

EXHAUST GAS CLEANING TECHNOLOGIES AND EMISSION LIMITS
FOR PLANTS IN THE CEMENT INDUSTRY USING THE CYCLONE PREHEATER PROCESS
ALPACEM CEMENT PLANT, ANHOVO, SLOVENIA

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- Expert's Report -

1 Introduction

Cements are hydraulic binders burned above sintering temperature. Due to their practical and economic importance, they are among the most important mortar binders [1]. Cement clinkers are important carriers of hydraulic properties. Together with additives, they are ground into a wide range of standard-compliant cements [2].

The carriers of the hydraulic properties are the various cement clinker minerals that form during the burning of the raw materials in the heat treatment plants at firing temperatures of more than 1450 °C. The heat required for this is provided by burning conventional fossil fuels (coal, oil, natural gas) and substitute fuels (plastic waste, used tyres, etc.).

The high flame temperatures during cement clinker burning result in exhaust gases with increased levels of thermal nitrogen oxides. Nitrogen oxides are considered to be direct and indirect air pollutants. Their main effect is as a strong oxidising agent. Among other things, they have an overfertilising and acidifying effect on water and soil (eutrophication) and contribute to the formation of ground-level ozone (tropospheric ozone) and secondary particulate matter (nitrogen-containing condensation aerosols). The release of nitrogen oxides must be minimised in accordance with applicable emission control guidelines through air pollution control measures, whereby secondary emissions such as those from ammonia (NH₃) must be kept as low as possible.

By using substitutes (secondary raw materials and secondary additives, as well as substitute fuels), cement plants can conserve natural resources and thus make a sustainable contribution to environmental protection. Cement plants can support waste management in the handling of residual materials within the framework of local waste disposal networks.

The use of substitute materials brings chemical compounds into the production process (such as sulphur compounds, organic compounds, heavy metal compounds) that require intensive exhaust gas treatment in order to comprehensively reduce the resulting air pollutant emissions.

Nevertheless, it must be noted that substances (e.g. sulphur compounds such as pyrite and marcasite, compounds of volatile metallic trace elements such as thallium and mercury, organic hydrocarbon compounds such as natural carbonisation products in clays) are also brought into the kiln system via the natural composition of the raw materials used, which can result in harmful gas emissions.

The share of emissions from the cement industry in total national emissions is illustrated in Table 1 using the example of the Austrian cement industry [3].

air pollutant	year	national mass flow* [t]	mass flow cement industry*** [t]	share 2021 [%]	share 2022 [%]
carbon dioxide** (CO ₂) (without biogenic emission)	2022	73 439 000	2 982 304	3,64	4,06
ammonia (NH ₃)	2022	67 990	132	0,18	0,19
sulfur dioxide (SO ₂)	2022	10 780	120	1,70	1,12
carbon monoxide (CO)	2022	480 600	3 478	0,80	0,72
nitrogen oxides (calculated as NO ₂)	2022	114 400	2 273	2,01	1,99
total organic carbon (TOC, NMVOC)	2022	100 000	155	0,17	0,15
total suspended particulate matter (TSP) (only kiln line)	2022	45 160	20	0,05	0,05
mercury (Hg) (gaseous and particle bound emission)	2022	0,99	0,1360	13,82	13,74

* UBA: "Emissionstrends 1990 - 2022 (Datenstand 2024)", Report REP-0917, Wien 2024

** UBA Wien: "Treibhausgas-Emissionen in Österreich 1990-2023", Klimaschutzbericht, Datenstand Jänner 2025

*** G. Mauschitz: "Emissionen aus Anlagen der österreichischen Zementindustrie - Bilanzjahr 2024", VOZ, Wien 2025

Table 1: Shares of various air pollutants emitted by the Austrian cement industry in total national emissions in the reference year 2022

Through cooperation with innovative plant engineering companies, existing exhaust gas cleaning technologies are being improved and new exhaust gas cleaning technologies are being developed in order to keep air pollutant emissions as low as possible.

2 Question

This expert opinion provides information on modern secondary separation measures for dust, conversion processes for nitrogen oxides (NO_x), carbon monoxide (CO), organic pollutants (TOC) and mercury (Hg) from exhaust gases in the cement industry that operate according to the cyclone heat exchanger process, and provides information on possible emission limit ranges that can be permanently complied with using these exhaust gas abatement techniques.

3 Findings

Alpacem Cement operates a Portland cement manufacturing plant in the settlement of Anhovo in the Republic of Slovenia (Figure 1).

