

Adiox™ is an innovative material for removing toxic dioxins from combustion gases, making it an ideal absorbing material for tower packings and demisters in wet scrubbers. Adiox can also be used as a police filter to reduce the memory effect, as well as the primary dioxin removal technology. Sven Andersson, Siegfried Kreis and Hans Hunsinger discuss this novel technology for the cleaning of flue gases.

Innovative Material Technology Removes Dioxins from Flue Gases

Dioxins, or polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDD/Fs), are a group of persistent and extremely toxic chlorinated organic compounds. Major emission sources are known to be processes like waste incineration, metal production, bio-fuel incineration and uncontrolled combustion. Under stable combustion conditions, dioxins are almost completely destroyed during incineration, but are re-formed during the cooling of the flue gas [1] and during dust separation at temperatures above 200 °C by de-novo synthesis [2]. A review of the formation mechanisms involved is given by Tuppurainen et al. [3].

Dioxin concentrations are commonly reported as toxic equivalents (TEQ), which is the sum of the congener concentrations multiplied by their specific TEQ-factors. The extreme toxicity of 2,3,7,8-Tetra-CDD (also known as Seveso-dioxin) is the reference and has a TEQ-factor of one. Dioxins and furans containing higher numbers of chlorine atoms (including the 2-, 3-, 7- and 8-positions) have lower TEQ-factors.

State-of-the-art dioxin removal

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. Waste incineration plants commonly use bag house filters (fabric filters), equipped with activated carbon injection, or fixed bed carbon filters in order to fulfil the emission limits for dioxins. SCR-catalysts (selective catalytic reduction) for NO_x-reduction

combined with an oxidation catalyst are also known to be an effective method to destroy dioxins. This method, however, requires a costly gas re-heating if used after wet scrubbers (gas-liquid contactors for removing acid components).

Other methods for dioxin removal include catalytic bag filters, as well as the injection of activated carbon or tensides in wet scrubbers.

Memory effect

Plastics, such as polypropylene (PP), are widely used as construction material in wet scrubbers because of their excellent corrosion resistance and low price. Significant amounts of dioxins can initially be transferred from the flue gas to the plastics until an equilibrium loading is reached. However, this equilibrium can be disturbed by changes in temperature or dioxin concentration. An increase in the temperature or decrease in gas concentration will lead to dioxin desorption to the gas phase. This absorption/desorption behaviour is known as the 'Memory Effect' (Figure 1a).

The equilibrium concentration in the plastic is very temperature dependent. An increase in temperature from 65 °C to 90 °C increases the desorption rate of dioxins from PP by a factor of ten [4]. Both the vapour pressure [5] and the diffusivity [6] increase with a decreasing degree of chlorination. The desorption rates are therefore higher for the lower chlorinated dioxins and furans. The lower chlorinated dioxins contribute the most to the TEQ-value. Subsequently, the Memory Effect can contribute significantly to the emission value.

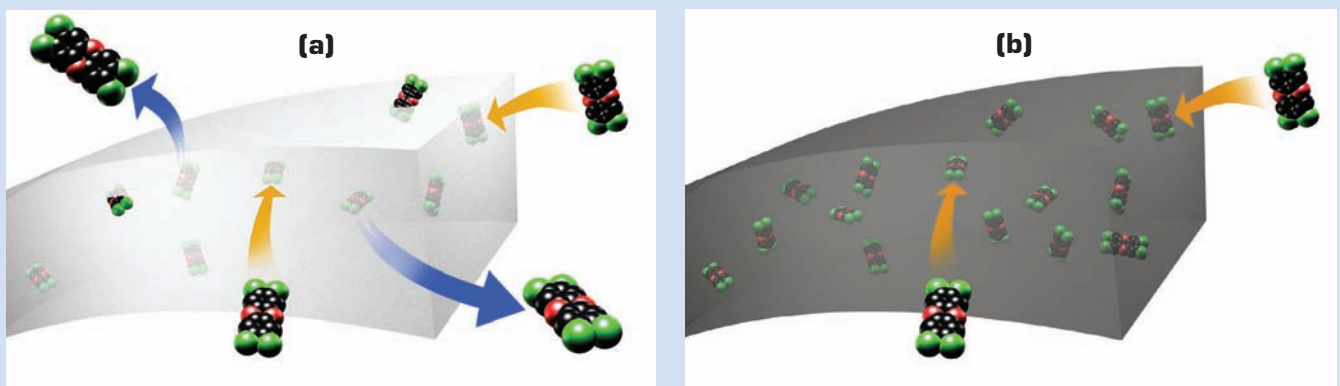


Figure 1: Schematic view of (a) absorption/desorption in polypropylene and (b) absorption/adsorption in Adiox (polypropylene containing carbon particles).

