Sulfur Recirculation for Reducing Dioxin Formation in Waste-to-Energy plants

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Introduction

Under controlled combustion conditions, PCDD/Fs are almost completely destroyed in the combustion chamber of modern Waste-to-Energy plants¹, but some PCDD/Fs are formed in the ash deposits of the boiler section^{1,2}. The EU emission limits for Waste-to-Energy plants are prescribed in the Industrial Emissions Directive, IED (2010/75/EC). New, more stringent, requirements will however likely be the result of the now ongoing review process of the Best Available Technology (BAT) Reference Document on Waste Incineration from 2006 (WI BREF). Techniques for meeting the emission limit for PCDD/Fs include the use of catalysts and adsorbents. Dosage of activated carbon into a bag house filter is the most commonly used method. An alternative is the ADIOX technology, which utilises tower packings produced from carbon filled polymers³. Due to the high absorption capacity of this material, the typical life time is 5-8 years depending on application. The tower packings can be incinerated after use, thus destroying the PCDD/Fs, rather than landfilling them as is the case with other adsorption technologies.

Higher sulfur dioxide concentration suppresses PCDD/F formation⁴. Permanently high SO₂ concentrations in the flue gas cause sulfation of the boiler ash deposits, which leads to low chlorine concentrations in the deposits, which in turn suppresses the dioxin formation⁵. Such high SO₂ concentrations can be obtained by dosing sulfur with the fuel, resulting in increased amounts of flue gas treatment residues. Another way of achieving high SO₂ concentration is by recirculating sulfur from the flue gas treatment to the boiler: Sulfur Recirculation is a patented technology using this method for reducing high temperature boiler corrosion and dioxin formation in Waste-to-Energy plants. Sulfur Recirculation was initially demonstrated in the 0.5 MW waste incineration pilot plant "TAMARA" at KIT^{5,6} as well as in full-scale tests at a Waste to Energy plant in Göteborg (Sweden) during nearly two months of operation⁷. During the pilot tests, the PCDD/F raw gas concentration decreased steadily from a few ng TEQ/Nm³ d.g. to approximately 0.1 ng TEQ/Nm³ d.g. during a two-weeks long campaign. During the full scale tests, the raw gas concentration decreased by approximately 25%. In 2016, the first permanent full-scale installation was taken into operation.

Materials and methods

Babcock & Wilcox Vølund AB (previously Götaverken Miljö AB) has installed the Sulfur Recirculation technology in one of the two Waste-to Energy lines at Måbjerg Energy Center (MEC) in Denmark in order to combat high temperature corrosion, decrease dioxin formation and eliminate the sulfate waste water. This is the first commercial installation of this kind and it has been in operation since mid-October 2016.

The Waste-to-Energy plant produces electricity and district heating and consists of two incineration lines with a capacity of 10 tons/h of waste each. The fuel consists of mainly household waste, with some addition of industrial waste and sludge. Both lines are operating with the same fuel mix, fed from one bunker. A third straw fired line is not covered in this paper. The flue gas treatment consists of an Electrostatic Precipitator, a HCl scrubber and a multistage scrubber for SO₂ removal, dioxin removal using ADIOX and flue gas condensation for producing additional district heating. The flue gas treatment has been operating with this configuration since 2004 and the PCDD/F emission limit has been met at all measurements so far.

In 2016, Sulfur Recirculation was installed at Line 1 (L1) shown in Figure 1. The Sulfur Recirculation installation consists mainly of a storage vessel and dosage system for hydrogen peroxide (H_2O_2), a raw gas analyzer for SO₂, equipment for transport and dosage of sulfuric acid into the furnace. SO₂ is now separated in the wet scrubber using H_2O_2 , producing a 15-25wt% H_2SO_4 solution, which is injected into the boiler producing SO₂, thus creating a sulfur loop. The sulfuric acid is sprayed through nozzles with atomization air, which produces a fine mist which evaporates rapidly. The dosage rate is controlled by a regulator, which maintains a fixed SO₂ setpoint. The recirculated sulfur will increase the gas concentration of SO₂ in the boiler and decrease the Cl/S ratio of the deposits and ashes, thus lowering chlorine content of the boiler deposits, in order to decrease the high temperature corrosion and the dioxin formation rates as well as dioxin emissions. The dioxin emissions are normally measured two times per year and two samples per line. During the first two years of operation with ADIOX, 2004-2005, the dioxin concentration was additionally measured downstream of the ESP, but upstream of the scrubbers in order to measure the dioxin removal efficiency of ADIOX.



