Adiox® for dioxin removal in wet scrubbers and semi-wet or dry absorbers

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Abstract

Adiox® is a state-of-the-art dioxin removal technology that has established itself as a cost-effective way to reduce dioxin emissions to the atmosphere. Adiox is a construction material in which carbon particles are dispersed in a polymer such as polypropylene. Several types of components such as tower packings for wet scrubbers, demisters (droplet separators) and dry or semi-wet fixed bed fillings can be produced from Adiox material.

The majority of the Adiox installations can be divided into three main categories:

a) Adiox as police filter to reduce or eliminate the "memory effect" in scrubber systems with upstream dioxin removal in bag house filters.
b) Adiox in combination with other dioxin removal technologies in order to improve the overall dioxin removal and increase the safety margins.
c) Adiox as the primary dioxin removal system for meeting the EU waste incineration directive with an emission requirement of < 0.1 ng TEQ/m^3 (n., d.g., 11% O_2). At Måbjergværket in Denmark, wet Adiox scrubbers in combination with one electrostatic precipitator per line act as the main dioxin filter since the fall of 2004. The dioxin measurements carried out so far show stack concentrations far below the emission limit.

If Adiox is employed in a dry absorber instead of a wet scrubber, the specific removal efficiency is higher, which leads to smaller equipment sizes. A full-scale dry absorber has been in operation at the Linköping municipal waste incineration facility since the end of 2006. After use, Adiox can be incinerated, thereby destroying the dioxins.

Keywords: PCDD/F, dioxin removal, flue gas cleaning, air pollution control, memory effect, wet scrubber, Adiox.

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1 Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are a group of carcinogenic, extremely toxic and persistent, chlorinated organic compounds. There is strong public concern about this group of compounds, commonly denoted as dioxins. Major emission sources are known to be processes such as waste incineration, metal production, biomass incineration and uncontrolled combustion.

A number of technologies are available for removing or destroying dioxins from gases, but the investment and/or running costs of these technologies are usually very high. Adiox® is a state-of-the-art dioxin removal technology which has proven itself as an efficient, reliable and competitive method with reference installations at some 65 municipal and hazardous waste incinerators. It can be applied as a stand-alone technology as well as integrated in existing flue gas cleaning devices. The Adiox construction material is based on a polymer, such as PP (polypropylene), in which carbon particles are dispersed in a polymer. Different components such as tower packings, demisters (droplet separators) and dry fixed bed fillings can be produced from Adiox material.

2 Material

The background for inventing Adiox was the observation that polymers can absorb large amounts of dioxins from gases, which can later be desorbed. This absorption/desorption equilibrium is also known as the Memory Effect.

2.1 Dioxin absorption and desorption in polymers

Polymers are widely used in flue gas cleaning devices, such as wet scrubbers, due to the excellent chemical resistance and low cost. The absorption/desorption process of dioxins in polymers can cause a long period of dioxin desorption from the polymer surfaces after operational disturbances or start-up, since the dioxin concentrations may be very large during e.g. start-up [1]. The system “remembers” the previous high concentrations. The dynamic behaviour of the adsorption/desorption of dioxins is governed by the equilibrium of dioxins in gas/polymer and the diffusion of dioxins in the polymer. The equilibrium constant and diffusivity for PeCDFs (Penta Chlorinated Dibenzo Furans) were estimated by studying absorption and desorption of dioxins in PP test rods [2]. PeCDF was used as a model substance for the TEQ value, since penta chlorinated congeners accounted for the largest contribution to the TEQ value. The test rods were exposed to flue gas with a known mean dioxin concentration during one year. After that, the test rods were exposed to a very low dioxin concentration. The 4 mm thick test rods were exposed to flue gas of a municipal waste incinerator with an average dioxin concentration of 8 ng TEQ/m^3 (n., d.g.) (according to EN1948) in the gas during one year and an average of 0.04 ng TEQ/m^3 (n., d.g.) for more than two years. The dioxin concentrations in the test rods were analysed after 1, 3, 6, 9, 12, 18, 30 and 40 months of exposure. The equilibrium constant and diffusivity were estimated by solving the unsteady diffusion equation for this case. The governing partial differential equations were solved numerically [2] in order to model the memory effect in a wet scrubber at a hazardous waste incinerator. The model was compared to measured stack emission data.

