Removal of Dioxins and Furans from Incinerator Flue Gases by Non Flammable Adsorbents in a Stationary Bed

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1. Introduction

Under certain conditions of combustion, polychlorinated dioxins and furans occur in the flue gas of thermal waste processing plants. Laws in Germany limit the concentration of these to less than 0.1 ng toxicity equivalents (TE) per cubic metre of gas. Dioxins and furans are not peculiar to incineration plants; they can originate from metallurgical or other thermal processes as well when these are operated under unfavourable conditions.

If formation of these extremely toxic organic compounds cannot be prevented by controlling combustion, specific measures must be taken to remove them from the flue gas.

Alternatives to afterburners for incineration of flue gases or catalytic and oxidation methods of destroying dioxins and furans coupled with measures to prevent them from reforming are adsorptive processes as the processes to be described.

2. Problems involved

Polychlorinated dioxins and furans (referred to here as dioxins) create problems due to their high toxicity and the correspondingly low emission levels permitted. Whereas normal emission standards for dusts are of the order of a few mg/m^3, dust-combined and free dioxins must be retained to no more than a few ng/m^3 in order to ensure a toxicity equivalent lower than 0.1 ng/m^3.

Adsorption methods employing activated carbon are particularly well suited for removal of dioxins. Precleaned flue gases generally contain a certain amount of SO_2 that is similarly adsorbed on the carbon and is catalytically oxidized by the residual oxygen in the flue gas to SO_3, which reacts with the moisture present in the gas to form sulphuric acid. This sulphuric acid absorbs additional moisture until the activated carbon finally becomes soaked, when its adsorptive capacity declines and corrosion problems set in.

As a means of overcoming these problems, pure activated carbon is practically no longer employed in fixed-bed adsorbers for cleaning flue gases. Instead, the adsorbent is continuously exchanged, as in the moving-bed or turbulent-contact method.

Another fundamental problem associated with use of pure carbonaceous adsorbents for cleaning flue gases containing oxygen is the risk of fire. Heat generated in the adsorber may not be completely removed, resulting in formation of hot spots within the bed, which may lead to spontaneous ignition. Licensing authorities therefore usually make the use of carbon-containing adsorbents contingent on the provision of appropriate safety measures, which in Germany are summarized in LIS Report No. 97 issued by the North Rhine-Westphalian State Institute for Source Emission Control. Commonly this covers carbon monoxide monitoring, automatic fire extinguishing and inertization facilities.

Owing to these problems, efforts have long been directed at developing nonflammable adsorbents

3. Process development, pilot plants, test results

In the quest for a suitable alternative to flammable carbonaceous adsorbents, LURGI first undertook preliminary trials on a laboratory scale with a wide variety of organic and inorganic substances.

In regard to inorganic substances these were subsequently continued in a focused direction and in close cooperation with DEGUSSA using a modified zeolite specially developed by the latter.

Zeolites are crystalline alkaline aluminosilicates exhibiting a three-dimensional open lattice structure which forms defined micropores with a closely limited pore radius distribution. Before now, zeolites were excluded from use in adsorptive cleaning of waste gases by the types commercially available being highly selective to water vapor adsorption, resulting in very quick exhaustion of their adsorptive capacity. By special synthesis or dealumination processes it is however possible to manufacture zeolites that are extremely hydrophobic, catalytically inactive, resistant to high temperatures, and stable to acids. Moreover they do not adsorb SO_2 or HCl, thus ruling out corrosion problems due to acid formation. Nonflammability of zeolites prevents spontaneous ignition of the adsorbent. With appropriate binders, zeolites can be preformed in any desired geometry to achieve optimum pressure drop. DEGUSSA zeolites utilized in the MEDISORBON® process are preferably extruded in cylindrical shape with particle sizes of a few millimetres.

Another well suited process for this task by using organic material is the LURGI KOMBISORBON adsorption method which employs granular activated carbon which is mixed with an inert material. This kind of fixed-bed filters has been used for several years with great success in a sewage sludge incineration plant. Contrarily to plain carbon the mixture of carbon and inert material is very safe against the risk of hot spots and fire. Therefore special instruments like carbon monoxide monitoring and automatic fire extinguishing or inertization facilities are not absolutely necessary.

In both processes removal of dioxins takes place by purely adsorptive mechanisms, like removal of other organic compounds and solvents.

A pilot MEDISORBON® plant fed with 130 Nm^3/h of precleaned flue gas from a hazardous waste incinerator has already logged over 23,000 hours of long-term trial operation for removal of polychlorinated dioxins.