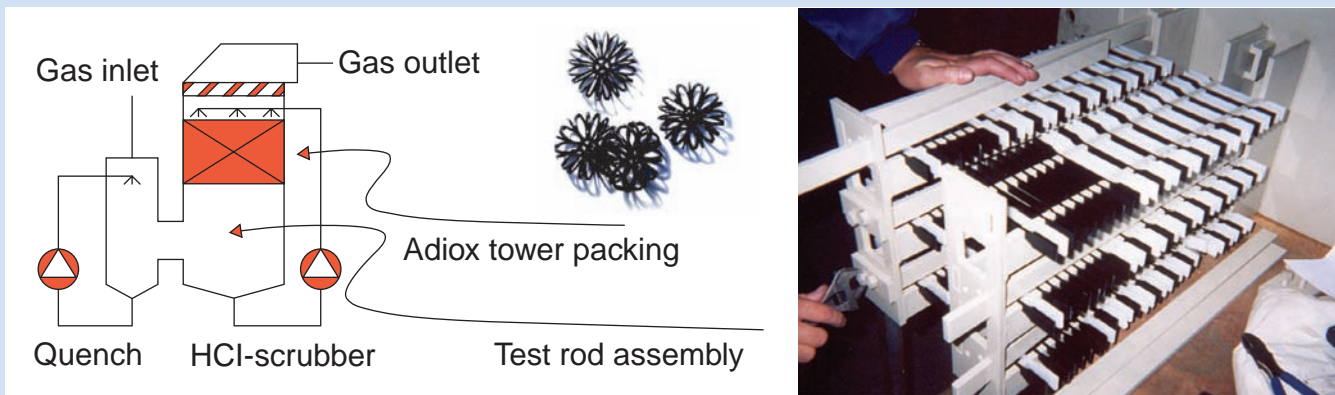


Figure 2: Adiox tower packings in the wet HCl-scrubber of the municipal solid waste incineration plant in Thisted, Denmark. A test rod assembly is placed downstream of the quench, below the tower packings.

A typical situation where these phenomena can occur is if an existing wet flue gas cleaning system is retrofitted with an upstream dioxin removal device. In this case the construction materials downstream of the device may contain large amounts of absorbed dioxins, which can be desorbed over a long period of time.

Adiox: carbon filled plastics

In order to avoid the dioxin release from the polymers, a new construction material was developed, in which carbon particles are dispersed in a polymer (such as PP). In this new material, called Adiox (patent pending), the dioxins are first absorbed in the PP. Then they diffuse to the surface of the carbon particles, where they are irreversibly adsorbed (Figure 1b). The PP acts as a selective barrier, which protects the carbon from other contaminants such as mercury (Hg).

The absorption of dioxins in pure PP and in Adiox, respectively, was tested in laboratory experiments [7]. Gas containing dioxins was passed through a fixed bed of pure PP granules at 80 °C. A break-through of the lower chlorinated dioxins was detected after one month. Upon heating the granules to 120 °C, a substantial part of the dioxins were desorbed. The experiment was repeated with Adiox granules. No break-through was detected and desorption at 120 °C was negligible.

Several types of components, such as tower packings and demisters (droplet separators), can be produced from Adiox material. Adiox tower packings can be applied in existing wet scrubbers, with a minimum of effort, producing a simple means of reducing dioxin emissions and avoiding the Memory Effect. The dioxin removal capacity of Adiox tower packings and demisters is favoured by the large specific surface area, selectivity for dioxins and high absorption capacity. It is possible to incinerate the material after usage: the dioxins are then destroyed.

Adiox has so far been installed at more than ten full-scale waste incineration lines. The old PP-tower packings in the existing scrubbers and/or droplet separators were replaced by new ones made of Adiox material.

First full-scale installation

The first Adiox installation was made at the municipal solid waste incineration plant in Thisted, Denmark, which consisted

of a grate-fired furnace, boiler, electrostatic precipitator (ESP), an acid scrubber and a neutral scrubber [8]. The flue gas flow is 40 000 m³/h (normal, dry gas).

The wet scrubbers, equipped with PP tower packings, were installed in 1991. Normally, the removal efficiency of dioxins in wet scrubbers operated over such a long time is not significant (equilibrium loading) or even negative (Memory Effect) [4]. A first measurement before replacing the tower packing confirmed these suspicions.