Figure 1 The flue gas treatment of MEC consists of an ESP (Electrostatic Precipitator), a HCl scrubber and a multistage scrubber for SO₂ removal, dioxin removal using ADIOX and flue gas condensation

Results and discussion

Sulfur Recirculation decreased the high temperature corrosion rates of the superheaters in this full-scale installation by approximately 50%, which may prolong the service life of the superheaters and/or increase the electricity production from combustion of biomass and waste in the future. In addition, at this plant, Sulfur Recirculation almost entirely decreased the need for costly road transports of effluent sulfate water for the Sulfur Recirculation line, since most sulfur from the waste now ends up in the ashes instead of creating a surplus dilute Na₂SO₄ solution. The sulfur content of the waste varies with time, which may create periods of sulfur surplus and deficit respectively. Most of these variations are being evened out by a storage vessel for H_2SO_4 . With Sulfur Recirculation in operation, the mean dioxin stack concentration decreased from 0.020 ng TEQ/Nm³ d.g. @11% O₂ to 0.0055 ng TEQ/Nm³ d.g. @11% O₂, corresponding to a decrease of 72% as seen in Table 1.

Table 1: PCDD/F emissions in ng TEQ/Nm³ d.g. @11% O₂ from the MEC Waste-to-Energy plant (DK) for line L1 with Sulfur Recirculation in operation (rec) and in normal operation (ref), as well as for line L2 without Sulfur Recirculation (ref).

	L1 rec	L1 ref	L2 ref
2013-11-20		0.029	0.038
2014-01-08		0.030	0.041
2014-02-25		0.021	0.042
2014-02-25		0.019	0.038
2014-09-12		0.013	0.016
2014-09-13		0.013	0.017
2015-03-17		0.014	0.018
2015-03-18		0.014	0.017
2015-11-11		0.005	0.006
2015-11-12		0.004	0.008
2016-03-09		0.013	0.022
2016-03-10		0.010	0.021
2016-11-03	0.005		0.045
2016-11-04	0.005		0.046
2017-01-11	0.006		0.013
2017-01-11	0.006		0.013
2017-09-19	0.007		0.008
2017-09-20	0.005		0.009
2018-03-21	0.006		0.012
2018-03-22	0.005		0.012

In order to assess the influence of the dioxin formation rate, the raw gas concentration upstream of the dioxin removal technology ADIOX, two measurements were performed with Sulfur Recirculation in operation and

compared to previous measurements at the same sampling position. The mean raw gas concentration decreased from 1.87 ng TEQ/Nm³ d.g. @11% O₂ to 0.47 ng TEQ/Nm³ d.g. @11% O₂, corresponding to a decrease of 75% according to Table 2.

Table 2: PCDD/F raw gas concentrations in ng TEQ/Nm³ d.g. @11% O₂ (downstream of the ESP) from the MEC Waste-to-Energy plant (DK) for line L1 with Sulfur Recirculation in operation (rec) and in normal operation (ref), as well as for line L2 without Sulfur Recirculation (ref).

	L1 rec	L1 ref	L2 ref
2004-10-26		1.1	
2004-11-17		1.3	0.71
2004-12-08		2.2	1.18
2005-08-02		4.8	2.3
2005-11-08		1.6	1.6
2017-09-19	0.45		
2017-09-20	0.49		

The dioxin concentrations upstream of the dioxin removal system decreased by 75% and the dioxin emissions decreased by 72% in the MEC Waste to Energy plant with Sulfur Recirculation in operation. In addition to decreasing the high temperature corrosion, Sulfur Recirculation can also decrease dioxin formation and emissions.

Acknowledgements:

The Måbjerg Energy Center Waste to Energy plant is gratefully acknowledged for providing the dioxin emission data.

References:

- 1. Hunsinger H., Jay K. and Vehlow J. (2002) Chemosphere 46: 1263-72
- 2. Stieglitz L. Zwick G., Beck J., Roth W., Vogg H. (1989) Chemosphere 18(12): 1219-1226
- 3. Andersson, S., Kreisz, S., Hunsinger, H., (2005) 42(10): 22-25
- 4. Gullett B.K., Environ. Sci. Tech. (1992) 26(10): 1938-1943
- 5. Hunsinger H., Seifert H. and Jay K. (2007) Environ. Eng. Sci., 24: 1145-1159
- Hunsinger H., Andersson S., (2014) Journal of Material Cycles and Waste Management, Oct 2014, Vol. 16: 657-664
- Andersson S., Blomqvist E., Bäfver L., Jones F., Davidsson K., Froitzheim J., Karlsson M., Larsson E., Liske J., (2014), Waste Management 34 pp. 67-78