2.2 The Adiox material

In order to avoid the dioxin release from the material, carbon particles are dispersed in a polymer, such as PP. In this new material, called Adiox, the dioxins are first absorbed in the PP. Then they diffuse to the surface of the carbon particles, where they are practically irreversibly adsorbed. The PP acts as a selective barrier, which protects the carbon from other contaminants such as Hg. Glass fibres may also be added in order to improve the mechanical properties at higher temperatures.

Figure 1: From the left: Adiox granules, Adiox Hiflow tower packings and Adiox Telpac tower packings. A number of different geometrical shapes and sizes can be used in order to optimise pressure drop and removal efficiency for a given application.

Several types of components, such as tower packings and demisters (droplet separators) and dry fixed bed fillings can be produced from Adiox material [3]. Some examples are shown in Figure 1. The dioxin removal efficiency of Adiox tower packings and demisters is favoured by the large specific surface area, selectivity for dioxins and high absorption capacity. By analysing the dioxin concentration of the Adiox material, it is possible to estimate the total amount of dioxins captured. By applying a mass balance, an estimate of the mean dioxin concentration removed from the gas during the operating period can be made.

The life time of the material depends on the application, but is normally 2-4 years. The life time is limited by ageing of the base polymer, surface scaling or dioxin absorption capability. Ageing of the polymer, which leads to embrittlement of the material, is the most likely life time limiting factor. It is possible to incinerate the material after usage. Practically no residues are produced during incineration of the material and the dioxins are destroyed and thereby removed from the eco cycle.

3 Results

Adiox allows the design of multifunctional wet scrubbers, where HCl, HF, SO_2 and oxidised Hg as well as dioxins can be removed simultaneously in one unit. Elemental Hg can be oxidised and captured in the scrubber using the MercOx process based on hydrogen peroxide [4]. Extended energy recovery by condensation of the flue gas can be integrated in the scrubber as well. Provided that there is need for low temperature heat, such as a municipal heating net, flue gas condensation can increase the overall energy efficiency of the plant significantly.

Areas where Adiox is particularly well suited for removing dioxins from gases include municipal waste incineration, hazardous waste incineration, chemical industry and biomass industry. Today, Adiox has been installed in all of these application fields.

The first full-scale test installation was made at the MSWI plant of Thisted (Denmark) in 2001. PP tower packings were replaced by Adiox tower packing in two existing scrubbers. The dioxin removal efficiency was constant during one year of operation [3]. Since the market introduction in 2002, Adiox has been installed at approximately 65 full-scale incineration lines. The gas flows range from 5 000 to 186 000 m^3/h (n, w.g.). The majority of the present Adiox installations can be divided into three main categories described in the following sections:

> **3.1 Adiox as police filter** to reduce or eliminate the "memory effect" in scrubber systems with upstream dioxin removal in bag house filters.
> **3.2 Adiox in combination with other technologies** in order to improve the overall dioxin removal and increase the safety margins.
> **3.3 Adiox as the primary dioxin removal system** for meeting the EU waste incineration directive with an emission requirement of < 0.1 ng TEQ/m^3 (n., d.g., 11% O_2). At Måbjergværket in Denmark, wet Adiox scrubbers in combination with one ESP (Electrostatic Precipitator) per line act as the main dioxin filter since the fall of 2004.

3.1 Adiox as police filter

The use of Adiox tower packing as police filter in a scrubber downstream of a primary dioxin removal system, such as a bag house filter, will result in additional security to guarantee low emission values. In that case, Adiox will increase the margins in the case of e.g. carbon dosage failure, filter leakage or increased dioxin concentrations during start-up, where also the memory effect may lead to prolonged periods of increased emission concentrations in the stack. Adiox has been installed in the MercOx-scrubber at Sakab, Sweden, downstream of a bag house filter in combination with carbon injection as seen in Figure 2.

3.2 Adiox in combination with other technologies

Adiox is in some cases used in combination with other dioxin removal technologies in order to improve the overall dioxin removal and increase the