(i) Removal efficiency

In 2001 the PP tower packings were replaced by Adiox tower packings (Figure 2). Two dioxin measurements were taken before and two measurements after the scrubbers were carried out according to EN1948 during start-up and then after one, three, six, nine and 12 months of operation. The start-up measurement was characterized by a low flue gas flow and low temperatures, resulting in a high removal efficiency. The clean gas concentrations was <0.1 ng TEQ/m³ (n, dg) in spite of elevated raw gas concentration typical for start-up conditions. An almost constant high removal efficiency of 70% was observed at normal operation over the 12 months (Figure 3). No indication of saturation or decreasing removal efficiency

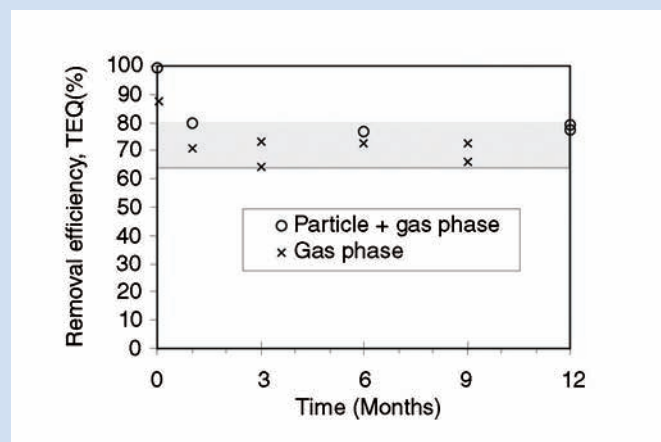


Figure 3: The removal efficiency of two wet scrubbers in series equipped with Adiox tower packings (0 months = start-up).

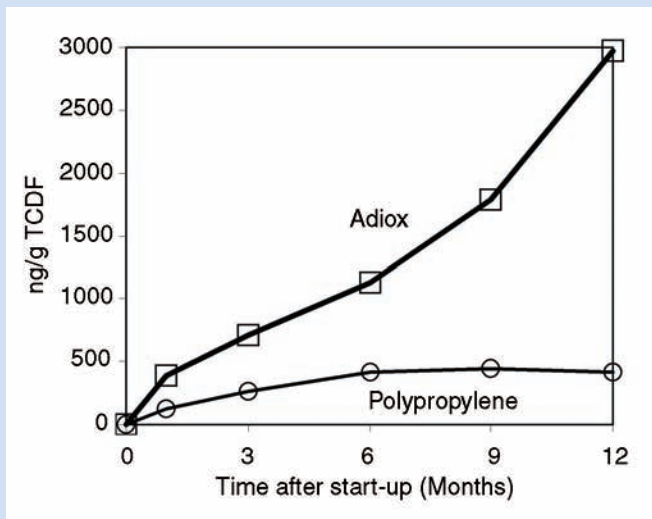


Figure 4: The concentration of tetrachlorinated dibenzo furans (TCDFs) in the test rods shown in Figure 1 after different exposure times.

could be detected, in spite of the relative high raw gas concentrations (typically 6-10 ng TEQ/m³ (n, dg)). The dioxin concentrations in the gas-phase were much higher compared to the particle phase, both before and after the scrubbers. The removal efficiencies of the different congeners were practically constant during the 12 months. A decreasing removal efficiency of the lower chlorinated dioxins, typical for pure PP, was not observed.

After the 12-month test period, the ESP was replaced by a bag house filter with carbon injection. The dioxin concentration of the flue gas entering the wet scrubbers was reduced from 10 ng TEQ/m³ (n, dg) to <0.1 ng TEQ/m³ (n, dg), i.e. by more than two orders of magnitude. The highly dioxin loaded Adiox tower packings were, however, not replaced. In the case of dioxin loaded PP tower packings, a significant release of low chlorinated dioxins would have taken place in this situation. Despite the high dioxin loading of the tower packing, the dioxin concentrations of the flue gas were reduced from 0.073 ng TEQ/m³ (n, dg) at the scrubber inlet to 0.028 ng TEQ/m³ (n, dg) at the outlet. During an additional measurement, the operation of the bag house filter was disturbed. Under these unfavourable conditions the dioxin concentrations also fell from 0.25 ng TEQ/m³ (n, dg) to 0.058 ng TEQ/m³ (n, dg) over the scrubbers. This demonstrates the effectiveness of Adiox as a police filter.

(ii) Material testing

The main objective of the first full-scale installation was to determine the lifetime of Adiox tower packings, taking into consideration the mechanical properties and PCDD/F absorption capacity.

A test rod holder (Figure 2) was installed in the acid scrubber in order to study the properties of different Adiox material compositions. It is located in a manhole directly under the support grid of the tower packing. The test rods are exposed to the acid scrubbing liquid, as well as the dioxin concentration of the raw gas.

(a) Dioxin absorption

The concentration of tetra-chlorinated dibenzo furans (TCDFs) in the test rods is plotted against time in Figure 4. It is obvious from Figure 4 that Adiox absorbs TCDFs during the entire test period, while an equilibrium concentration is reached for pure PP after a few months.

(b) Mechanical properties

The tensile strength, yield strength, E-modulus and Charpy impact strength were tested for Adiox and pure PP, respectively, after zero, three, six and 12 months. All measured values varied within $\pm 10\%$ and no trends indicating degradation could be seen. Some single tower packings were compressed at a constant speed between two metal surfaces and the force was measured. No differences could be detected between new and old Adiox tower packings in the resulting force-compression diagram.

