

REMOVAL, REFORMATION AND DESTRUCTION OF DIOXINS AND RELATED COMPOUNDS IN WASTE INCINERATOR FLUE GAS

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Introduction

Low temperature (150°C) catalytic destruction of dioxins by the Shell Denox System in simulated waste incinerator flue gas has been demonstrated at very high levels of efficiency (>99.5%) using the Umeå laboratory-scale apparatus [1]. A key feature of these and related studies [3] has been the clear evidence of dioxin destruction provided by ¹⁴C-labelling and catalyst bed dioxin measurements [2] even at operating temperatures as low as ~100°C [3].

The Shell Denox System (SDS) developed for NO_x Selective Catalytic Reduction was installed as the final part of the off-gas cleaning system at the full-scale WATCO MWI (200 Mt/day) in Roosendaal, The Netherlands in 1996. After a year's successful DeNO_x operations the dioxin removing potential of SDS was investigated in detail.

Materials and Methods

The WATCO MWI contains, in addition to SDS, an electrostatic precipitator (ESP) and a lime/activated carbon injection system, Fig.1. Flue gas was sampled at points A-D and dioxin measurements carried out by TAUW, The Netherlands, using standard VDI methodology.

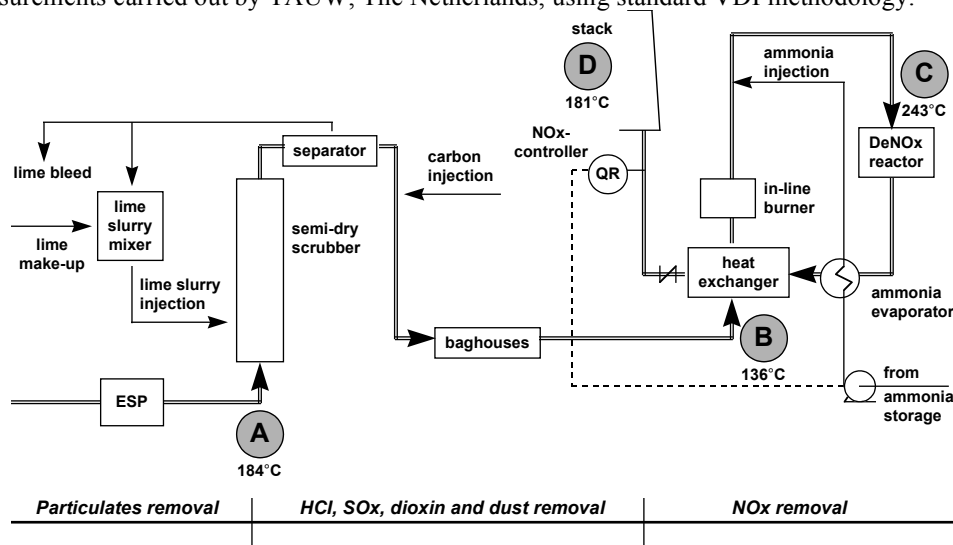


Fig.1. Schematic drawing of off-gas cleaning system at WATCO MWI

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The SDS typically operates at 225-230°C following reheating of the flue gas from the baghouses via a heat exchanger and an in-line burner. Two trials were carried out:-

1. Without activated carbon injection,^a to ensure that sufficiently high dioxin concentrations were present in flue gas prior to the DeNOx reactor to enable dioxin removal efficiency measurements; flue gas samples were taken at the scrubber inlet (A), DeNOx reactor inlet (C1) and stack (D1);
2. With normal activated carbon injection, to elucidate results from 1st trial indicating unexpected dioxin formation between sampling points A and D; samples were taken at the heat exchanger inlet (B), DeNOx reactor inlet (C2) and stack (D2).

Results and Discussion

1st trial: The flue gas dioxin concentration (expressed as Teq) before the DeNOx system (C1) is more than two orders of magnitude greater than that at the stack after the SDS (D1), Table 1. Concentrations of total PCDFs (polychlorinated dibenzofurans - the main component) are reduced by a similar amount, and that of total PCDDs (polychlorinated dibenzo-*p*-dioxins) to below the detection limit. The dioxin removing efficiency of the SDS is 99.7%.