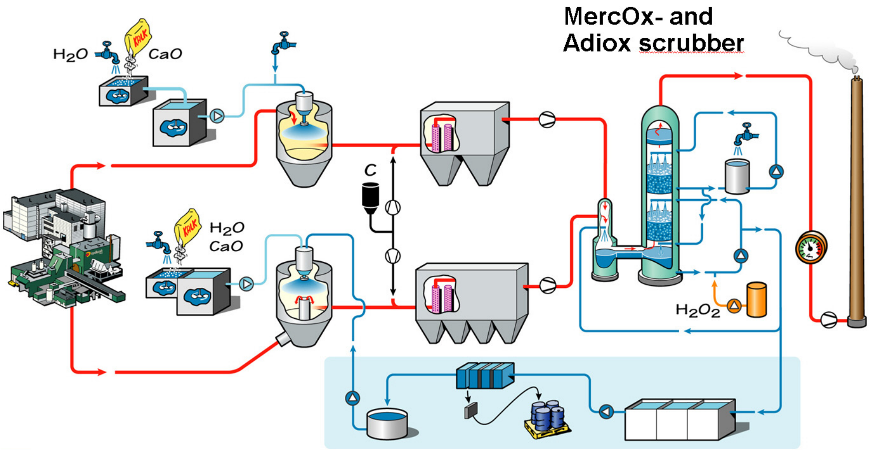

Figure 2: MercOx and Adiox scrubber for simultaneous HCl, SO_2, Hg and dioxin removal at the Sakab hazardous waste incinerator. Figure by Holmberg.

safety margins. For example, at the AVR Duiven MSWI (Municipal Solid Waste Incineration) plant in the Netherlands all three lines have integrated the Adiox system in the existing system for dioxin removal, which comprises circulation of activated carbon slurry.

3.3 Adiox as the primary dioxin removal system

A pilot scrubber was installed in series with a full-scale, two-stage Adiox scrubber after an ESP at the Kolding MSWI plant in Denmark. The aim of this installation was to demonstrate how economic and operational benefits can be gained by complete integration of the dioxin removal into the wet scrubbing process downstream of an ESP. The experiences from these pilot tests served as a design basis for the full-scale installation at the Måbjergværket MSWI plant in Denmark, where wet Adiox scrubbers in combination with one ESP per line act as the main dioxin filter since the fall of 2004 (Figure 3). The plant is located in Holstebro and has an incineration capacity of 2 x 9 tonnes per hour. The scrubber system is designed for a maximum gas flow of 2 x 105 000 Nm^3/h. All dioxin measurements done so far show that the concentrations in the stack are far below the emission limit of 0.1 ng $I\text{-}TEQ/m^3$ (n., d.g.), as can be seen in Table 1.

The amount of Adiox material required for achieving the desired dioxin removal is determined on the basis of the dioxin concentration in the raw gas. Using Adiox as a primary dioxin removal system, this amount is typically larger than the amount of normal tower packings required for HCl and SO_2 removal. Using Adiox in a dry absorber instead, would make the installation more compact, since Adiox is more efficient under dry conditions.

Figure 3: Adiox has been in operation as a primary dioxin removal system since 2004 at Måbjergværket Holstebro (Denmark) operated by Dong Energy. From left to right: ESP, HCl scrubber with Adiox and finally SO_2 and condensing scrubber with Adiox.

Table 1: Dioxin measurements upstream and downstream of the Adiox scrubbers at Måbjergværket Holstebro (Denmark).

	Line 1 (ng I-TEQ/m^3 (n., d.g. @ 11% O_2))			Line 2 (ng I-TEQ/m^3 (n., d.g. @ 11% O_2))		
Date	**Raw gas**	**Clean gas**	**Efficiency**	**Raw gas**	**Clean gas**	**Efficiency**
Oct. 2004	1.1	0.0038	99.7%	-	-	
Nov. 2004	1.3	0.0025	99.8%	0.71	0.0039	99.5%
Dec. 2004	2.2	0.0048	99.8%	1.18	0.0036	99.7%
March 2005	-	0.0056	-	-	0.0074	
Nov. 2005	1.6	0.0058	99.6%	1.6	0.0052	99.7%
March 2006	-	0.010	-	-	0.021	-
Feb.-March 2007	-	0.0096	-	-	0.022	-
Oct. 2007	-	0.011	-	-	0.023	-
Guarantee	≤ 5	≤ 0.09	98.2%	≤ 5	≤ 0.09	98.2%

3.4 Wet, semi-wet and dry operating modes

In addition to the use of Adiox in wet scrubbers described above, which represents the largest portion of installations to this date, Adiox can also be used in semi-wet and dry operating modes. Semi-wet operation in this respect means that flue gas saturated with water vapour passes through a fixed bed of Adiox tower packings without liquid circulation. Alternatively, intermittent flushing can be used to prevent dust build-up. The advantages are lower energy cost from pumps and pressure drop due to lower liquid hold-up compared to wet packings with liquid circulation.