With a kiln capacity of approx. 3180 tons of clinker per day (limitation of the environmental permit), the Anhovo cement plant produced approx. one million tons cement in the reference year 2024. The cement plant employed approx. 260 people in the reference year.



Figure 1: Photographic view of the Alpacem cement plant in Anhovo, Slovenia

At the Alpacem cement plant in Anhovo, limestone and marl from the company's own deposits on the left bank of the Soča River are first coarsely crushed and then transported to the plant by conveyor belts, where they are mixed with corrective substances and grinded into raw meal by two ball mills. The raw meal is then fed into a five-stage cyclone heat exchanger equipped with an inline calciner and a tertiary air duct, before being burned in an approx. 68 m long rotary kiln with a diameter of approx. 4.5 m at approx. 1450 °C. The cement clinker is cooled in a grate cooler, temporarily stored and ground with standard main components in accordance with SIST EN 197-1:2011 Cement – Part 1 and SIST EN 413-1:2011 Masonry cement – Part 1 in two ball mills to produce standard cements.

The various additives (which are used as alternative raw materials for clinker production or as cementitious additives for cement production, etc.) are transported to the plant by rail or lorry.

The furnace exhaust gas is dedusted in a bag filter system. With a total filter area of approx. 4070 m² (PPS needle felt), the daily dust emission limit in the clean gas is reduced to approximately <5 mg/m³ (Vn) at 10.0 vol.% O₂ in daily average. Dust separation from the clinker cooler exhaust gas is also carried out using a bag filter system.

In 2019, the daily nitrogen oxide exhaust gas limit value was reduced to less than 500 mg/m³ (Vn) at 10.0 vol.% O₂ (calculated as NO₂) by using an SNCR (selective non-catalytic reduction) system, using aqueous urea solution as reducing agent. By the end of 2025 aqueous ammonia solution shall be used as reducing agent.

To reduce SO₂ emissions, a dry sorption process is used at the Alpacem cement plant in Anhovo, whereby sodium hydrogen carbonate (NaHCO₃) is injected into the flue gas stream.

The cement produced is transported by rail and truck, approx. 88 % as bulk solid and approx. 12 % in bags.

With a view to conserving natural resources as much as possible and given the current economic conditions, the Alpacem cement plant continues to aim to increase its use of substitute materials in the form of secondary raw materials, secondary additives and substitute fuels. While the substitute raw materials are transported to the plant exclusively by truck, petroleum coke is transported to the plant by rail.

The rotary kiln is fired by a low-NO_x multi-component burner (conventional fossil fuels and RDF-2D, particle size: height: 2 mm and the other two dimensions up to 30 mm). Coarse-grained substitute fuels (RDF-3D, used tyres...) are burned using a hot disc.

In 2024 approx. 110000 t of alternative fuels (e.g. refuse-derived fuels, used tyres) were used.

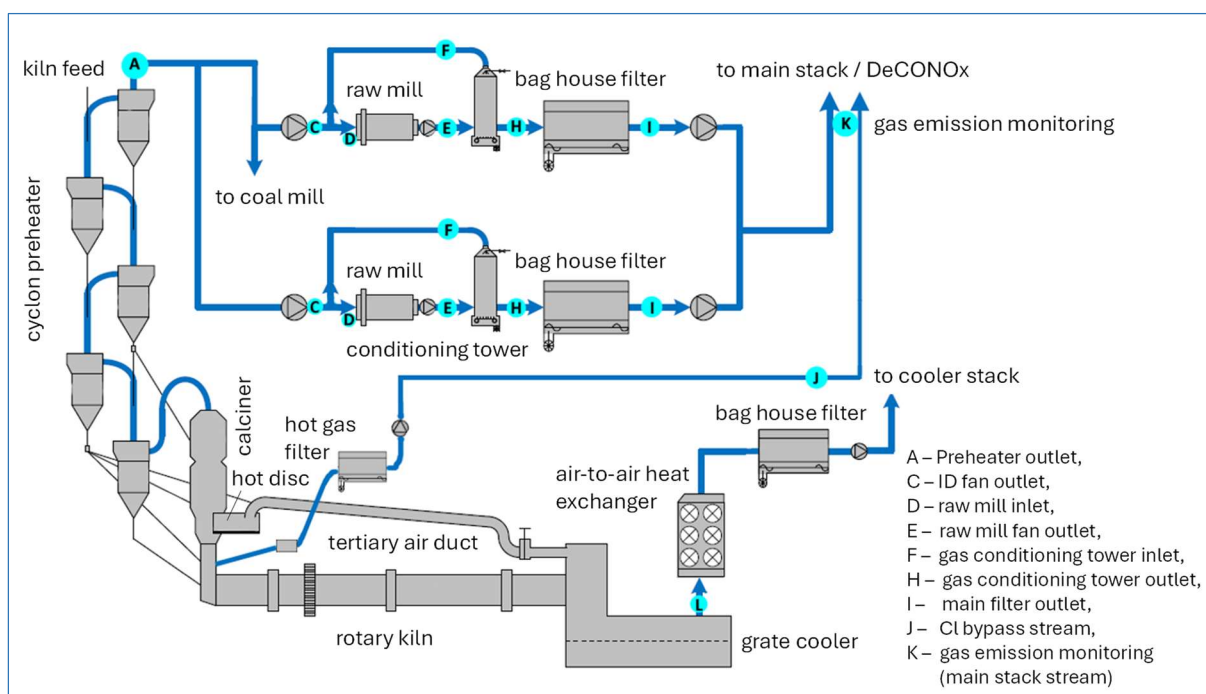
Over the last ten years, 60 % to 65 % of the total heat demand at the Alpacem cement plant has been met by burning substitute fuels (i.e. used tyres, RDF from commercial and industrial sources).

