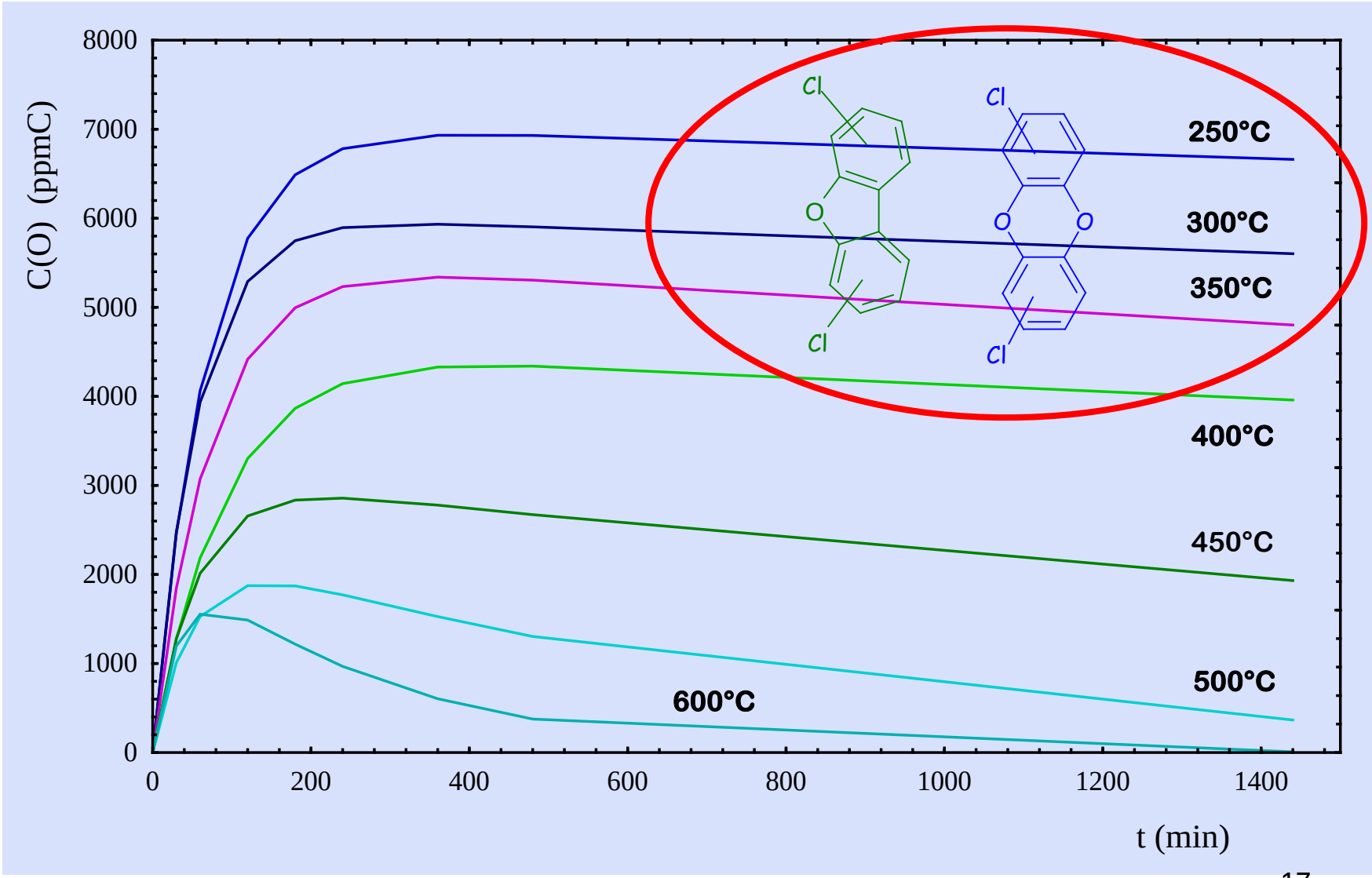
$$\frac{TOC}{TOC^0} = \frac{[C]+[C(O)]}{[C]_0}$$

$$\frac{TOC}{TOC^0} = \frac{k_1}{(k_1+k_2-k_3)} \exp(-k_3 t) + \frac{(k_2-k_3)}{(k_1+k_2-k_3)} \exp[-(k_1+k_2)t]$$

Agreement between calc. and exp. data






C(O) (ppmC)
8000
7000
6000
5000
4000
3000
2000
1000
0
0
200
400
600
800
1000
1200
1400
t (min)
250°C
300°C
350°C
400°C
450°C
500°C
600°C
Cl
O
Cl
O
O
Cl
Cl

MAIN CONCLUSION ABOUT MECHANISM

Measured conversion of FA **native carbon** to CO_2 is the result of two processes:

