

# PDDD/Fs DECONTAMINATION FOR AN INCENERATOR WASTEWATER TREATMENT PLANT

Guerriero E<sup>1</sup>, Olivieri F<sup>1</sup>, Rossetti G<sup>1</sup>, Rotatori M<sup>1</sup>, Cincinelli A<sup>2</sup>, Ferrini M<sup>3</sup>, Piga L<sup>3</sup>, Saviano G<sup>3</sup>, Manni A.<sup>3</sup>

<sup>1</sup>CNR-Istituto sull'Inquinamento Atmosferico Via Salaria, Km 29m300, 00016 Monterotondo Scalo (Rome)

<sup>2</sup>Dept. of Chemistry, University of Florence, Sesto Fiorentino (Firenze)

<sup>3</sup>Dept. ICMA, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Rome

## Summary

A wastewater treatment plant, receiving incinerator plant effluents, was showing a high level of PCDD/Fs in the outgoing stream. Those level were near the limits of the Italian directive (0,3 ngTE/L<sup>1</sup>). Reduction of the pollutants was obtained by the means of zeolitized powdered tuffs, simulating their addition to the pond where the final step before the releasing into the environment, is performed.

The influence of residence time, solid/liquid ratio were studied.

## Introduction

Many incineration plants use wet scrubber as system for the abatement of macro and micro pollutants<sup>2</sup>. Wet scrubbers perform better than dry ESPs in capturing small particles and have the highest removal efficiencies for soluble acid gases among the demonstrated techniques but waste water can cause problems, especially if PCDD/F emissions are present. In fact this water has to be cleaned in wastewater treatment plants. At the end of the process they release the treated stream in small river showing, especially in summer, very small capacity. Plants often do not manage to meet the limits, specified by law and reported above, for the PCDD/F's content in the outgoing stream.

In the past years the ability of zeolitized tuffs to remove dioxin<sup>3</sup> and PAH<sup>4</sup> was demonstrated on spiked samples. In the present work the possibility to use the same material on a real case study it has been assessed.

## Materials and methods

Zeolitized tuffs from the Roman province, being a waste of the quarrying production for building materials, was only sieved and the size distribution was -500 +100  $\mu$ m.

Polluted water was obtained from a plant after its treatment of industrial effluent and showed minor amount of suspended solids having a dimensions ( $d_{80}$ ) of 0.34  $\mu$ m.

Labelled internal standards were added to the water; precisely EPA 1613-LCS (Wellington Laboratories, Canada); 1liter of polluted wastewater and zeolitized tuff were in contact, in a continuously stirred batch reactor, with different residence time and at different solid/liquid ratio, as reported in table 1.

Residence time (min)	Liquid / Solid (w/w)= 15	Liquid / Solid (w/w)= 50	Liquid / Solid (w/w)= 250	Liquid / Solid (w/w)= 500
60	60/15	60/50	60/250	60/500
120	/	120/50	/	/
240	240/15	240/50	240/250	240/500
480	/	/	480/250	480/500

Table 1. – Schematics of the tests performed.

Liquid-liquid extraction of the contaminants from the wastewater was performed in 3 times by the means of dichloromethane, with a contact time of 1 night for first time and 3 hours for second and third times.

Automated GPC clean-up and automated concentration of the different phases were performed using Accuprep<sup>TM</sup> and Accuvap<sup>TM</sup> from J2 Scientific, Missouri, USA, and an alumina column (Alumina Super B, IGN) according the procedure reported in Guerriero et al.<sup>5</sup>.

Analysis were performed by the means of a GC/MS/MS TSQ from ThermoFisher Scientific, USA, directly interfaced to a ThermoFisher Scientific ultra trace GC oven. Chromatographic separation was achieved with a

RTX-5 (Restek) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 mm film thickness) with helium as carrier gas in the splitless injection mode.

## Results

Wastewater originally showed a PCDD/F's concentration reported in table 2.

Table 3 and table 4 show the residual amount of the PCDD/F's in the wastewater, as percent of the original concentration, in the different experimental condition.