The adsorbent is distributed in two layers so as to permit detection of progressive saturation. The bar diagram of individual measurements reproduced in Fig. 1 shows analytical data upstream of the first treatment stage (raw gas), downstream of the first stage and downstream of the second stage (clean gas).

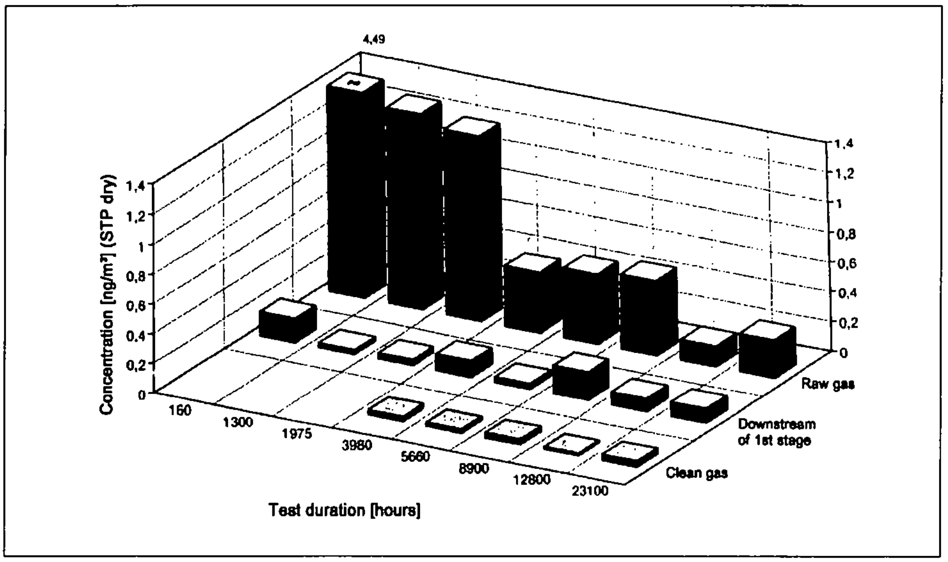

fig. 1 LURGI Pilot Plant. Results of tests for Dioxin removal to date

Reduction of dioxin concentrations in the raw gas is attributable to measures undertaken on the incineration plant and demonstrates that pollutant levels can be lowered alone by specific modifications to the combustion system.

Residual dioxin content of the precleaned flue gas was still reduced from 0.25 to 0.04 ng TE/Nm^3 after 23,100 hours of operation. Operation of the pilot plant is being continued in order to gather additional experience, especially regarding run time of the adsorbent, effects on it by other flue gas components, and like aspects.

4. Description of process and plant

With the MEDISORBON®/KOMBISORBON process, adsorptive removal of dioxins from the flue gas of incineration plants takes place at a temperature of about 40-100°C. In order to avoid increased retention of water by the adsorbent, relative humidity of the flue gases must not exceed 80-85%. This also rules out condensation of moisture in the adsorber. Optimum utilization of the theoretical adsorbent run time requires that the dust burden be kept as small as possible. Although finest dust particles mostly pass through the adsorbent bed, dust concentration in the flue gas to be cleaned should not be more than 10 mg/m^3 so as to reliably preclude excessive pressure drop across the bed and with it the necessity to replace the adsorbent prematurely.

The heart of a MEDISORBON®/KOMBISORBON plant is the packed adsorber. This is either a horizontal-flow vertical adsorber (Fig. 4) or a vertical-flow horizontal adsorber. Horizontal adsorbers are normally packed with a single layer of adsorbent, thickness of which may vary over a wide range. Vertical adsorbers contain one or several layers of defined thickness, through which the gas flows successively.

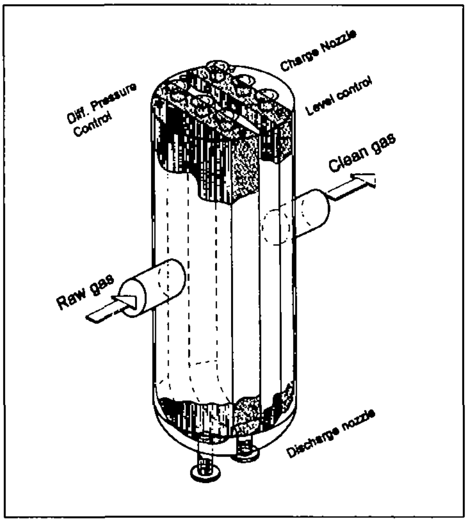

fig. 4 Vertical MEDISORBON®/KOMBISORBON adsorber

A particular advantage of the vertical type is the possibility of replacing only the first, possibly thin layer of the bed in the event of a high dust burden causing premature increased pressure drop, leaving the remaining layers in place. Another obvious point is easier discharge of the separate layers from a vertical adsorber, which can be accomplished by gravity through a rotating-vane gate on a vertical adsorber. Both types of adsorber are built as very compact units and do not contain any valves or similar controls needing to be actuated regularly in normal operation.