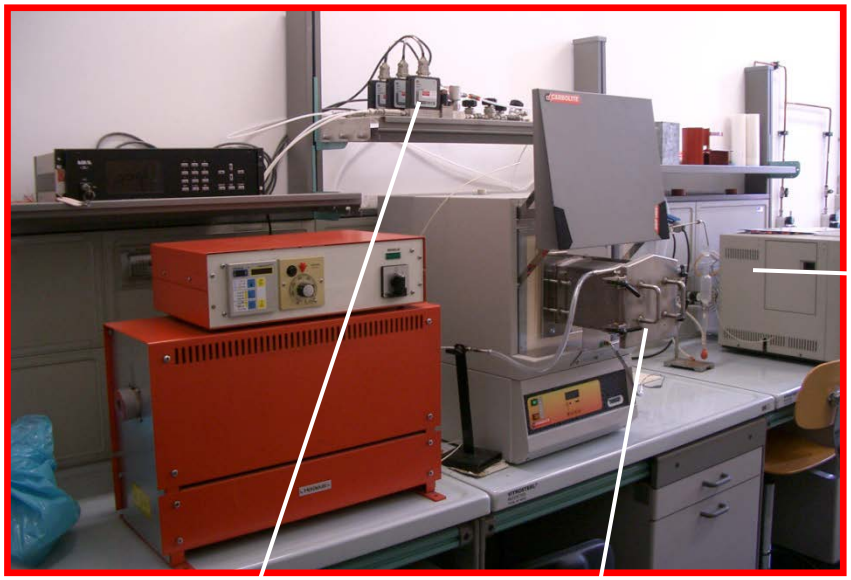
1. **The dissociative oxygen chemisorption (k_1) followed by the gasification of the intermediate complexes (k_3).**

2. **The direct carbon gasification (k_2).**

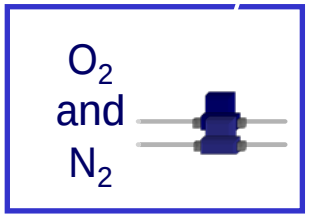
Due to $\Delta G_1^{\neq} \cong \Delta G_2^{\neq} < \Delta G_3^{\neq}$, the two reactions become concurrent on FA surface.

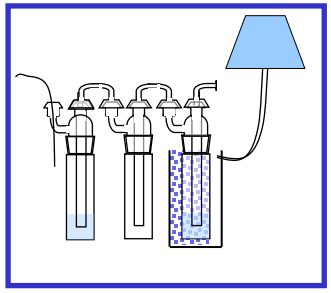
TOWARDS A GLOBAL REACTION MECHANISM OF NATIVE CARBON THERMAL OXIDATION AND PCDD/PCDFs FORMATION

EXPERIMENTAL SYSTEM



GC-TCD for on line determination of CO/CO_2





Reaction matrix: Fly ash (AMSA, MI)

Gas mixture: 80% v/v N_2, 20% v/v O_2

Flow: 100 mL/min

Temperature: 230-350°C

Time: 0-24 h

HYPOTHESIZED REACTION MECHANISM

$$C + O_2 \xrightarrow{k_1^0} C(O)$$

$$C + O_2 \xrightarrow{k_2^0} CO_2$$

$$C(O) + O_2 \xrightarrow{k_3^0} CO_2$$

$$C + O_2 \xrightarrow{k_4^0} CO$$

$$C(O) + Cl^- \xrightarrow{k_5^0} C(O)(Cl)$$

$$C(O)(Cl) \xrightarrow{k_6} (PCDD/F)_s$$

$$(PCDD/F)_s \xrightarrow{k_7} (PCDD/F)_v$$

$$(PCDD/F)_s \xrightarrow{k_8} P_{deg}$$

$$(PCDD/F)_v \xrightarrow{k_9} P_{dec}$$

RATE EQUATIONS

$$d[C]/dt = -(k_1 + k_2 + k_3)[C]$$

$$d[C(O)]/dt = -k_1[C] - (k_3 + k_5)[C(O)]$$

$$d[CO]/dt = k_4[C]$$

$$d[CO_2]/dt = k_2[C] + k_3[C(O)]$$

$$d[C(O)(Cl)]/dt = k_5[C(O)] - k_6[C(O)(Cl)]$$

$$d[(PCDD/F)_s]/dt = k_6[C(O)(Cl)] - (k_7 + k_8)[(PCDD/F)_s]$$

Where

$$k_1 = k_1^0[O_2]^{n_O} \qquad k_4 = k_4^0[O_2]^{n_O}$$

$$k_2 = k_2^0[O_2]^{n_O} \qquad k_5 = k_5^0[Cl_2]^{n_{Cl}}$$

$$k_3 = k_3^0[O_2]^{n_O}$$

$$\frac{[O_2]}{[C]} = 22 \Rightarrow [O_2]^{n_O} = \text{cost}$$

$$\frac{[Cl^-]}{[C]} = 14 \Rightarrow [Cl_2]^{n_C} = \text{cost}$$

$$n_C = 1$$

PCDD/F reaction order = 1

INTEGRATION BOUNDARY CONDITIONS

The system was analytically integrated by partial fraction method under the following boundary conditions

$$t = 0$$

$$[C] = [C]_0$$

$$[CO]_0 = [C(O)]_0 = [C(O)(CI)]_0 = 0$$

$$[(PCDD/F)_S] = [(PCDD/F)_S]_0$$

INTEGRATED EQUATIONS

$$\frac{[C]}{[C]_0} = \left\{ \exp\left[-(k_1+k_2+k_4)\,t\right] \right\}$$

$$\frac{[C(O)]}{[C]_0} = \frac{k_1}{(k_1+k_2+k_4)-(k_3+k_5)} \left\{ \exp\left[-(k_3+k_5)\,t\right] - \exp\left[-(k_1+k_2+k_4)\,t\right] \right\}$$

$$\frac{[CO]}{[C]_0} = \frac{k_4}{(k_1+k_2+k_4)} \left\{ 1 - \exp\left[-(k_1+k_2+k_4)\,t\right] \right\}$$

