

5 A method for ozone-assisted dioxin removal

The present invention relates to a method for removing dioxins from a gas, especially a flue gas, using ozone (trioxygen, O_3) and a catalytic dust filter.

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Selective catalytic reduction (SCR) is a means, by which nitrogen oxides, also referred to as NO_x , can be converted into diatomic nitrogen (N_2) and water (H_2O) with the aid of a catalyst. A gaseous reductant, which typically is anhydrous ammonia, aqueous ammonia or urea, is added to a stream of flue gas or exhaust gas and adsorbed onto a catalyst. Carbon dioxide (CO_2) is a reaction product when urea is used as reductant.

20 It is known that SCR catalysts, dual function SCR catalysts ($V_2O_5 + Pd$) and also noble metal catalysts and Cu/Mn catalysts can oxidize volatile organic compounds (VOCs) at ambient temperatures if ozone is added to the gas. Within the field of catalytic
25 filtration and specifically in the areas of waste incineration, metal sintering plants and cement plants (if waste is used as fuel), dioxin removal is required, which is a challenge for many plants.

30 Ozone is known as a strong oxidizing agent for waste and drinking water treatment, sterilization and deodorization. It is an allotrope of oxygen that is much less stable than the diatomic allotrope O_2 , as it is

breaking down in the lower atmosphere to yield normal dioxygen. As mentioned, ozone is a powerful oxidant (far more so than dioxygen), and so it has many industrial applications related to oxidation. Because
5 of the considerable oxidizing power of ozone and the formation of molecular oxygen as a by-product, ozone is sometimes chosen for oxidation. In fact, oxidation using ozone offers at least the following advantages over chemical alternatives:

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- ozone can be generated on-site,
- ozone rapidly decomposes to oxygen,
- reactions do not produce toxic halogenated compounds, and
- 15 - ozone acts more rapidly and more completely than other common oxidizing agents.

However, due to the fact that ozone itself is toxic, the residual ozone from these oxidation processes must
20 be removed. Moreover, being quite harmful to animal and plant tissue even in concentrations as low as around 100 ppb, ozone is a pollutant that cannot be emitted. For these reasons, much research is devoted to find suitable catalysts for oxidation reactions using ozone
25 and also to find effective ways of removing residual ozone following such oxidation reactions.

Dioxins and dioxin-like compounds are compounds that can be characterized as highly toxic environmental
30 persistent organic pollutants (POPs). They are mostly by-products of various industrial processes or - in case of dioxin-like polychlorinated or polybrominated biphenyls - part of intentionally produced mixtures.

The substances referred to as dioxins are grouped into dioxin-based compounds such as polychlorinated dibenzo-p-dioxins (PCDDs), in which two benzene rings containing two replaced chlorine atoms are connected through two oxygen atoms, and furan-based compounds such as polychlorinated dibenzofuran (PCDF), which is connected through one oxygen atom, but also the above-mentioned polychlorinated and polybrominated biphenyls (PCBs and PBBs). Dioxins include their isomers which comprise as many as 75 types for dioxin-based compounds and 135 types for furan-based compounds depending on the position and the number of replaced chlorine atoms. In other words, a total of 210 dioxin compounds are known to exist.

Today, most plants use low temperature (below 180°C) injection of activated carbon to capture the dioxins by adsorption or, in certain cases, catalytic units are used at higher temperatures (around 180-240°C) to destroy the dioxins through catalytic oxidation. In many cases, however, the activated carbon is expensive and unable to satisfy the requirements for dioxin removal, but increasing the temperature to facilitate the catalytic dioxin oxidation is expensive in OPEX and may also require extensive construction work.

The present invention makes dioxin removal from a gas, especially a flue gas, possible through destruction at low temperature, facilitated by injection of ozone and use of a catalytic dust filter.

The need for removing dioxins from flue gases is known in the prior art. Thus, EP 1 940 546 B1 discloses a

- method for removing nitrogen oxides and dioxin from flue gas using an ammonia reducing agent and a V/TiO₂ catalyst comprising natural manganese ore (NMO) within a wide operating temperature range from low
- 5 temperatures (250°C or less) to high temperatures of 300-400°C. The V/TiO₂ catalyst is mixed with NMO to increase the activity of nitrogen oxides removal in the low temperature range.
- 10 In EP 1 214 971 B1, a spent catalyst comprising an alumina support with a large specific surface area and impregnated with over 5% of vanadium is recycled in order to prepare a catalyst with a high efficiency for removing dioxin.
- 15 US 6.077.431 A describes a process for decomposition and removal of dioxins contained in sludge, which comprises slurring the sludge to be treated, applying ultrasonic radiation to the slurry to decompose dioxins contained in the sludge in a reaction field developed
- 20 by the ultrasonic radiation and to transfer pollutants to a liquid phase of the slurry, and then separating the slurry into a liquid phase containing the pollutants and a solid phase which is free from dioxins.
- 25 JP H0775720 A describes a method for removing dioxins from a gas in a gas treatment plant comprising a catalytic unit by injecting ozone into the gas at a point upstream the catalytic unit which comprises a bag
- 30 filter for capturing dust. So the gas passes first through a bag filter and then through a catalytic unit housing a catalyst comprising 72 wt% TiO₂, 7 wt% V₂O₅ and 5 wt% WO₃. Further, Pt or Pd may be present in

amounts of 0.01 to 3 wt%. The gas is re-heated before passing through the catalytic unit, so it is in its essence something rather different.

