DIOXIN-FURAN RECOVERY INCINERATION PROCESSES

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ABSTRACT

Dioxin-furan emissions created both in the combustion of municipal waste and subsequent formation in the boiler were reduced by chemisorption in the R-C Teller system. Initial operation of a 400 TPD MSW-Industrial waste incinerator, the reduction was from 28.5 ng/Nm^3 to 1.87 ng/Nm^3. After 18 months of operation, at the same combustion conditions, the system inlet rose to 739 ng/Nm^3 with an outlet of 1.94 ng/Nm^3.

PROCESS

The emission control system, applied to both MSW and Industrial Wastes, consists of 3 components, a Quench Reactor[8], a Dry Venturi[8], and a Fabric Filter, in series. There are two reaction zones. The Quench Reactor neutralizes a portion of the acid gases by contact with a slurry of calcium hydroxide. the fabric filter is converted by the Dry Venturi to a second reactor, a fixed bed.

The Dry Venturi, where the dried Quench Reactor gases flow, adds crystalline hydrophobic particles to both capture fine particulate and to add a non-compressible solid to the filter cake. This permits the accumulation of cake thickness 3 to 10 mm, over a period of 6-12 hours, without any adverse effect on pressure drop.

This fixed bed containing unreached reagent provides 95% recovery of the acid gases entering the fabric filter and provides for adsorption of organic compounds.

Studies on the adsorbed phase vapor pressure of dioxin-furan cogeners indicated that with a fixed bed temperature between 120°-130°C, effective reduction of these compounds could be achieved[7,9] when the bed contained flyash and other silica-alumina crystals.

Thus, the MSW-hazardous waste incinerators systems were designed for inlet temeprature of 155°-900°C, quench temperature of 130-150°C and the fabric filter operates at 120-135°C.

PERFORMANCE

A system was installed downstream of the boiler on a 400 TPD combined service muncipal-industrial waste incinerator. Three months after start-up, the following results were obtained, with the furnace operation at 900-1000°C with 2 seconds residence time.[6,10]

TABLE I

EMISSIONS ACHIEVED IN NEW OPERATION

(Reagent Stoichiometic ratio 1.4-1.6)

Component	Concentration	Reduction Per Cent
Total Particulate	9.8 mg/Nm^3 - 12% CO$_2$	
Fine Particulate	0.9 mg/Nm^3 - 12% CO$_2$	
Hydrochloric Acid	5.5 ppmdv - 7% O$_2$	99.0
Sulfur Oxides	1.3 ppmdv - 7% O$_2$	99.5
Hydrofluoric Acid	<0.02 ppmdv - 7% O$_2$	98.0
Heavy Metals		99.9
Dioxins + Furanes	<1.87 ng/Nm^3 - 12% CO$_2$	93.5
Dioxins · Toxic Eq.	<0.009 ng/Nm^3 - 12% CO$_2$	

The emissions of dioxins (PCDD) using the basic system, were approximately 6% of that achieved using an electrostatic precipitator for an identical furnace under the same combustion conditions.[4]

After 18 months of oepration, the system was retested. The combustion conditions were statistically the same as in the previous test and the CO remained under 50 PPM.

Although the average acid gas and particulate concentrations, both inlet and outlet, remained in the same range, there was a radical increase in the dioxin-duran emissions from the boiler, rising to 739 ng/Nm^3. This increase was attributed to the seasoning of the flyash on the boiler tubes and subsequent catalytic formation of dioxins and furans as suggested by others.[2,3,5,11]

The system reduced the dioxins and furans to < 1.94 ng/Nm^3, essentially to the same level as achieved with the lower inlets.

CONCLUSION

The very large increase in dioxin emissions from an incinerator from startup to 18 months later, at statistically constant combustion conditions, strengthens the implication that dioxins and furans are formed in the boiler by catalysis on flyash.

The reduction of dioxin-furan emissions by the control system to the same level for a 26 fold variation inlet, further confirms the hypothesis that an equilibrium-temeprature chemisorption is a primary recovery mechanism.

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SIGNIFICANCE OF CHLORINE SOURCES FOR THE GENERATION OF DIOXINS DURING
INCINERATION OF MSW.   J. Vikelsoe*, P.R. Nielsen, P. Blinksbjerg, H. Madsen
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ABSTRACT: Known amounts of PVC, NaCl and lime were added to municipal waste
during a series of incineration experiments. The results showed increased
dioxin emission at high levels of PVC and NaCl, and decreased emission at
high lime levels. After a boiler cleaning, the dioxin emission rose
dramatically, but returned to normal after two days.