$$\frac{[CO_2]}{[C]_0} = \frac{k_2}{(k_1+k_2+k_4)} \left\{1 - \exp\left[-(k_1+k_2+k_4)\,t\right]\right\} + \frac{k_1 * k_3}{(k_1+k_2+k_4)-(k_3+k_5)} \left\{ \frac{1-\exp\left[-(k_3+k_5)\,t\right]}{k_3+k_5} - \frac{1-\exp\left[-(k_1+k_2+k_4)\,t\right]}{k_1+k_2+k_4} \right\}$$

$$\frac{[C(O)(Cl)]}{[C]_0} = \frac{k_1 * k_5}{(k_1+k_2+k_4)-(k_3+k_5)} \left\{ \frac{\exp[-k_6\,t] - \exp\left[-(k_3+k_5)\,t\right]}{(k_3+k_5)-k_6} - \frac{\exp[-k_6\,t] - \exp\left[-(k_1+k_2+k_4)\,t\right]}{(k_1+k_2+k_4)-k_6} \right\}$$

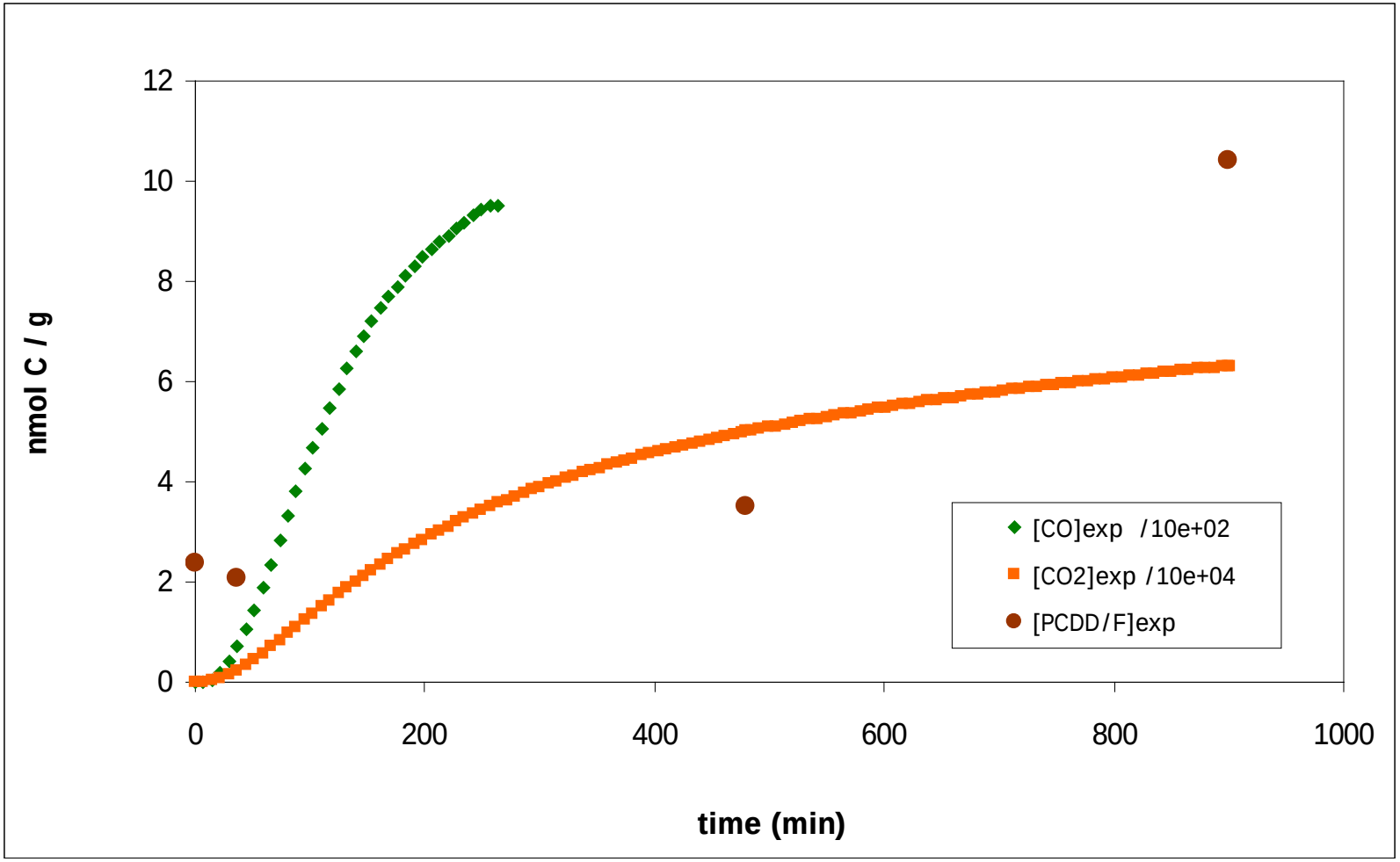
$$\frac{[(PCDD/F)_S]}{[C]_0} = \frac{[(PCDD/F)_S]_0}{[C]_0} \exp[-k_8\,t] +$$

$$\frac{k_1 * k_5 * k_6}{(k_1+k_2+k_4)-(k_3+k_5)} \left\{ \frac{1}{(k_3+k_5)-k_6} \left[\frac{\exp[-k_8\,t] - \exp[-k_6\,t]}{k_6-k_8} \right] - \frac{\exp[-k_8\,t] - \exp\left[-(k_3+k_5)\,t\right]}{(k_3+k_5)-k_6} \right\} -$$

$$\frac{k_1 * k_5 * k_6}{(k_1+k_2+k_4)-(k_3+k_5)} \left\{ \frac{1}{(k_1+k_2+k_4)-k_6} \left[\frac{\exp[-k_8\,t] - \exp[-k_6\,t]}{k_6-k_8} \right] - \frac{\exp[-k_8\,t] - \exp\left[-(k_1+k_2+k_4)\,t\right]}{(k_1+k_2+k_4)-k_6} \right\}$$