5 Finally, US 2014/0170046 A1 discloses a method and an apparatus for the reduction of organic compounds and other emissions from an industrial plant utilizing a cement or minerals kiln that has a high level of organic compound emissions. The apparatus consists of a
10 filter for the control of particulate emissions which has been treated with a catalyst to provide catalytic destruction of gaseous emissions as process gases are passed through the porous medium of the filter. Both dioxins and ozone are mentioned, but the ozone is for
15 hydrocarbon reduction, and the leap to ozone-assisted dioxin removal is not obvious. Also, nothing about an ozone decomposition catalyst is mentioned.

A standard solution for dioxin removal from a flue gas
20 consists in injection of activated carbon into the gas, e.g. as described in EP 0 930 091 B1. According to the method of the present invention, the dioxin removal from flue gas is effected through low-temperature destruction facilitated by ozone injection and the use
25 of a catalytic dust filter.

So the invention relates to a method for removing dioxins from a gas, especially a flue gas, in a gas treatment plant comprising a filter unit, wherein ozone
30 is injected into the flue gas at a point upstream the filter unit, and the filter unit includes a catalytic dust filter.

More specifically, the present invention relates to a method for removing dioxins from a gas in a gas treatment plant comprising a catalyst unit for emissions abatement, wherein

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- ozone is injected into the gas at a point upstream the catalyst unit, and

- the catalyst unit includes a dust filter.

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Preferably the gas is a flue gas and the catalytic unit is a catalytic dust filter unit.

The catalytic dust filter is preferably a bag filter.

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Bag filters are well suited for the removal of dust and particulate matter from gas streams. Catalytic bag filters have the double utility of being able both to remove particulates from a gas stream and to catalyze one or more desired reactions in the gas. A catalytic bag filter typically comprises two or three layers of filter fabric. Each layer can contain different catalysts optimized for removal of a specific kind of compound from the gas that passes through it. Dust and other particulate matter will settle on the surface of the outer bag, from where it can easily be removed. The two or three-layer structure provides the flexibility to protect the catalytically impregnated fabrics and tailor different catalytic combinations for different purposes. A catalytic bag filter can also contain fabric layers that are not catalytically impregnated, for example an outer fabric layer without catalytic impregnation to remove the dust and then with one or

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more catalytically impregnated fabric layers positioned on the inside of the outer fabric layer. The catalytically impregnated fabrics can contain the same catalyst or different types of catalyst depending on
5 application.

Preferably a known ozone decomposition catalyst, such as manganese or oxides thereof, is added to the filter to remove any residual ozone. This known ozone
10 decomposition catalyst is preferably added downstream from the filter unit.

The catalytic oxidation of dioxin compounds is very sensitive to temperature. Thus it is known that the
15 catalytic activity for known catalysts drops dramatically when the temperature decreases. Further, it is known that ozone is not stable at temperatures above 250°C. Most industrial flue gas filtration units are operating at temperatures below 200°C, and many are
20 operating around 140-160°C. At these temperatures, to a certain extent, the dioxin is absorbed on activated carbon which is often injected into the filter housing. However, the degree of dioxin removal is limited, and the more stringent emission control requirements cannot
25 be fulfilled using activated carbon alone. Furthermore, the dioxin components are not destroyed by using activated carbon. The dioxin is just absorbed on the carbon, which leads to the fact that all the spent activated carbon and the rest of the dust from the
30 process, that it is removed together with, must be disposed of as hazardous waste. In order to increase the dioxin removal, a catalytic filter can be used, and it can replace the standard filters in the filter

housing, but for the catalyst to become effective, the temperature has to be increased. This may require that the plant is revamped and that some of the construction material is replaced. Furthermore, the removal
5 efficiency regarding acid gas (HCl, SO₂ etc.) is higher at lower temperatures. By introducing ozone injection into the flue gas prior to the filtration unit together with a catalytic dust filter, the need for a revamp, construction work and safety will be eliminated,
10 thereby ensuring a high dioxin destruction efficiency.

It is preferred that the catalytically active material in the catalytic unit consists of one or more metal oxides, in which the metal is selected from the group
15 consisting of V, W, Mn, Cu, Ce, Mo, Fe, Ca and Mg, and one or more porous supports selected from the group consisting of Al₂O₃, SiO₂, SiC and TiO₂, optionally in the presence of other elements in a concentration below 1 wt%. Said catalytically active material preferably
20 comprises from 1 wt%, 2 wt% or 3 wt% to 4 wt%, 5 wt%, 10 wt%, 25 wt% or 50wt% V₂O₅. Another preferred catalytically active material comprises from 1 wt%, 2 wt% or 3 wt% to 4 wt%, 5 wt%, 10 wt%, 25 wt% or 50wt% MnO₂.

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Preferably the porous support comprises TiO₂, especially in the form of anatase.

The catalytically active material preferably further
30 comprises from 0.01 wt%, 0.02 wt% or 0.05 wt% to 1wt% of a noble metal, preferably Pd or Pt.