PCDD/F <i>Congener</i>	Concentration pg TEQ/liter
2,3,7,8-TCDD	13,43
1,2,3,7,8-PCDD	30,59
1,2,3,4,7,8-HxCDD	8,05
1,2,3,6,7,8- HxCDD	8,47
1,2,3,7,8,9- HxCDD	8,23
1,2,3,4,6,7,8-HpCDD	19,56
OCDD	3,50
2,3,7,8-TCDF	6,95
1,2,3,7,8-PCDF	2,51
2,3,4,7,8-PCDF	44,57
1,2,3,4,7,8-HxCDF	15,15
1,2,3,6,7,8-HxCDF	11,77
2,3,4,6,7,8-HxCDF	38,05
1,2,3,7,8,9-HxCDF	7,82
1,2,3,4,6,7,8-HpCDF	17,43
1,2,3,4,7,8,9-HpCDF	3,57
OCDF	1,72
<b>PCDD/F sum</b>	<b>241,37</b>

Table 2 – PCDD/F's concentration originally present in the water after the treatment of industrial effluent

Residence time (min)/ Liquid-Solid ratio	60/15	60/50	60/250	60/500	120/50
2,3,7,8-TCDD	1,3	2,3	7,2	13,2	0,4
1,2,3,7,8-PCDD	1,7	6,5	11,0	11,1	0,4
1,2,3,4,7,8-HxCDD	1,3	3,1	22,3	23,7	0,1
1,2,3,6,7,8- HxCDD	0,9	6,8	23,3	27,9	0,2
1,2,3,7,8,9- HxCDD	1,4	3,2	22,5	22,9	0,1
1,2,3,4,6,7,8-HpCDD	0,9	9,9	19,2	16,0	0,6
OCDD	0,3	6,4	34,1	53,0	0,7
2,3,7,8-TCDF	0,7	3,4	16,9	18,3	0,0
1,2,3,7,8-PCDF	0,0	2,1	12,1	11,7	0,2

2,3,4,7,8-PCDF	0,0	2,3	11,0	12,1	0,2
1,2,3,4,7,8-HxCDF	1,3	3,8	13,3	16,6	0,4
1,2,3,6,7,8-HxCDF	0,4	3,2	27,9	21,8	1,1
2,3,4,6,7,8-HxCDF	0,2	8,6	15,9	26,5	0,1
1,2,3,7,8,9-HxCDF	0,3	5,4	22,3	24,1	0,6
1,2,3,4,6,7,8-HpCDF	0,1	3,6	10,5	8,8	0,1
1,2,3,4,7,8,9-HpCDF	0,1	2,9	9,7	9,1	0,1
OCDF	0,0	0,0	0,6	0,1	0,0

(a) % = [PCDD/F recovered amount/PCDD/F initial amount ]\*100

Table 3 –% Residual amount of the PCDD/F's in the wastewater

Residence time (min)/ Liquid-Solid ratio	240/15	240/50	240/250	240/500	480/250	480/500
2,3,7,8-TCDD	0,0	1,5	6,7	5,5	0,5	13,2
1,2,3,7,8-PCDD	0,6	1,2	7,6	5,4	1,6	15,4
1,2,3,4,7,8-HxCDD	0,0	0,0	11,8	15,6	3,2	37,4
1,2,3,6,7,8- HxCDD	0,0	0,0	14,0	16,8	2,7	33,8
1,2,3,7,8,9- HxCDD	0,0	0,0	11,6	15,7	3,3	34,6
1,2,3,4,6,7,8-HpCDD	2,6	1,1	14,5	8,4	2,2	31,0
OCDD	1,8	0,2	1,5	20,9	4,9	54,7
2,3,7,8-TCDF	1,8	0,0	7,8	5,3	1,3	12,3
1,2,3,7,8-PCDF	0,6	0,6	5,1	8,8	1,2	12,4
2,3,4,7,8-PCDF	0,7	0,5	5,7	9,0	0,6	21,6
1,2,3,4,7,8-HxCDF	1,0	0,1	7,2	12,1	3,4	43,4
1,2,3,6,7,8-HxCDF	1,2	0,6	11,4	21,8	0,9	35,9
2,3,4,6,7,8-HxCDF	1,5	0,2	12,6	12,6	2,8	36,9
1,2,3,7,8,9-HxCDF	1,2	0,3	12,8	18,4	1,6	34,5
1,2,3,4,6,7,8-HpCDF	0,9	0,0	5,2	6,1	0,4	3,1
1,2,3,4,7,8,9-HpCDF	0,7	0,0	4,8	5,4	0,3	3,4
OCDF	0,2	0,0	0,0	0,0	0,0	0,0

(a) % = [PCDD/F recovered amount/PCDD/F initial amount ]\*100

Table 4 – % Residual amount of the PCDD/F's in the wastewater

## Discussion

Zeolitized tuff from the Roman province was able to reduce the amount of PCDD/Fs discharged in the environment.