EXPERIMENTAL DATA

$[C]_0$= 3.268 10^{+5} nmol C/g $[(PCDD/F)_S]_0$=2.381 nmol C/g T=280°C

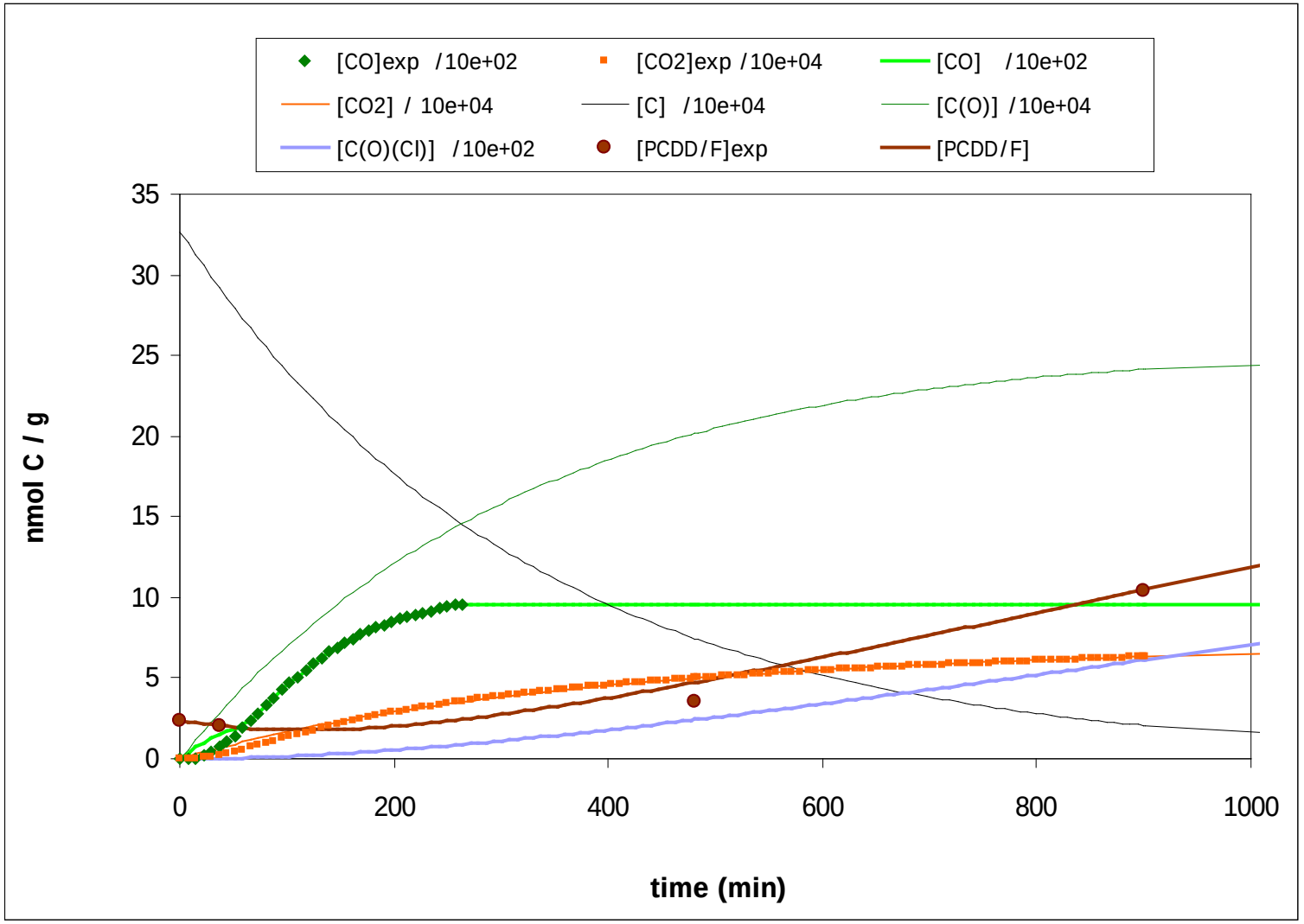


CALCULATED RATE CONSTANTS

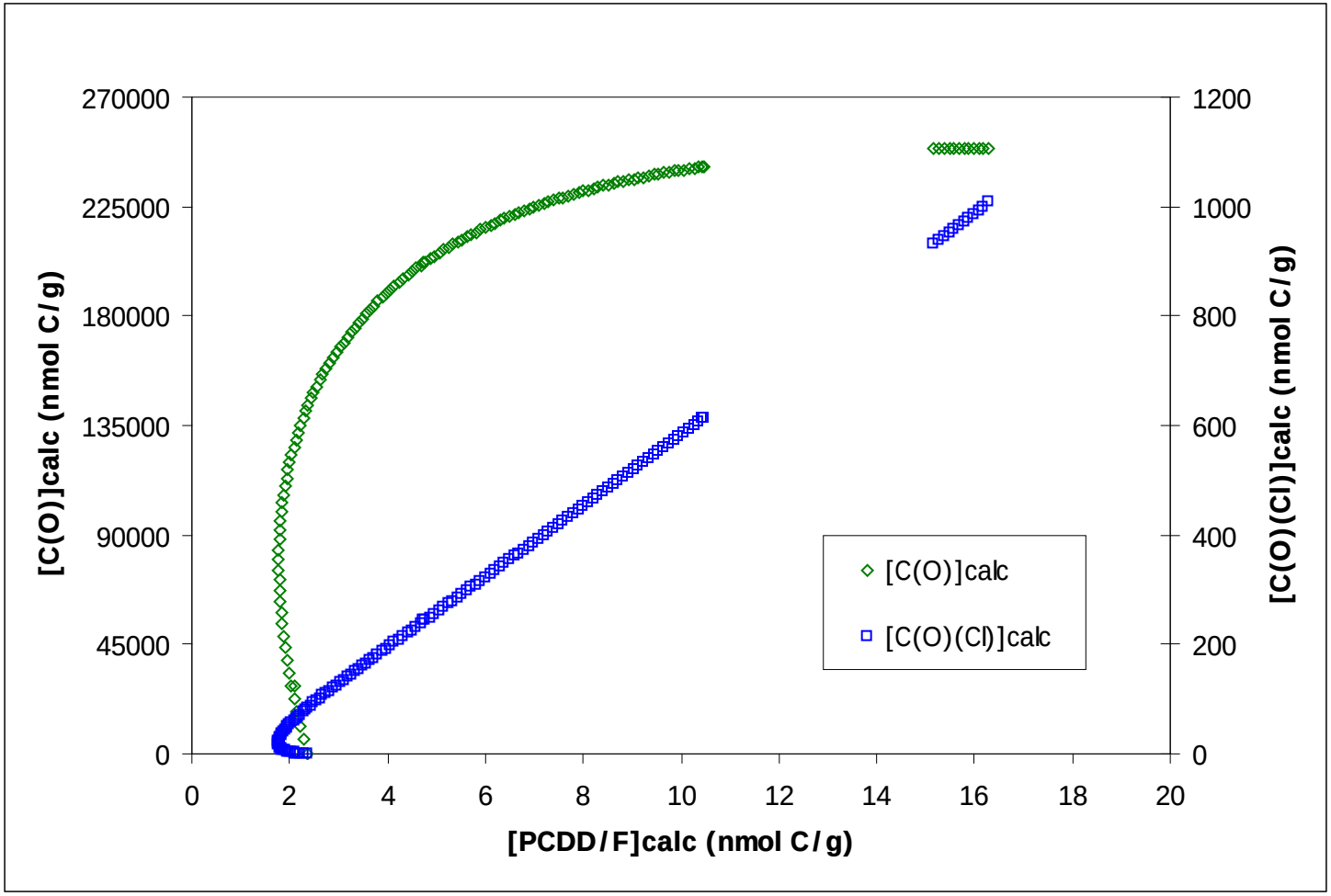
The kinetic constants were determined with a step by step procedure using a trial and error technique

k_1	min^{-1}	$2.49\ 10^{-3}$
k_2	min^{-1}	$5.85\ 10^{-4}$
k_3	min^{-1}	$3.16\ 10^{-5}$
k_4	min^{-1}	$1.85\ 10^{-5}$
k_5	min^{-1}	$4.05\ 10^{-6}$
k_6	min^{-1}	$6.99\ 10^{-5}$
k_8	min^{-1}	$4.87\ 10^{-3}$