In 2024 approx. 43000 t of secondary raw materials (e.g. construction demolition waste, incineration ashes) and approx. 295000 t of secondary additives (e.g. slag, fly ash, bypass dust) were used.

In the reference year 2024, the resource conservation factor of the cement plant was approx. 443 kg of substitute materials per ton of cement. The resource conservation factor illustrates the amount of substitute fuels, secondary raw materials and secondary additives used in the production of one ton of cement. The Alpacem cement plant in Anhovo has therefore contributed to the conservation of natural resources by using approx. 446000 tons of substitute materials per year (reference year 2024).

The clinker factor in the reference year 2024 was 720 kg of Portland cement clinker per ton of cement.

Figure 2 shows a process flow sheet of Alpacem cement plant in Anhovo.



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*** G. Mautschitz: "Emissionen aus Anlagen der österreichischen Zementindustrie - Bilanzjahr 2024", VÖZ, Wien 2025

Table 2: Emissions of various air pollutants from plants in the Austrian cement industry and their share of the national freight

Based on the relative contributions of Austrian cement industry to Austrian emissions (Table 2) it is particularly important to remove sulphur dioxide (SO₂), carbon monoxide (CO), nitrogen oxides (NO_x), total organic carbon compounds (TOC), volatile heavy metal compounds (in particular mercury (Hg)) and dust from the exhaust gas of cement plants [4].

3.1 Measures to minimize dust emissions

Exhaust gases from the cement industry contain particulate matter that must not be released into the atmosphere. This includes raw material particles, cement clinker particles, carbon particles and additive material particles. The removal of the solid dispersed fraction from the gas phase is referred to as dedusting or dust separation. The process engineering units used for this purpose are called dust collectors or dust separators.

In cement industry plants, bag filter systems with high-performance filter media and/or electrostatic precipitators are predominantly used for this purpose.

The electric dust collector developed by *F. G. Cottrell* was first used in the cement industry in 1909 (*Riverside Portland Cement Co.* (US)). Electrostatic precipitators use an electric field to transport dust particles via the displacement space to the precipitation electrode after they have been electrically charged by a corona discharge, where they are then separated. An electrostatic precipitator normally works optimally when the specific dust resistance is approx. 10⁴ ohm cm to approx. 10¹¹ ohm cm, thus preventing the dust particles from rebounding and spraying back from the precipitation electrodes. Continuous operation can be ensured if the precipitation plate-shaped electrodes are periodically cleaned from the deposited dust by shaking and tapping. Electrostatic **dust** precipitators can also be used successfully at operation temperatures above 260 °C, although their effectiveness decreases with increasing exhaust gas temperature due to changing physical conditions (in particular: change in specific dust resistance, decrease in corona voltage, decrease in breakdown voltage, increasing gas viscosity).

It should be noted that dust separators can contribute to the de novo synthesis of dioxins and furans (Figure 3).