Table 1. Summary of dioxin analyses

	1 st trial			2 nd trial			used catalyst	
	flue gas samples						Samples	
	A	C1	D1	B	C2	D2	front	Back
	ng/Nm ³						ng/g	
ΣPCDDs	5.9	2.2	<1.4	<1.5	<1.6	<1.8	0.46	<0.5
ΣPCDFs	14	490	2.4	<1.5	10	<1.8	<0.05	<0.05
ΣPCDDs+Fs	20	490	3.8	<3.0	12	<3.6	<0.51	<0.55
PCDF:PCDD	2.5	220	>1.7	n.a.	n.a.	n.a.	n.a.	n.a.
	ng/Nm ³						ng/g	
Teq*(min)	0.46	29	0.10	0.017	0.48	0.023	0.011	Nil
Teq*(max)	0.47	32	0.11	0.025	0.48	0.032	2.883	2.882

*. methodology does not provide for non-detection of some 2,3,7,8-congeners - a common occurrence at low concentrations, min: non detects calculated as zero, max: non detects calculated for detection limit.

Surprisingly, the flue gas dioxin level at the DeNOx reactor inlet is considerably more than that at the scrubber inlet (A). There is also a change in the dioxin constituents from a small predominance of PCDFs (PCDF:PCDD of 2.5) before the scrubber to a large excess (PCDF:PCDD of 220) prior to the DeNOx reactor. PCDD levels are actually lower at A than C, whereas PCDF concentrations increase dramatically. Dioxin homologue distributions are shown, Fig.2: clearly TCDF, PeCDF and HxCDFs are being formed between A and C, presumably during the reheating stages.

2nd trial: The dioxin concentration (expressed as Teq) at the DeNOx reactor inlet (C2) is ~25 times higher than that before the heat exchanger (B). Subsequently at the stack (D) the dioxin

^a Approval was gained from the Dutch Government regulatory authority to carry out this test. Normal operations were carried out without carbon injection for two days prior to sampling so that activated carbon would be purged from the scrubber and baghouses.

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concentration is reduced to almost the same level as that at B with a removal efficiency of 99.98%, Table 2. Concentrations of PCDFs are reduced by a similar amount, and PCDDs to below the detection limit. PCDFs are clearly being generated between the heat exchanger and DeNOx reactor and then removed by the DeNOx catalyst.

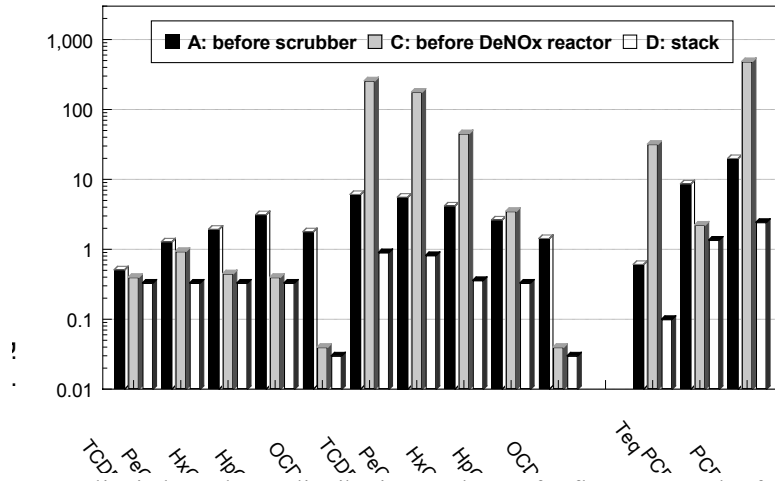


Fig. 2. Mean dioxin homologue distributions and Teqs for flue gas samples from 1st trial