T = 280 °C

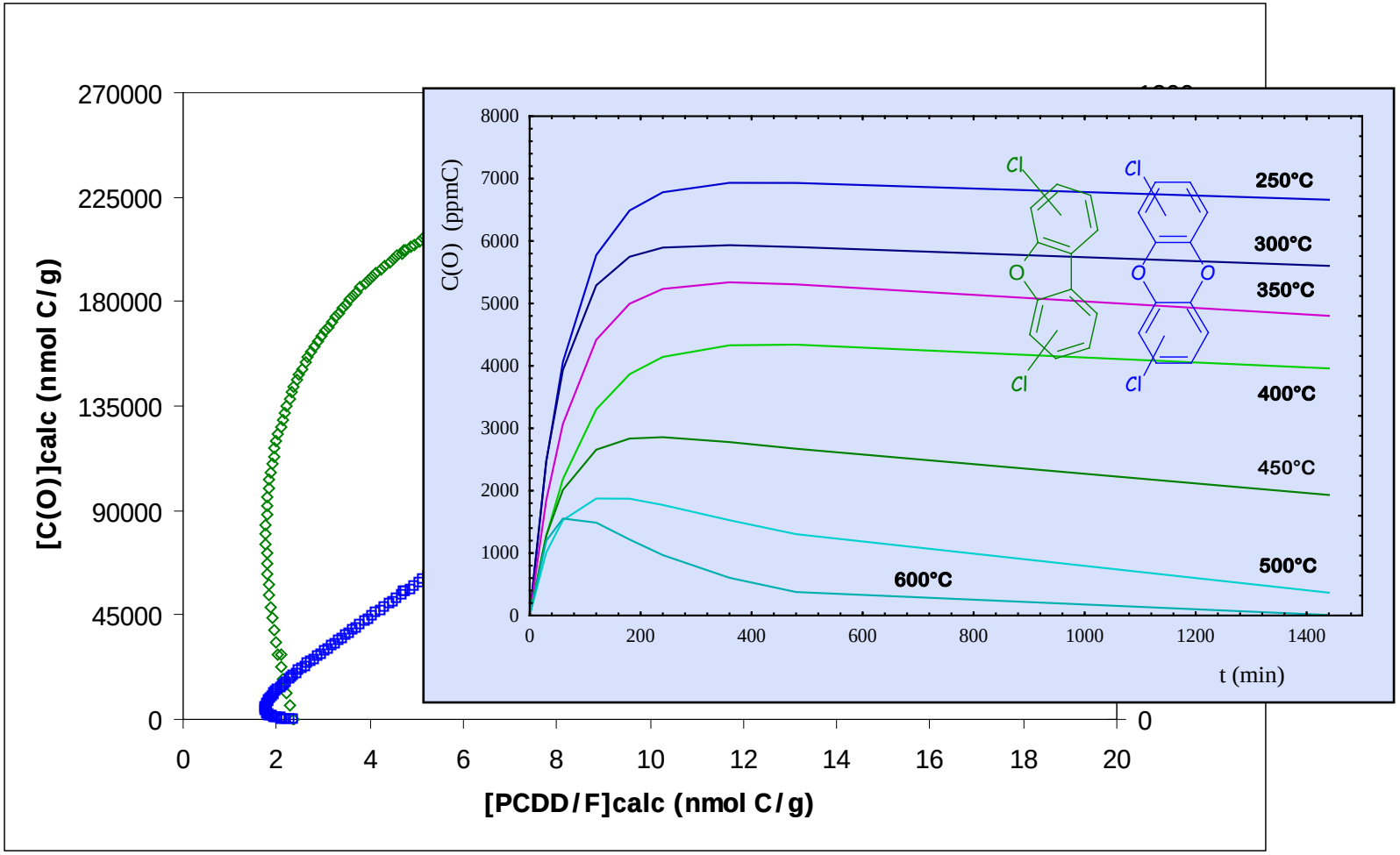

[CO]exp /10e+02
[CO2]exp /10e+04
[CO] /10e+02
[CO2] / 10e+04
[C] /10e+04
[C(O)] /10e+04
[C(O)(Cl)] /10e+02
[PCDD/F]exp
[PCDD/F]
nmol C / g
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
time (min)

!!!! [C(O)] and [C(O)(Cl)] *vs* [PCDD/F] !!!!



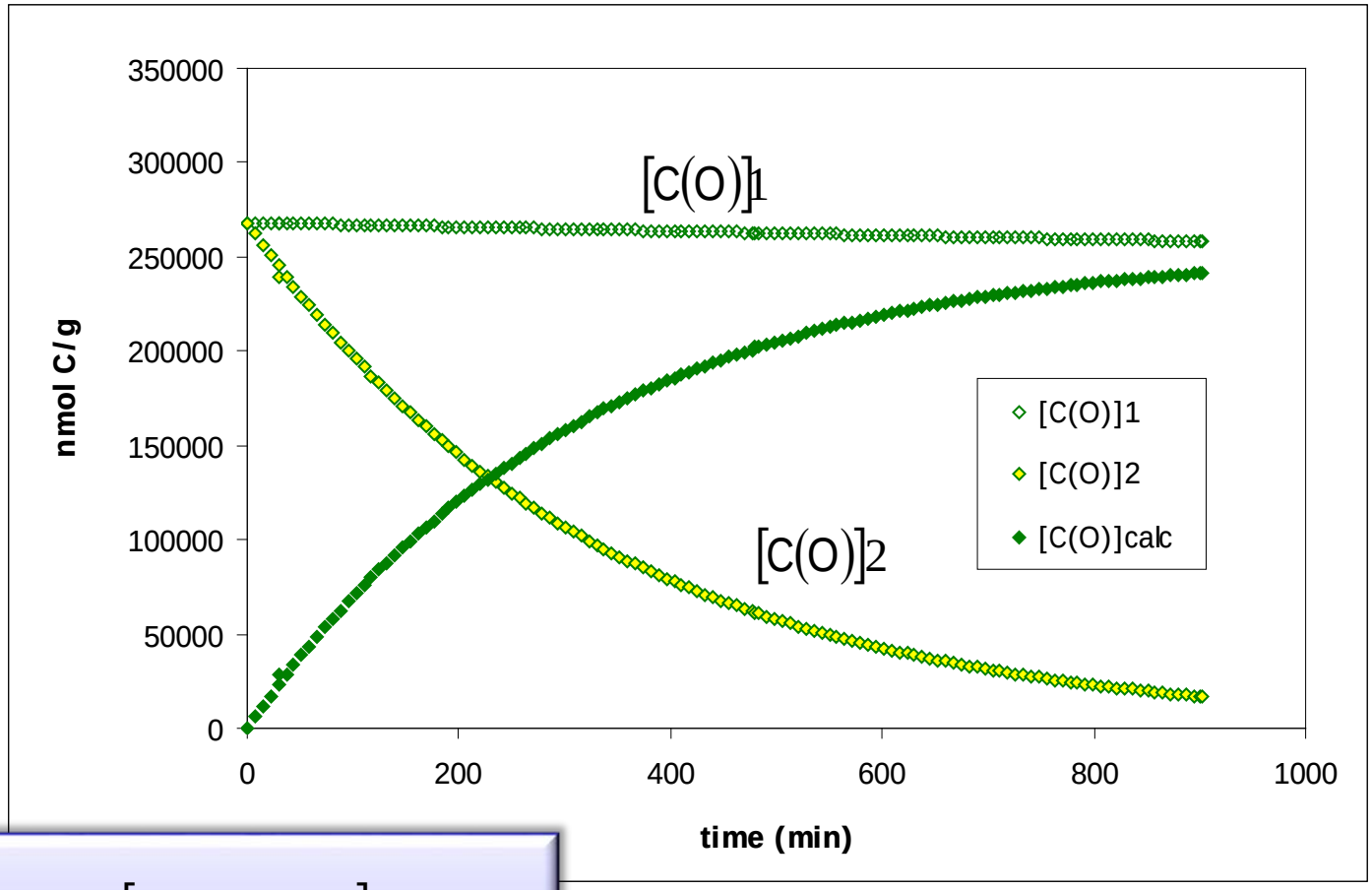
[PCDD/F] increase whit increasing C(O)] and [C(O)(Cl)]