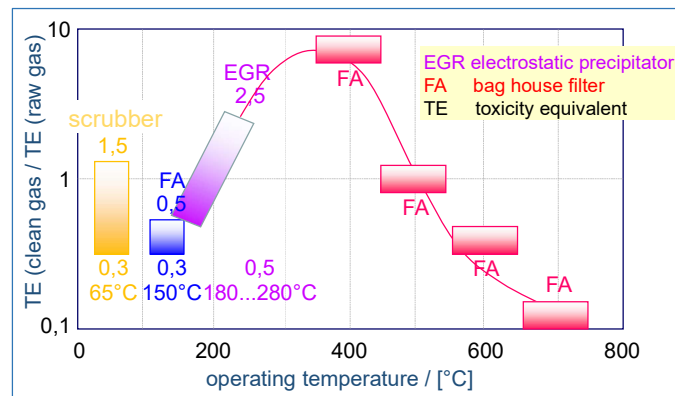


Figure 3: De novo synthesis of dioxins and furans in dust separators

Semi-permeable filter media are used in filtering dust separators to retain dust particles through surface filtration and depth filtration. The dust particles collect in the depth and on the surface of the filter medium, forming a dust cake at higher dust concentrations. The dust cake must be removed periodically, usually by a pulse of compressed air (pulse jet cleaning), to ensure continuous operation. The filter medium is usually converted in the form of filter bags 5 m to 10 m long with a diameter of approx. 15 cm, mounted vertically in the bag housings of the dust collectors. Teflon-laminated glass fibre fabrics or polyimide needle felts are often used as conventional filter media in the cement industry. These filter media are temperature-resistant up to approx. 260 °C.

In hot gas filtration, e.g. metal needle felts or ceramic filter elements made of high-temperature wool or fine ceramic granulates are often used as self-supporting filter elements to enable dust removal at temperatures up to approx.

1100 °C. These materials are insensitive to flying sparks, non-flammable and have good thermal shock resistance. Nevertheless, there are only a few examples of applications in the operation range above 500 °C because of the high operating costs. Hot gas filters with ceramic filter cartridges are often used successfully in the chlor-alkali bypass of cement plants.

Figure 4 shows that electrostatic precipitators have a minimum separation efficiency in a particle size range from 0.1 µm to 1 µm. This minimum separation efficiency is due to a change in the charging mechanisms of the particles. This minimum separation efficiency is less pronounced in filter separators. This is the reason why filter separators have been preferred over electrostatic precipitators in the cement industry in recent years.

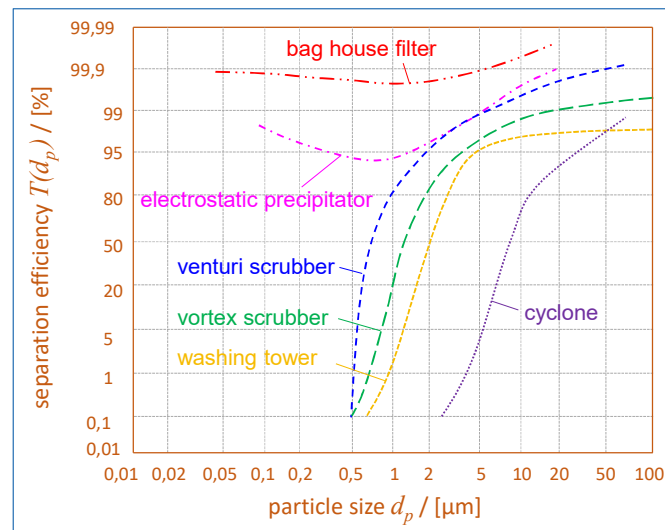


Figure 4: Single particle separation efficiency of different types of dust separators

However, it should be noted that when using conventional textile filter media, an operation temperature of 220 °C must not be exceeded continuously (thermal instability). For this reason, it is often necessary to cool the dust-laden exhaust gas stream before it enters the filter separator. In order not to impair the overall energy efficiency of the system, waste heat recovery is recommended. Direct dust passage through the textile filter medium (holes) into the clean gas chamber must absolutely be prevented. Special dust monitors are used for this purpose.

Despite the minimum separation efficiency of between 0.1 µm and 1 µm, electrostatic precipitators can be used, but they require numerous electric field areas, which result in correspondingly high investment and operating costs.

Operation experience with the use of electrostatic precipitators in cement industry plants shows that a daily emission limit of 10 mg/m³(Vn) at 10 vol.% O₂ in the clean gas can be maintained permanently.

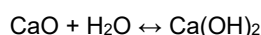
Operation experience with the use of filter separators with high-performance textile filter media in cement industry plants shows that a daily emission limit of 5 mg/m³ (Vn) at 10 vol.% O₂ in the clean gas can be maintained permanently. It has been found that, with newly installed textile filter media, clean gas dust concentrations of less than 1 mg/m³ (Vn) can initially be measured. These values deteriorate over time due to incomplete cleaning of the filter elements, so that the individual filtration cycles between cleaning operations become shorter. Increased cleaning can result in greater dust penetration into the clean gas.