Applications

Adiox allows the design of multifunctional scrubbers, where HCl, HF, SO₂ and oxidized Hg, as well as dioxins can be removed simultaneously. Elemental Hg can be oxidized and captured in the scrubber using the MercOx process [9]. Extended energy recovery by condensation of the flue gas can be integrated into the scrubber as well.

(i) Wet scrubber

Adiox has been installed in the wet flue gas treatment downstream of an ESP in order to reduce dioxin emissions (e.g. in Thisted and Kolding, Denmark).

The use of Adiox tower packing as a 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 this instance, Adiox will increase the margins in cases of carbon dosage failure, filter leakage or increased dioxin concentrations during start-up.

Adiox has been installed in a scrubber downstream of a bag house filter equipped with catalytic bags (hazardous waste incineration in Salaise, France), as well as normal bags in combination with carbon injection (e.g. Umeå, Sweden).

(ii) Primary dioxin removal system

The second Adiox installation was made in a two-stage scrubber after an ESP at the Kolding MSW incineration plant in Denmark. A pilot scrubber was installed in series with the full-scale scrubber. The aim of this flexible installation was to demonstrate how economical and operational benefits can be gained by a complete integration of the PCDD/F removal into the wet scrubbing process downstream of an ESP.

The results of the tests clearly demonstrate that the Adiox process, in combination with upstream particle removal, can meet the EU-directive exhaust gas limit requirements on dioxin at 0.1 ng TEQ/m³ (n, dg). Such a simple air pollution control system can consist of an ESP followed by a multifunctional scrubber (Figure 5). The required amount of Adiox material is typically larger than for a traditional

scrubber, and is determined on the basis of the dioxin concentration after the electrostatic precipitator. The first full-scale installation with this configuration will go into operation in 2004.

(iii) Dry 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 granules instead of carbon pellets would overcome these disadvantages. Earlier experiences with a fixed bed adsorber showed high removal efficiencies using PP granules [7, 10]. Based on these findings and taking the high loading capacity of Adiox into account, the new material could be an interesting alternative to fixed bed carbon filters.

Conclusions

Adiox is well suited for selective absorption of dioxins in wet gas scrubbers. It can be integrated in new or existing wet scrubbers without the need for additional equipment. The Memory Effect caused by the absorption/desorption equilibrium of dioxins in the tower packing can be eliminated.

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

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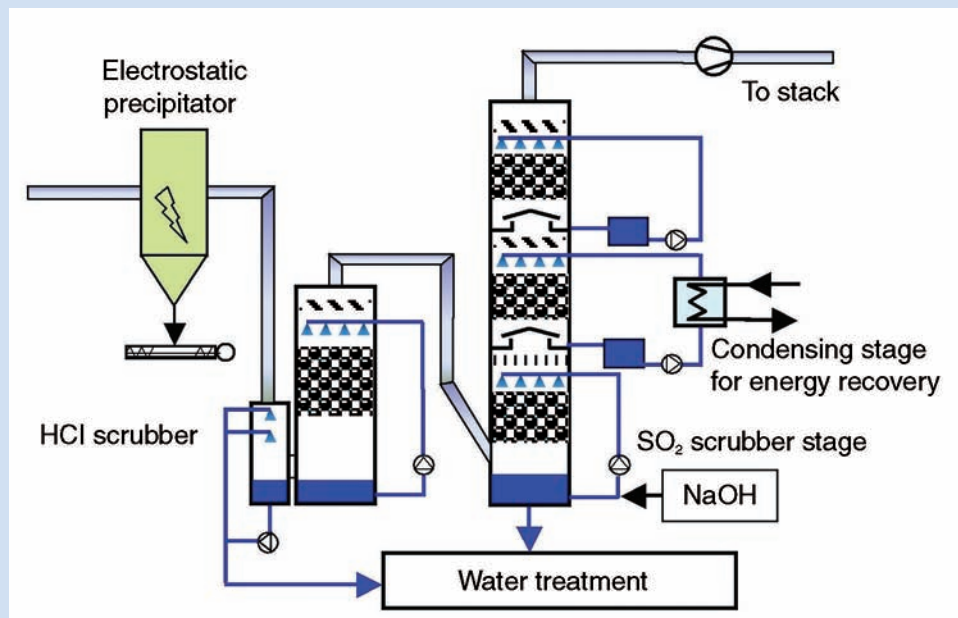


Figure 5: Schematic view of a flue gas treatment with ESP for dust removal, wet scrubbers for HCl, HF, SO₂ and Hg (oxidised) removal and Adiox tower packings for dioxin removal. Flue gas condensation for energy recovery can be integrated in the system.

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