!!!! [C(O)] and [C(O)(Cl)] *vs* [PCDD/F] !!!!



[PCDD/F] increase whit increasing C(O)] and [C(O)(Cl)]

CONTRIBUTION OF C(O) COMPLEXES

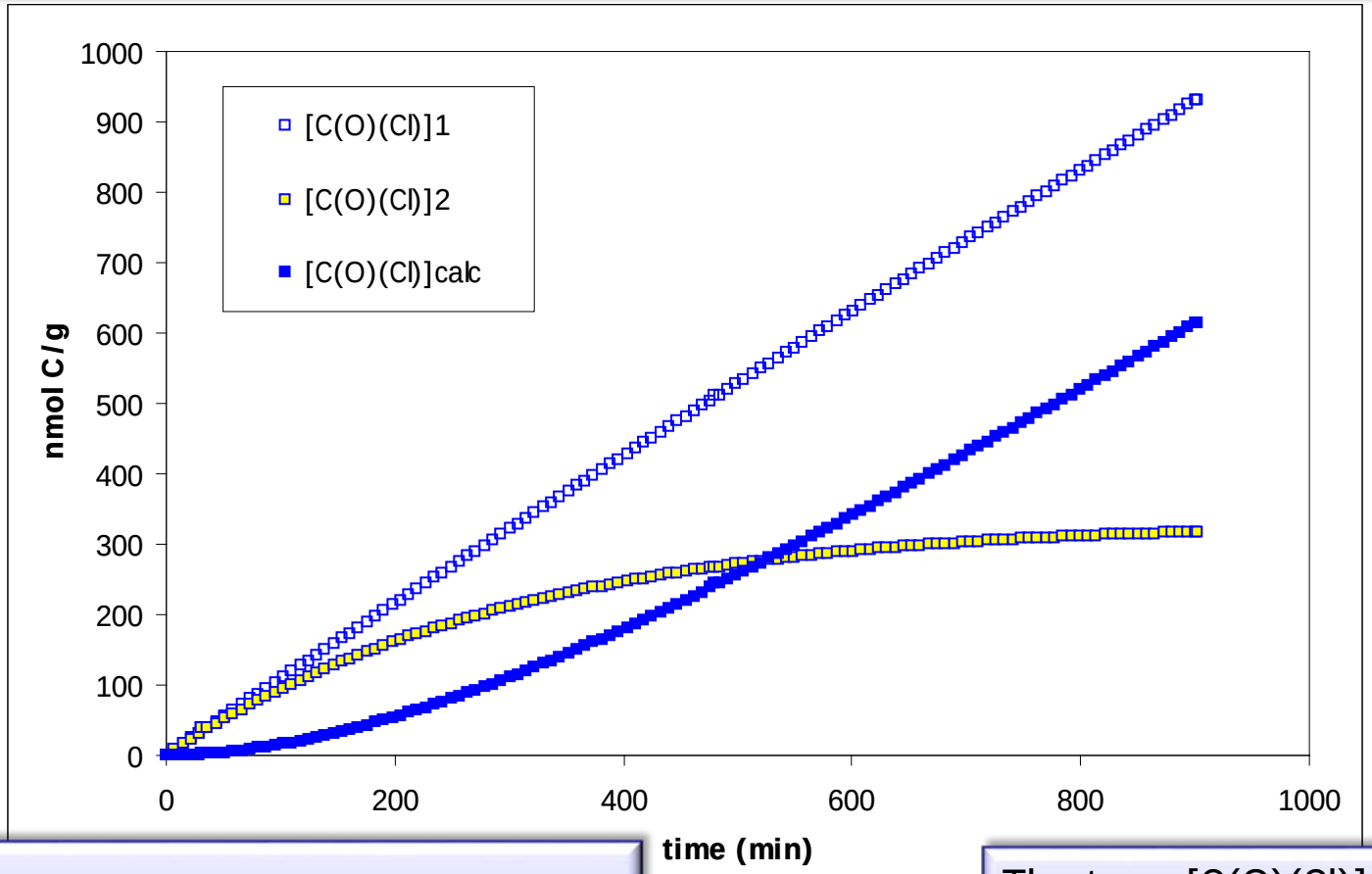


$$[C(O)]1 = \exp[-(k_3 + k_5)\, t]$$

$$[C(O)]2 = -\exp[-(k_1 + k_2 + k_4)\, t]$$

C(O) derives almost only from [C(O)]2 term (negative) of the rate equation.