At the Anhovo Alpacem cement plant, bag filters with high-performance textile filter media are used to remove dust from the kiln exhaust gas and the clinker cooler exhaust gas. The filter medium consists of polyphenylene sulphide (PPS). The filter area of the furnace filter is approx. 4070 m². More than 50 additional filter separators (e.g. silo top filters) are also used in the cement plant.

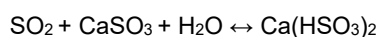
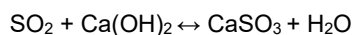
A conventional bag filter is used in the Alpacem cement plant to remove dust from the chlor-alkali bypass flow after the kiln gas has been cooled to approx. 180 °C.

3.2 Measures to reduce sulphur dioxide emissions

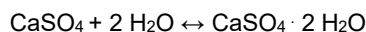
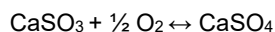
Sulphur dioxide emissions arise in cement industry plants through the combustion of sulphur-containing fuels (in particular sulphur-containing coal and heavy oils) and/or the use of sulphur-containing raw materials. For example, iron sulphide (FeS₂) may be present in the raw material in form of marcasite or pyrite, which release SO₂ during thermal treatment. Dry additive processes, semi-dry processes and wet processes are used as technical SO₂ flue gas treatment systems. In the cement industry, wet processes based on a calcium washing process (chemical sorption process, *Gea-Bischoff process*) are predominantly used, with gypsum (CaSO₄·2 H₂O) **production**, which is ground into the cement as a setting regulator. In the calcium washing process, calcium oxide is dispersed in water to produce an aqueous calcium hydroxide suspension:



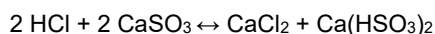
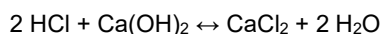
The calcium hydroxide (Ca(OH)₂) suspension reacts with SO₂ in the flue gas to form calcium sulphite (CaSO₃) and calcium hydrogen sulphite (Ca(HSO₃)₂):



If there is enough oxygen in the flue gas, calcium sulphite reacts to form calcium sulphate (CaSO₄), which combines with water to form gypsum:

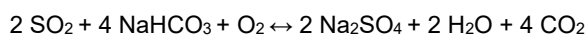


In addition to SO₂, hydrogen chloride (HCl) is also removed from the exhaust gas stream as calcium chloride (CaCl₂):



Monitoring the concentration of chlorine-containing compounds is particularly important in cement production. Soluble chlorine compounds, mostly present as CaCl₂, can be added to cements as accelerators for compressive strength development or to achieve shorter setting times. However, chlorine-containing compounds in reinforced cement can cause corrosion of steel girders and ultimately lead to premature structural damage (material fatigue). Sulphur in cement is often controlled by adding gypsum to the cement mixture. The sulphur content partly determines the degree of drying and the drying strength as well as the ability of the cement to dry out even at higher humidity. For these reasons, it is important to monitor both the chlorine and sulphur concentrations in cements.

In the drying additive process, which is also used in the cement industry for the desulphurisation of exhaust gases, sorbents (such as sodium hydrogen carbonate (NaHCO₃, *SolvAir process*) or limestone (CaCO₃) are injected into the exhaust gas stream to bind sulphur oxides as sodium sulphate (Na₂SO₄):



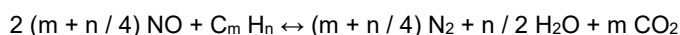
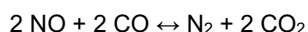
At the Alpacem cement plant in Anhovo, the dry additive process with sodium hydrogen carbonate is used to desulphurise the exhaust gas stream.

The exhaust gas partial flow from the chlor-alkali bypass was identified as the main source of SO₂ in the Anhovo cement plant. So sodium hydrogen carbonate is added to this exhaust gas partial flow and the resulting sodium sulphate particles are removed from the exhaust gas flow by a filtering dust separator.

Operation experience with the dry additive process in cement industry plants shows that a daily SO₂ emission limit of 20 mg/m³ (Vn) can be maintained continuously at 10 vol.% O₂ in the clean gas (without natural inclusions of marcasite and/or pyrite in raw materials).