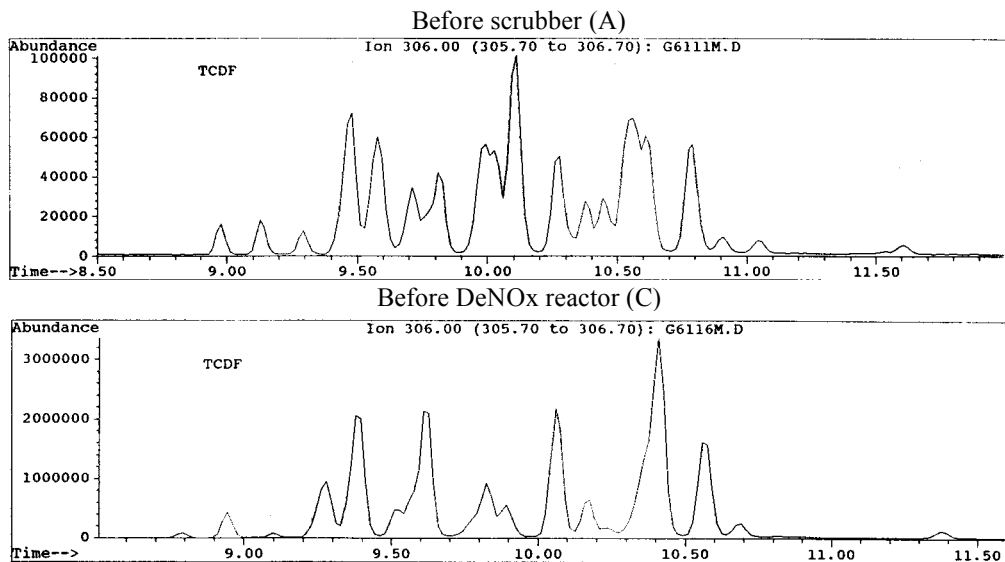


Fig.3. TCDF isomer profiles for flue gas samples

Dioxin isomer PCDF chromatographic profiles have been compared in detail; those for tetrachlorodibenzofurans (TCDFs), Fig.3, are distinctive, repeatable and almost identical during both trials, but are clearly different at the scrubber inlet (A) than before the DeNOx reactor (C). More dioxins were formed in the 1st trial, indicating that activated carbon is removing most of the

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precursors to this additional dioxin formation route. The dioxins formed prior to the DeNOx reactor, presumably at high local temperatures in the in-line burner, are almost exclusively PCDFs, so it is possible that they have been formed from chlorinated aromatic hydrocarbons which have not been adsorbed in the scrubber (e.g. polychlorobiphenyls, PCBs).

Used catalyst: Dioxin concentrations in both samples are very close to detection limits, however the corresponding maximum limits for both samples are 2.9 ng[Teq]/kg, Table 1. A rough estimate of the destruction efficiency of the catalyst system has been made, assuming that the flue gas dioxin concentrations at C and D during the 2nd trial are typical of normal operations. Thus ~140 mg[Teq] dioxins are removed by the catalyst during a year's operation. Applying the worst-case catalyst dioxin concentration of 2.9 ng[Teq]/kg to the total catalyst weight (6000 kg) accounts just for 17.4 µg[Teq] dioxins. Thus >99.98% of the dioxins (as Teqs) to which the catalyst has been exposed must have been destroyed.

Removal and Destruction of dioxin-related compounds: In a complementary laboratory rig [1] study at Umeå [1,2] removal and destruction efficiencies have been determined not only for dioxins, but also for dioxin precursors and related compounds, Table 2. This indicated that dioxins are removed and destroyed at efficiencies > 98%, and that:-

- PCPs (polychlorophenols) and PAHs (polycyclic aromatic hydrocarbons) are removed and destroyed almost as effectively as dioxins.
- PCBzs (polychlorobenzenes) are partially removed but all removal is destruction.
- PCBs are removed (>87 %) and destroyed (>69%) fairly successfully.

Table 2. Removal and destruction efficiencies for various dioxin-related compounds

	Flue gas concentration (ng/Nm ³)			Efficiency (%)	
	Before catalyst	After catalyst	On catalyst*	Removal	Destruction
dioxins	77.9	0.93	0.05	98.81	98.74
PCP	3.4 x 10 ⁴	6.8 x 10 ²	29	98.0	97.9
PCBz	7.5 x 10 ⁴	5.0 x 10 ⁴	2.0 x 10 ²	32.6	32.4
PCB	82	6.5	130	87.8	69.5
PAH	1.8 x 10 ⁴	82.6	52.9	99.5	99.2

Umeå lab-scale incinerator rig (233 °C, 40,000 GHSV); * calculated as equivalent flue gas concentration

Conclusions

Reformation of dioxins during reheating in the late stages of a typical MWI off-gas cleaning system has been demonstrated, together with their subsequent efficient destruction by the Shell Denox System. The benefits of utilising low temperature DeNOx catalyst as a fail-safe end-of-pipe technology are clear, particularly where carbon injection systems are employed, for in addition to dioxin reformation, there is always a risk of carbon carryover releasing adsorbed dioxins into the atmosphere, particularly during incinerator start-up.

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References

1. Andersson, P., Rappe, C., Maaskant, O., Unsworth, J.F., and Marklund, S., *Organohalogen Compounds (Dioxin '99)*, **1998**, 36, 109.
2. Clark, D.M., Andersson, P., Marklund, S. and Unsworth, J.F., Using the Shell Dioxin Destruction System in Process Flue Gas Streams, 1st Singapore Chem. Conf., 7-9 Dec 1998.

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