INTRODUCTION: The present work is a part of the Danish Incinerator Dioxin
Program (ref.1), this paper appearing as no. 6 in a series. The purpose was
to study the influence of chlorine sources in MSW on the dioxin emission.
Earlier research conducted during the same program on MSW in large
incinerators had shown a correlation between HCl in the flue gas and the
dioxin emission, which rose by 14% when the HCl concentration doubled. For
hospital waste in hospital incinerators the increase was 25%. A similar
correlation has been reported for incineration of chlorinated organic
solvents (ref.2), but several investigations on incineration of MSW had
failed to show such a relationship (ref.3).
In the present investigation, PVC and NaCl were studied, as they are the most
prominent organic and inorganic chlorine sources in MSW. Since PVC gives off
HCl when incinerated, a correlation between dioxin emission and PVC level was
to be expected. In contrast, the influence of NaCl was unknown. It was
further the aim to study the influence of lime addition on dioxin and HCl
emissions, as well as the correlation between chlorine sources and HCl
emission, and between HCl and dioxin emission.

EXPERIMENTAL PART: Advanced statistical methods were applied in the
planning of the experiments, and in analyzing and evaluating the results
(ref.5). To avoid bias and systematic errors, a pre-randomized plan was
followed, involving a total of 26 individual experiments.
PVC, NaCl and lime were added to the refuse in different doses alone or
combined. PVC doses were 0, 10, 33 and 100 kg per ton MSW, NaCl doses and
lime doses 0, 10 and 33 kg per ton. The lowest chlorine doses added
correspond to 1200 mg/Nm^3 HCl, 3 times the average concentration earlier
found in flue gas (400 mg/Nm^3). The planned chlorine amounts ranged from 0.2%
to 6% by weight in the MSW. This large range was judged necessary to observe
the small expected effects.
The experiments were performed on a 3 tons per hour incinerator to the north
of Copenhagen. The MSW was fed by crane equipped with a calibrated weighing
cell, and the calculated amount of chemicals applied manually in each batch.
The plant was intended to be operating at normal and stable conditions.
During incineration, O_2, HCl, CO, CO_2, H_2O, furnace and flue gas temperatures
as well as heat rate were measured as combustion parameters.
The same methods of sampling and dioxin analysis were used throughout the
Danish Incinerator Program, and has been evaluated on a large number of
samples (ref.1).
The Nordic sampling procedure (ref.4) was modified by lowering the filter
temperature to 120 degr. C (quartz-wool particle filter). Flue gas was
sampled (about 2 hours) isokinetically between the boiler and the cleaning

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system, to avoid the latter disturbing the results. The extraction was done
with toluene, clean-up by chromatography on silica gel and aluminum oxide,
GC/MS on a Finnigan 4500 quadropole instrument using SE-54 capillary column.
Carbon labelled furans were used as spikes, 2 field spikes and 2 lab spikes
(on the particle filter), and 5 carbon labelled dioxins as internal
standards. Standards employed were manufactured by CIL. Results were
calculated by an internal standard ratio method, using these internal
standards relative to external standards, and the results corrected for
laboratory recovery. Group-specific analysis were preferred because of the
better repeatability demonstrated previously (C.V. = 14% including sampling,
ref.1). This is significant since small relative changes are studied,
absolute levels being unimportant.
The dioxin analysis were conducted as a blind experiment, the identity of
samples being unknown to the analysts.
At the course of the series of experiments, an unintended event occurred, as
a heat exchanger in the flue gas path of the boiler system clogged. After
shutdown, cleaning, and start-up, the experiments were resumed.

RESULTS: The results were calculated as total PCDD+PCDF per normal cubic
meter of flue gas at 10% O_2 (TPCDD/Nm^3), the HCl at current O_2 (HCl/Nm^3).
As it turned out, the dioxin concentrations showed dramatically elevated
levels the two first days after the boiler cleaning, affecting 9 samples (the
'high episode'). They returned to normal on the third day. This was
surprising, since no indication of change during the episode in any of the
measured combustion parameters existed.
The statistical evaluation was performed by a combination of variance
analysis and regression analysis on the logarithms of the data (ref.5).
The following correlations were investigated:

- Influence of chlorine sources on dioxin and HCl emissions
- Influence of lime on dioxin and HCl emissions
- Influence of HCl on dioxin emission

The high episode, which required a special treatment, was handled as block
effects introduced for each day. In this way it was found that the emission
the two days was elevated by factors of 13 and 2 above normal, respectively.
The 4 results of the first day were excluded, since the factor of 13
indicated a situation too far from the normal. This omission, and the block
effect introduced for the second day, unfortunately reduces the confidence of
the evaluation.
Nevertheless, all correlations sought for were found statistically
significant. These can be expressed as the relative change in percent of
dioxin or HCl, when the concentration of the chlorine source doubles. In the
same way, the influence of lime and of HCl can be expressed, as shown in
table 1.