3.3 Measures to reduce nitrogen oxide emissions and carbon monoxide emissions

Through staged combustion in the calciner, the carbon monoxide (CO) produced can be used to achieve a partial reduction of the nitrogen oxides present:



Although the reducing agents carbon monoxide and hydrocarbons promote the partial decomposition of nitrogen oxides into environmentally neutral exhaust gas components nitrogen, carbon dioxide and, if applicable, water, the carbon monoxide concentration in the exhaust gas can nevertheless remain high (e.g. residence time in the calciner too short, turbulence level in the calciner too low).

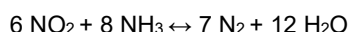
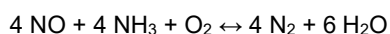
If the reduction in nitrogen oxide emissions is insufficient and above-average amounts of CO remain in the exhaust gas stream, further emission reduction measures must be taken.

One option is thermal post-combustion of the organic pollutants and carbon monoxide to CO₂ with simultaneous selective catalytic reduction of nitrogen oxides. The aim is to convert CO, TOC and NO_x emissions simultaneously in a single plant through two consecutive sub-processes in the same reactor. This plant concept is called the DeCONOX process. The DeCONOX plant is designed to couple an SCR DeNO_x plant with a regenerative post-combustion plant in a low-dust configuration. In the low-dust configuration, the exhaust gas is dedusted before entering the SCR DeNO_x plant.

3.3.1 Description of SCR DeNO_x technology

Burning temperatures of approx. 1450 °C with flame temperatures of more than 2000 °C are necessary for the formation of cement clinker minerals. This produces exhaust gases that contain increased levels of nitrogen oxides (NO_x, especially thermal NO) and must be subjected to exhaust gas cleaning.

In conventional SCR DeNO_x technology, nitrogen oxides are converted into nitrogen (N₂) and water vapour (H₂O) [5]. Since the reaction products are natural components of air, environmental problems can be ruled out. According to general opinion, the chemical reactions that take place during SCR DeNO_x technology can be summarized by the following sum reactions:



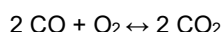
The dosing device of the reduction agent is very important for the equimolar conversion of nitrogen oxides. The control system must function quickly and reliably in order to keep NH₃ slip as low as possible. If the raw gas concentration of nitrogen oxides in the exhaust gas stream is lower and the added NH₃ is too high, the ammonia slip increases, unless excess ammonia is oxidized to NO_x by appropriately dimensioned catalyst layers. In this case, the reductant ammonia is partially consumed without being used. Operating costs will increase.

Catalyst materials for reducing NO_x emissions are already being used successfully in energy-generating plants to reduce NO_x emissions and are considered state of the art in this field. The use of catalyst materials to reduce NO_x emissions in exhaust gases from the cement industry has been attempted since 2009 and is problematic. This exhaust gas cleaning method is therefore not yet state of the art in the cement industry. The effects of exhaust gases from cement industry plants on catalyst materials are manifold (catalyst poisons). Using mobile pilot rigs operated with original flue gas, the plant operator selects a plant-specific catalyst material which, under the given plant conditions, should offer the greatest possible NO_x reduction potential with the longest possible service life. Finally, the suitability and availability of the large-scale SCR DeNO_x plant must be tested during a longer-term trial operation (a few years) on site under official supervision.

3.3.2 Description of conventional thermal post-combustion

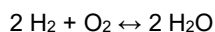
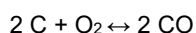
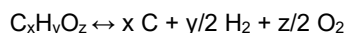
For quality reasons, cement clinker must be burned in an oxidizing atmosphere. However, furnace malfunctions (e.g. blocking of the kiln) can lead to incomplete combustion of carbonaceous substances in the rotary kiln, resulting in CO concentration peaks in the furnace exhaust gas when it leaves the rotary kiln and before it enters the preheater. Carbon monoxide (CO) can also be formed in the secondary combustion chamber if carbonaceous fuels are only partially combusted there due to low temperatures, a lack of oxygen or too short residence time. Carbon monoxide can also be produced as a decomposition product in the less hot upper cyclone stages of the preheater (250 °C to 400 °C) from organic raw meal components.

To avoid high CO emissions, CO-containing rotary kiln exhaust gases can be thermally post-combusted, whereby carbon monoxide is converted into carbon dioxide (CO₂):



Due to the incomplete conversion of carbon-containing input materials to CO₂ in the cement production process, organic compounds are also found in rotary kiln exhaust gases. These include polycyclic aromatic hydrocarbons (PAHs), dioxins/furans (PCDD/PCDF) and hexachlorobenzene (HCB). The total organic carbon (TOC) content is used as a measure of the organic compound content in the exhaust gas. Due to the very low concentrations of ultra-toxic pollutants (e.g. PCDD/PCDF) in the exhaust gas stream, the TOC value is not useful for evaluating ultra-toxic pollutant emissions.