Figures 1 shows the influence of residence time and liquid/solid ratio for has result of the consolidation of the data reported in table 2 and table 3 and their extrapolation: each data represents the percentage of the total PCDD/F sum reported in table 2. It shows that the effectiveness of PCDD/F's extraction increases both with the residence time and with the solid/liquid ratio. The correct choice of the final parameters will depend from the plant design, especially in relation to the flowrate and volume of the reaction-settling ponds.

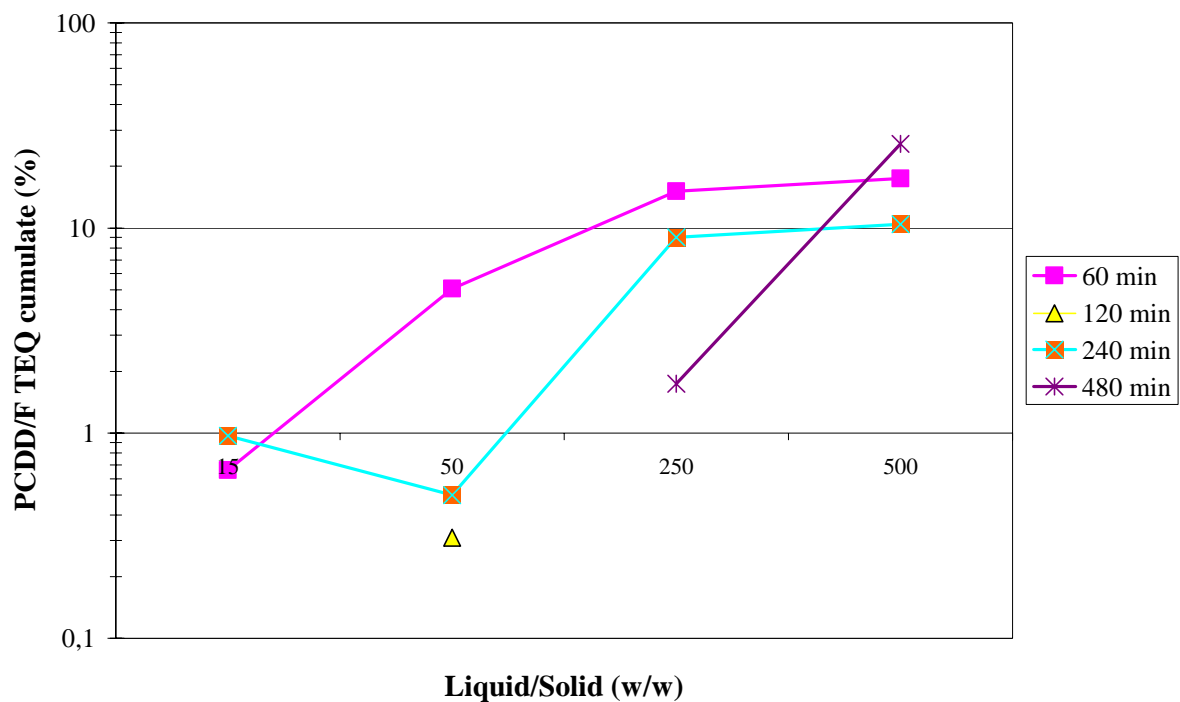


Fig. 1- % residual amount vs liquid-solid ratio at different residence time

## References

1. European Directive 2000/76/CE (Italian Legislative Decree 133/2005)
2. European Commission. 2004. Reference Document on the Best Available Techniques for Waste Incineration. BAT Reference Document (BREF), 2nd Draft, March 2004. European IPPC
3. Manni A., Saviano G., Rotatori M., Guarnieri A., Guerriero E., *Organohalogen Comp* 2006; 68: 2326
4. Manni A., Saviano G., De Casa G., Rotatori M., Guarnieri A., Guerriero E., *Organohalogen Comp* 2007; 69: 2938-2941
5. Guerriero E., Rotatori M., Mosca S., Rossetti G., Manni A., submitted for publication to *Organohalogen Comp* 2008; 70