Table 1: Correlations found between PVC, NaCL, Lime, HCl and TPCDD

Doubling	Implies variation of	
	TPCDD	HCl
PVC	32% +-10%	64%
NaCl	17% +- 6%	9%
Lime	-15% +- 5%	-20%
HCl	42% +-15%	-

As can be seen from the table, both PVC and NaCl can act as chlorine sources. In the evaluation, there were indications of a delayed response for NaCl, implying that this response is underestimated. It might be of the same order of magnitude as the PVC-response.

DISCUSSION: In the results (table 1), the influence of PVC on dioxin is of the same magnitude as that of HCl, the difference not being significant. Probably the PVC-effect is mediated through HCl (in agreement with the apparent high-yield conversion of PVC to HCl) which rapidly reaches the boiler region, where the dioxin-formation is believed to take place according to the theory of low-temperature dioxin synthesis (ref.6). A comparison of the present results with the earlier investigations in the Danish program is shown in table 2.

Table 2: Dioxin increase on doubling HCl, HCl-level and range compared with earlier studies

Investigation	TPCDD-incr.	HCl-level mg/Nm^3	
		Mean	Range
Large inciner.	14%	500	30 - 4000
Hospital incin.	25%	300	70 - 800
Present study	42%	1800	300 - 9000

The present study is showing the highest increase, but the differences are not statistically significant, meaning that the three investigations confirm the results of each other. As the present result is obtained using controlled HCl concentrations, it must be regarded as more reliable than the earlier ones, although the experimental HCl-span covered is above normal, the lower limit being about 300 mg/Nm^3. In contrast, the lower experimental HCl-limit of the large incinerator study was only 30 mg/Nm^3, making that study more relevant for normal situations. From a chemical point of view, table 2 makes sense supposed HCl at high levels act as the chlorine donor, sharing that activity with NaCl at lower levels.
Indeed, the results (table 1) indicate that NaCl can act as a chlorine donor. Since this substance in the combustion process evidently gives off amounts of HCl too minor to explain the dioxin increase, it can assumably act directly without gaseous intermediates. This view is supported by the observed time delay for NaCl, as it must take more time for a solid to be transferred to the dioxin-synthesizing boiler region, where it remains for a longer time, than a gas. Laboratory experiments conducted on fly ash showing NaCl alone to be a sufficient chlorine donor lend further support for this (ref.7).
The results (table 1) finally show a negative influence of lime on dioxin and HCl emissions. Doubling the lime leads to a decrease in HCl of 20%, which subsequently should lead to 11% dioxin decrease, in fair agreement with the 15% decrease observed. However, the lime reacts with the HCl to form CaCl$_2$, which assumably can act as a chlorine donor too, in which case the decrease remains unexplained.

The observed large increase in dioxin emission the two days after the boiler cleaning - the high episode - in a way impaired the carefully planned experiments. Nevertheless, it was possible to carry out the statistical evaluation to obtain significant results, albeit with lesser fidelity. The high episode is in itself a surprising and interesting finding. It clearly indicates that the conditions in the boiler zone - in agreement with the

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theory of low temperature dioxin synthesis - are important for the dioxin
emission. It could appear to be in disagreement with the view that the
dioxins are formed in a coating of ash deposited on the boiler tubes. The
earlier research showed (ref.1) that dioxin emission correlates with flue gas
temperature, which in turn is known to be dependant of the thickness of the
ash layer, so an influence of boiler cleaning must be expected. However,
no abnormal change in flue gas temperature during the high episode was
observed. More severe, the cleaning ought to improve heat transfers leading
to lower flue gas temperature, which in turn should lead to lower emission,
contrary to observation. The observed high episode clearly is a short-term
phenomenon, with a time scale of days, whereas the correlations between
boiler ash thickness, flue gas temperature and dioxin emission are long-term,
with a time scale of months. Possibly the cleaning has temporarily changed
the chemical properties of the boiler surfaces, maybe by leaving a thin layer
of crushed ash on the tubes or by exposing the construction material, thereby
introducing enhanced catalytic dioxin generating activity. Or perhaps the
much simpler explanation applies that the cleaning has exposed dioxins
previously formed deep within the boiler ash coating.

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