Catalytic Activated Ceramic Dust Filter – a new technology for combined removal of dust, NOx, dioxin, VOCs and acids from off gases.

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Principle
During the last three years, a Catalytic Activated ceramic Dust Filter (CADF) has been developed, patented and commercialized by Haldor Topsoe A/S together with Madison Filter Ltd under the trade name Cerafil TopKat (CTK). CTK combines highly efficient surface barrier filtration of dust with highly efficient catalytic destruction at 170 to 450°C of NOx, dioxin and VOCs in the off gas from thermal processes. The candles are installed as an alternative to conventional bags in pulse jet cleaned bag houses. As illustrated in Figure 1, the catalyst is microscopic particles embedded in the 10-20 mm thick walls of the CADF candles and protected by the surface barrier against any contact with dust from outside.

Figure 1. Schematic principle of the ceramic Catalytic Activated Dust Filter, CTK.

The catalyst particles are micro-porous and due to their small size, they catalyze the gas phase reactions without diffusion restriction (i.e. almost 100% utilization of the catalyst intrinsic activity) as opposed to usual pellet or monolithic catalysts. In industrial plants the conventional catalyst types typically operate with 5-15% catalyst effectiveness in the SCR (Selective Catalytic Reduction of NOx by NH3), and with even lower catalyst utilization in dioxin destruction. The latter is highly gas film controlled in usual catalysts due to the low diffusion coefficient of dioxins. As determined by microprobe analysis (EDS) the V and Ti components
of the catalyst are evenly distributed across the wall in the desired atomic ratio for optimal catalytic activity.

Typical SCR activity of industrial CADF candle are seen in Figure 2, which shows NOx-conversions and corresponding values of the first order rate constants ($k_{NOx}$) measured at 130-300 °C with excess NH$_3$ (NH$_3$/NOx =1.2). Compared to a conventional catalyst at the same NHSV, higher conversions are achieved in particular above 230°C due to elimination of diffusion restriction in the CADF catalyst.

![DeNOx activity for various V$_2$O$_5$/TiO$_2$ compositions](image)

**Figure 2.** NO$_x$ conversion (right axis) and first order NOx reduction rate konstant (left axis) of different CTK elements vs. operating temperature. NHSV = 5225 Nm$^3$/h/m$^3$. 200 ppm NO and NH$_3$/NO = 1.2.

V/Ti based catalysts are best for deNOx and de-dioxin applications. Other catalyst formulations developed for CADF embedment are more active at lower temperatures for CO and VOC oxidation but are not suitable for NOx reduction.

**Applications of CADF technology**

The CADF technology has great potential in particular for use in (waste) incinerations plants, diesel engines and combustion of bio mass and petroleum residues (petcoke, tar, heavy fuel oil).
Incinerators plants: A significant simplification and reduction in investments and operating cost can be obtained compared to the current BAT-technology, which involves an ESP, active carbon injection, a SO₂ scrubber and a tail-end SCR with gas reheat. High dust SCR deNOₓ and dioxin removal using monolith SCR catalysts is not possible due to the sticky fly ash from waste incineration. With CADF it is possible to combine removal of dust, SOₓ, HCl, HF, NOₓ and dioxin in the dust filter equipped with Cerafil TopKat CADF elements at temperatures from 180 to 400 °C, as seen in fig 3. In special cases, the operating temperature can be down to 160°C or up to 500-600°C. NH₃ or urea for the NOₓ reduction is injected in the gas upstream of the CADF as with ordinary SCR reactors. As with ordinary SCR catalysts, Hg in the gas will be oxidized to Hg⁺⁺ which can be adsorbed either at 100-140°C in a fixed bed with Hg-sorbent, or in a wet scrubber.

The CTK elements can operate at temperatures from 170-180° C, which is the minimum temperature of sufficient deNOₓ activity of the catalyst, and up to 400-450°C, which is the maximum long term operating temperature sustainable for the catalyst. 99% of the dioxin in the gas is destroyed at temperatures down to about 160°C.

Very often the dust in the flue gas from combustion of waste and biomass tends to foul the boiler tubes in particular when the gas is cooled to temperatures below 200–300°C. If that is the case, it is advantageous to cool the gas in two steps and insert the CADF treatment at, say, 300°C followed by further cooling of the dust-free clean gas in a more price-effective finned tube boiler for increased heat recovery down to 100-120°C, up-stream of a possible Hg-absorption, followed by a wet scrubbing tower in case that it is desired to remove high concentrations of HCl and SO₂ by a cheaper sorbent such as limestone. The Hg-absorption may be carried out in a fixed bed and is favoured by the low temperature and the fact that Hg is present in oxidized form.