CONTRIBUTION OF C(O)(Cl) COMPLEXES

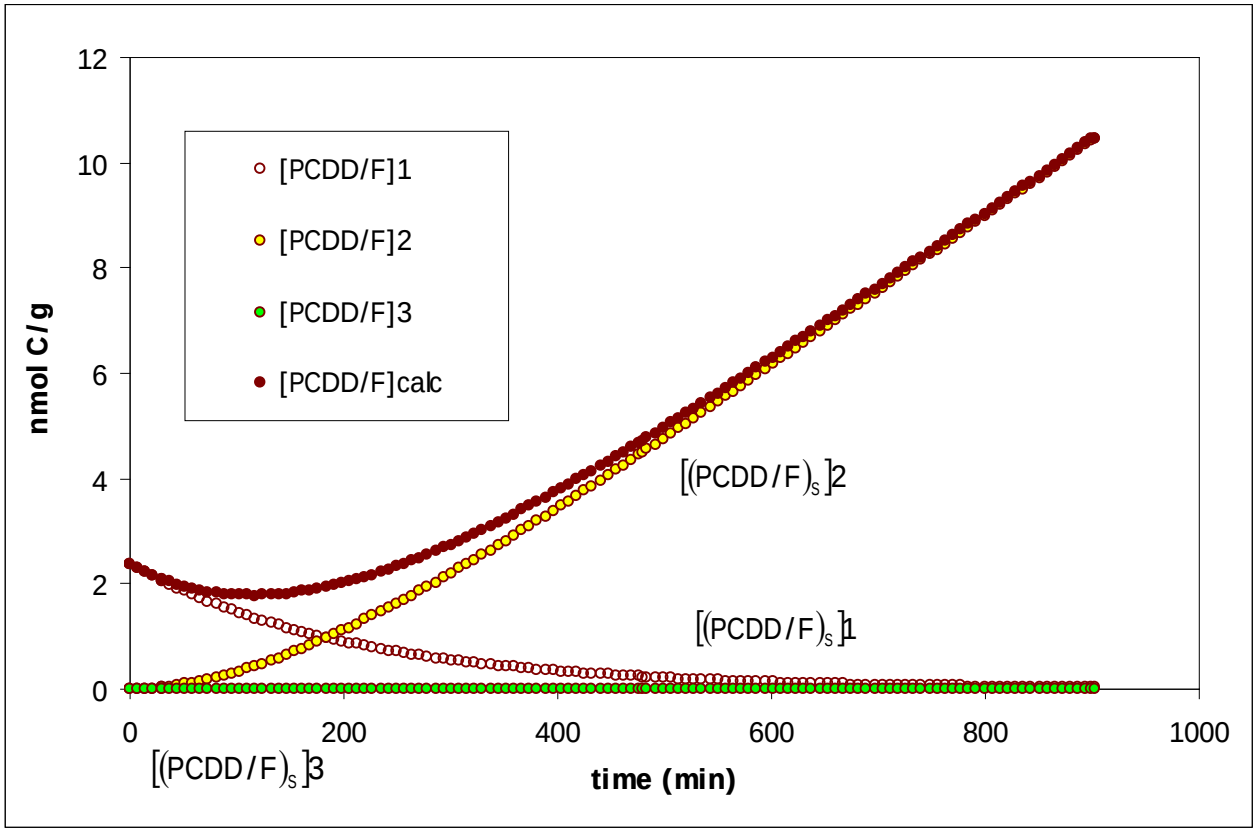


$$[C(O)(Cl)]_1 = \frac{\exp[-k_6\,t] - \exp[-(k_3 + k_5)\,t]}{(k_3 + k_5) - k_6}$$

$$[C(O)(Cl)]_2 = -\frac{\exp[-k_6\,t] - \exp[-(k_1 + k_2 + k_4)\,t]}{(k_1 + k_2 + k_4) - k_6}$$

The term [C(O)(Cl)]1 is partially counter balanced by the term [C(O)(Cl)]2 till the reaction times of about 400 min.

PCDD AND PCDF FORMATION



Balance between degradation of the congeners initially on the raw FA and the formation reaction.

The predominant term is [PCDD/F]2 **strongly** correlated to surface oxygen and oxy-chlorinated complexes formation.

$$\left[(PCDD/F)_S\right]1 = \frac{\left[(PCDD/F)_S\right]_0}{[C]_0}\exp[-k_8\,t]$$

$$\left[(PCDD/F)_S\right]2 = \left\{\frac{1}{(k_3+k_5)-k_6}\left[\frac{\exp[-k_8\,t]-\exp[-k_6\,t]}{k_6-k_8}\right] - \frac{\exp[-k_8\,t]-\exp[-(k_3+k_5)\,t]}{(k_3+k_5)-k_6}\right\}$$

$$\left[(PCDD/F)_S\right]3 = -\left\{\frac{1}{(k_1+k_2+k_4)-k_6}\left[\frac{\exp[-k_8\,t]-\exp[-k_6\,t]}{k_6-k_8}\right] - \frac{\exp[-k_8\,t]-\exp[-(k_1+k_2+k_4)\,t]}{(k_1+k_2+k_4)-k_6}\right\}$$