If exhaust gases contain organic pollutants, they can be cleaned by thermal oxidation (thermal post-combustion), whereby hydrocarbons can be converted into harmless reaction products. As the following reaction equations illustrate, the hydrocarbons first dissociate at high temperatures into the combustible components carbon and hydrogen as well as oxygen, and are then converted into water or carbon monoxide or carbon dioxide in a further reaction step:



In thermal post-combustion the raw gas is often preheated by indirect heat exchange while cooling the hot exhaust gases flowing out of the combustion chamber. If the heat exchange is insufficient, a relatively large amount of additional fuel must be burned to maintain the required combustion chamber temperature.

The amount of additional fuel is reduced when a regenerative post-combustion system is used. Depending on the size of the exhaust gas volume flow to be treated, a regenerative post-combustion system has three, five or seven

regenerators connected in parallel, which are either equipped with temperature-stable ceramic honeycomb modules or with pellets as ceramic heat storage masses. The raw gas flows through the first heat storage tower, which has been heated by the hot combustion gases. Heat exchange increases the raw gas temperature to 80 % to 100 % of the combustion chamber temperature. If the calorific value of the raw gas components is sufficient for complete combustion of the pollutants, this is referred to as autothermal plant operation, in which no additional fuel is required. If the calorific value of the raw gas components is too low, sufficient additional fuel must be burned in the combustion chamber. The hot exhaust gas leaves the combustion chamber through another regenerator, which has previously been cooled by the cold raw gas. This cools the exhaust gas and heats the regenerator. By switching the flow paths, the heat storage towers enable heat exchange between the cold, pollutant-rich raw gas and the hot, low-pollutant clean gas.

3.3.3 Description of the DeCONOx process

First, the daily average dust emission limit in the raw gas is reduced to $<5 \text{ mg/m}^3(\text{Vn})$ by a filter separator equipped with highly efficient textile cleaning filter media. A fan sucks the dedusted exhaust gas volume flow through the DeCONOx system (Figure 5) [6 ,7].

Depending on the volume of flue gas, the system has three, five or seven reactors, which are periodically fed with raw gas or clean gas. In order to avoid peaks in pollutant concentrations during the switching cycles, the remaining reactor is flushed with air and the exhaust gas that has not been completely converted is transported to the combustion chamber and incinerated there.

The number of reactor towers in a DeCONOx plant depends, among other things, on the exhaust gas flow rate, the state variables of the exhaust gas, the exhaust gas composition, the installed regenerator volume and its heat storage capacity, the materials used in the plant and the reactor heat insulation.

Each individual reactor has pneumatically operated flaps supplied with sealing air, through which the raw gas enters the thermally insulated reactor interior.

First, the raw gas flows through the lower regenerator layer to reach the catalyst inlet temperature ($250^\circ\text{C} - 350^\circ\text{C}$). This is followed by an intermediate chamber in which the pre-vaporised ammoniacal reducing agent is injected. The exhaust gas/reducing agent mixture then flows through the SCR DeNOx catalyst layer. Following successful pilot tests with original flue gas, a ternary mixture of $\text{TiO}_2/\text{V}_2\text{O}_5/\text{WO}_3$ is often used as catalyst material. The plant-specific catalyst material is available in the form of parallel flow catalyst elements.

Above the catalyst layer is another intermediate space and above that the upper regenerator layer, which raises the exhaust gas temperature to approx. 850°C .

The combustion chamber is mounted above the reactors. It is operated at a minimum temperature of 850°C to ensure that organic hydrocarbons and carbon monoxide are oxidized as completely as possible when the exhaust gases remain in the combustion chamber for more than three seconds.

During start-up of the DeCONOx plant and during non-autothermal operation, the minimum combustion chamber temperature is ensured by burning additional fuel.

The clean gas leaves the DeCONOx system at approx. 180°C and is therefore warmer than the raw gas entering the DeCONOx. Residual heat recovery will be recommended for energy efficiency reasons.