Operation on or below the NH₄HSO₄ (ABS) dew point may be possible when injecting the alkaline sorbent (preferably NaHCO₃ or Na₂CO₃ in reactive form) together with the NH₃ of the
CADF. SO\textsubscript{3} in the flue gas immediately forms ABS at temperatures on or below the ABS dew point. The ABS condenses on the particulates in the gas where after the ABS on alkaline particles is decomposed by the sodium carbonate under liberation of the NH\textsubscript{3}:

\[
\text{Na}_2\text{CO}_3(\text{s}) + \text{NH}_4\text{HSO}_4(\text{s}) \rightarrow \text{Na}_2\text{SO}_4(\text{s}) + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]

The reaction is slow and requires at least 10 minutes residence time in the dust layer accumulating on the surface of the CADF elements between the pulse jet cleanings. In this way, the use of gas surface filtration in CADF— in place of using ESP for dust removal – may make it possible to carry out SCR NO\textsubscript{x}-reduction with SO\textsubscript{3}-rich flue gases on or below the ABS dew point, where ordinary SCR catalysts would deactivate quickly by ABS condensation in the catalyst. This additional unique possibility with CADF may, as seen in the next example, be utilized in purification of diesel exhaust which is characterized by a high content of NO\textsubscript{x} and SO\textsubscript{3} in the flue gas.

**Figure 4.** 2-stroke diesel engine with CADF installed downstream gas turbine.

**Diesel engines:** In both two and four stroke engines, the use of CADF technology provides great advantages with regard to removal of both NO\textsubscript{x}, SO\textsubscript{3}, SO\textsubscript{2} and particulates in the flue gas and makes it possible to use fuel oils with high sulphur and high metal content without emission problems. This is illustrated in fig 4 with a two-stroke engine where the flue gas is cleaned by CADF installed downstream of the expansion turbine at 260-280°C. The flue gas typically contains 1600 ppm NO\textsubscript{x} (at 14% O\textsubscript{2}). With 3% S and 500 ppm vanadium and nickel in the fuel oil, the flue gas also contains 600 ppm SO\textsubscript{2}, 60 mg ash/Nm\textsuperscript{3} and 20-40 ppm SO\textsubscript{3} corresponding to an ABS dew point of about 330°C after injection of 1500 ppm NH\textsubscript{3}. The ABS condenses on the alkaline sorbent particles where the ABS will be decomposed in the dust cake on the filter elements, provided that the sorbent is sufficiently reactive and present in excess. If not, the cake will be sticky and difficult to remove by pulse jet. However, it remains to be
demonstrated in industrial practice how much the gas can be ABS under-cooled with specific brands of sodium carbonate.

The CADF and the injection of sorbent and NH3 can, alternatively, be placed upstream of the expansion turbine at 3.5 bar, 430-460°C. This placement is advantageous as the actual gas volume is nearly 3 times lower but not possible with ordinary SCR catalyst due to excessive formation of additional SO3 by SO2-oxidation in the vanadium rich ash fouling the catalyst surfaces and in the SCR catalyst itself. With CADF and injection of sorbent (could be Mg-Ca oxides), the SO3 will be adsorbed in the dust cake, and, furthermore, the rate of SO2-oxidation on the small catalyst particles will much lower relatively to the rate NOx-reduction because neither of the two reactions will be subjected to diffusion restriction in CADF, as opposed to ordinary SCR catalysts where the deNOx reaction is strongly diffusion restricted while the SO2-oxidation takes place un-restricted.

With 4-stroke diesel engines, the temperatures before and after the expansion turbine are 60-90°C higher which means that SCR deNOx can only be installed downstream of the expansion turbine. Also in this case, use of CADF will be advantageous compared to ordinary SCR catalysts combined with possible ESP dust removal.

**Biomass fired boilers:** Traditional SCR systems suffer from high deactivation rates up to 50% per 1000 hours in biomass fired boilers due to deactivation by alkali aerosols. With CADF the sodium and potassium containing aerosols do not come in contact with the catalyst since they are stopped in the surface barrier and the catalyst lifetime may be prolonged significantly.

**Industrial experience.** CADF elements have, so far, been installed in three relatively small industrial waste incineration plants:

- In a medical waste incineration plant in UK in which 50 ngTDE/Nm³ is reduced to 0.4 ng/Nm3 at about 155°C. Sodium carbonate is injected upstream the CADF in order to remove HCl and HF. An element was taken out after 14 months of operation with injection of sodium carbonate for removal of HCl, SO2 and HF. Its oxidation and deNOx activity was unchanged from new, and no Na had penetrated the filtration surface barrier.

- In an animal fat incineration plant in France where 0.01 ng TDE/Nm³ and 80% NOx-removal with 1-2 ppm NH3-slip are achieved at 220-240°C.

- In an iron scrap thermal treatment plant in France, where < 0.06 ng TDE is achieved at 380°C with 5-50 ng TDE/Nm³ inlet.