The third option is the dry operating mode. The initial laboratory tests of Adiox were performed with dry gas [5]. If Adiox is employed in a dry absorber instead of a wet scrubber, the removal efficiency is higher, since the water film in a wet scrubber poses a mass transfer limitation for the dioxins. Less material is thereby required for the same removal efficiency. A simple, cost-effective pollution control system can be obtained by combining an ESP, a multi-functional wet Adiox scrubber and a dry Adiox absorber as seen in Figure 4.

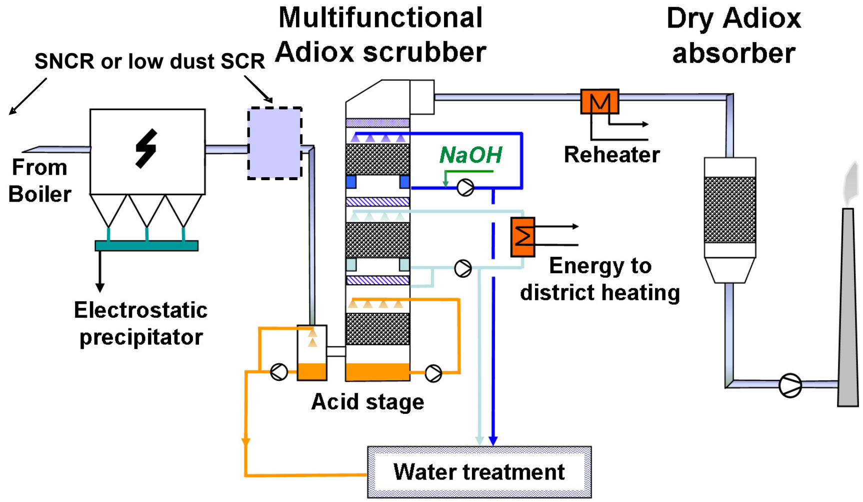

Figure 4: State-of-the-art flue gas cleaning system consisting of an ESP, multifunctional Adiox scrubber and dry Adiox absorber.

Fixed bed carbon filters are sometimes used as a final dioxin removal stage. There is a risk of fire in these filters, and contaminated dust particles may escape during operation or handling of the carbon pellets. Using Adiox material instead of carbon pellets would not have these disadvantages. The design of the absorber can be kept simple, since no material dosing system is required. Granular beds have porosities around 30%. If the gas contains particles, parts of the bed may be clogged, leading to channelling and increased pressure drop. Tower packings, originally designed for the use in wet scrubbers, can be used instead. The porosity is typically 95%, which reduces the risk for clogging. Intermittent rinsing may be used to reduce the risk further.

A dry pilot absorber, using Adiox tower packings, was installed at line 1 of the Renova municipal waste incinerator in Göteborg (Sweden). The flue gas treatment consists of an ESP, two wet scrubbers, reheater and a bag house filter. The pilot scrubber operates with a fraction of the total gas flow (approximately 3000 m^3/h) extracted after the reheater. The inlet concentrations ranged from 0.7 to 2.0 ng I-TEQ/m^3 (n, d.g., 11% O_2), and the clean gas concentrations ranged from 0.002 to 0.02 ng I-TEQ/m^3 (n, d.g., 11% O_2). No trend of decreasing removal efficiency with time could be seen [6].

Figure 5: A dry Adiox absorber at Tekniska Verken Linköping (Sweden).

A full-scale dry absorber has been in operation at the Linköping municipal waste incineration plant since December 2006 (Figure 5), serving three incineration lines with a total flue gas flow of 186 000 Nm^3/h. The measured removal efficiency is > 97%. The guaranteed emission value is < 0.1 ng I-TEQ/m^3 (n., d.g.) at 1.0 ng I-TEQ/m^3 (n., d.g.) in the inlet.

4 Conclusions

Adiox is well suited for selective absorption of dioxins in wet gas scrubbers and semi-wet or dry absorbers. It can be integrated in new or existing wet scrubber without the need for additional equipment. The Adiox material can be produced in a wide range of specific surface areas and geometrical shapes, which makes it possible to optimise pressure drop and removal efficiency for a given application. Using the material in a dry absorber can decrease equipment sizes due to the higher efficiency per volume.

The system is static which makes it robust and reliable. It is effective even during start-up and in stationary operating conditions, where other technologies may not work optimally. The carbon particles are encapsulated in polypropylene, which makes the material easy to handle. After use, Adiox can be incinerated, thereby destroying the dioxins.

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