The gas heater necessary for conditioning the flue gas is used together with fresh air intake during startup for heating the adsorber to operating temperature before admitting the moist flue gas as a means of preventing condensation in the adsorber. Depending on whether the flue gas blower is installed upstream or downstream of the MEDISORBON® / KOMBISORBON system, auxiliary provision of a fresh air blower may be required for startup, but it may be of much smaller capacity than the flue gas blower. This fresh air blower is then used during the operation of filling the adsorbent into the adsorber to exhaust air containing a small amount of adsorbent dust and clean it in a bag filter installed in an adsorber bypass before it is released to the atmosphere.

Trials can be undertaken prior to designing the full-scale plant in order to ensure guarantee levels of clean gas purity or pollutant removal rates, especially when treating unusual flue gases such as those originating from thermal soil reclamation or metallurgical processes.

In addition to laboratory test units, for which the flue gas is generated synthetically, mobile pilot plants are available with gas treatment capacities between 10 and 130 m^3/h. These are self-contained units and are normally operated on a sidestream taken from the main flow of gas.

Fig. 4 illustrates integration of the MEDISORBON® / KOMBISORBON process into the flue gas cleaning train of a three-stream industrial-scale sewage sludge incineration plant in the Netherlands. In two streams MEDISORBON® systems are installed, in one a KOMBISORBON type.

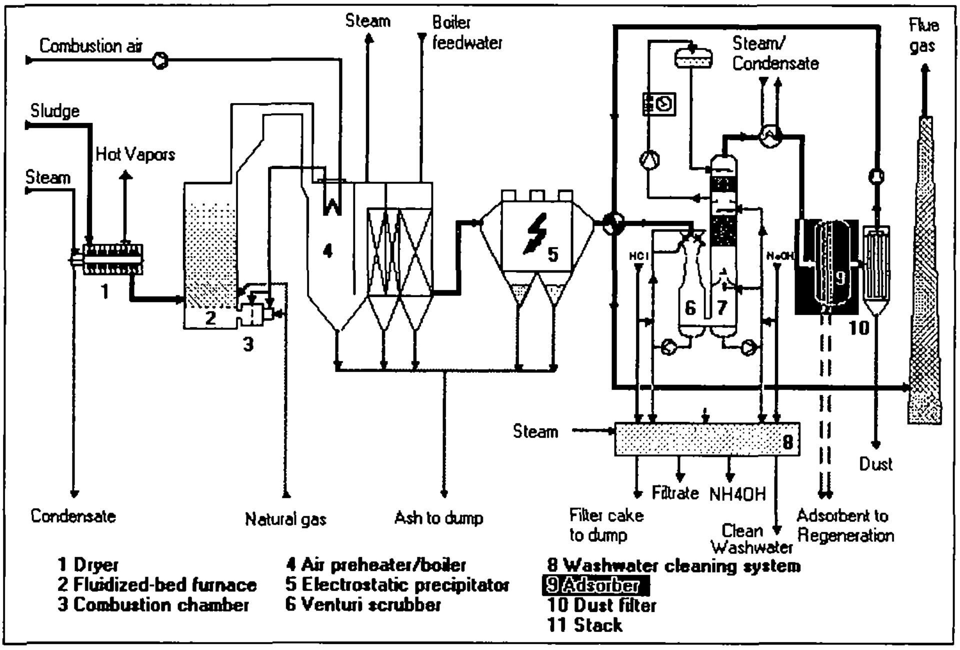

fig. 4 Use of MEDISORBON® / KOMBISORBON process in a sewage sludge incineration plant

Operating experience to date confirms that MEDISORBON® / KOMBISORBON constitutes a process low in operating and maintenance requirements.

5. Summary

Compared with other adsorption methods which mainly employ pure carbonaceous adsorbents, the main advantage of the MEDISORBON® / KOMBISORBON processes lie in the safety potential of the adsorbents they use. This means that they doe not require the safety devices, fire extinguishing facilities, extensive instrumentation and so on normally prescribed with other processes. There is no danger of spontaneous ignition.

The MEDISORBON® / KOMBISORBON plant is practically free from need for maintenance and supervision. Removal and refilling of the adsorbent is only necessary at intervals of a few years.