Analytical investigations show that although the DeCONOX plant does not influence the extent of Hg emission concentrations in the exhaust gas stream, it can fundamentally change the proportions of Hg species. If mercury is present at the inlet of the DeCONOX plant at approx. 91 % metallic and approx. 9 % ionic in oxidation state +II, mercury is present at the outlet of the DeCONOX plant at approx. 20 % metallic and approx. 80 % ionic in oxidation state +II. This fact must be taken into account when operating continuous Hg emission measuring devices.

The availability of existing DeCONOX installations has been gradually increased to more than 99 %.

There is currently no DeCONOX plant at the Anhovo cement factory as a secondary emission mitigation process, and one would have to be newly implemented. This would require the authorities to approve a trial operation, lasting several years, in order to increase the availability of the DeCONOX system from an initial average of <80% to an average of >99% through technical optimisation measures.

If the DeCONOX plant switches to bypass operation, the authorities must provide for correspondingly higher emission limits for NO_x, NH₃, TOC and CO in the event of such a failure. The time span for such technically unavoidable failure must be limited by the authorities to approx. 8% of the annual furnace operation time, whereby start-up and shutdown operation conditions must be included. The time span for failure operations should be kept as short as possible.

In the event of a DeCONOX failure, the existing SNCR system can be used to reduce NO_x emissions with correspondingly higher daily NO_x- and NH₃- emission limits (NO_x: 300 mg/m³(Vn), NH₃: 30 mg/m³(Vn), O₂: 10 vol.%).

Operation experience shows that when the DeCONOX process is used in plants in the cement industry, daily NO_x emission levels of 150 mg/m³ (Vn) at 10 vol.% O₂ in the clean gas, with a daily NH₃ slip emission levels of approx. 20 mg/m³ (Vn) at 10.0 vol.% O₂ and a daily CO emission level of 100 mg/m³ (Vn) at 10 vol.% O₂ in clean gas and a daily average TOC emission level of approx. 20 mg/m³ (Vn) at 10.0 vol.% O₂ in clean gas can be maintained permanently.

To reduce higher NO_x emission peaks in the raw gas flow of secondary NO_x reduction technologies (e.g. DeCONOX, SCR- DeNO_x technology) can prove useful in conjunction with an upstream SNCR system.

Benzene, toluene, ethylbenzene and xylenes undergo extensive degradation at approx. 99 % under the given operation conditions in the DeCONOX plant. In contrast, halogenated aromatic hydrocarbons such as pentachlorobenzene and hexachlorobenzene undergo lower conversion rates. The same applies to dioxins and furans as well as their precursor substances (biphenyls).

The exhaust gas is thoroughly dedusted by a filtering separator, before entering the DeCONOX plant. This is advantageous for the sub-process of catalytic nitrogen oxide emission reduction. The absence of dust particles in the raw gas stream prevents erosion of the parallel flow elements of the catalyst layers and also of the regenerator layers. The risk of clogging due to dust deposits is low. The cell division of the parallel flow catalyst elements (pitch) can be kept small. This increases the specific catalyst surface area and enables a more compact plant design with a high NO_x conversion rate. A disadvantage is the necessary reheating of the exhaust gases after intensive dust removal to the temperature level of the SCR catalyst material. However, this can be kept to a minimum by the heat release due to the oxidation of the combustible gas components contained in the exhaust gas with simultaneous regenerative waste heat utilisation. A deterioration in the combustion efficiency must be avoided. Only during start-up and bypass operation and in the absence of autothermal operation (depending on the calorific value of the exhaust gas) are additional fuels burned.

The heat distribution in the reactors must be monitored particularly closely to prevent permanent thermal degradation of the catalyst elements (mineral conversion of anatase to rutile); if necessary, emergency cooling of the catalyst elements must be provided. During regenerative heat exchange in the reactors, the temperature at the reactor outlet must not fall below 180 °C to prevent the formation of ammonium salts. This prevents blockages caused by ammonium salts (NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$) and prevents increased NH_3 emissions. The number of catalyst elements installed in the DeCONOX system should not be too small in order to ensure high NO_x emission reduction with as little NH_3 slip as possible. Too much NH_3 can be oxidized by the catalyst elements.

Persistent organic hydrocarbon compounds (POPs, e.g. dioxins and furans) are only partially oxidised to CO_2 in the combustion chamber of the DeCONOX plant. When selecting POP-contaminated substitute materials, it is essential to bear in mind that the DeCONOX plant is not a conventional high-temperature combustion chamber ($>1100\text{ °C}$, residence time of $>5\text{ s}$, with high oxygen content and good exhaust gas mixing) (Figure 6) and therefore does not allow complete destruction of ultra-toxic substances. When conventional high-temperature post-combustion chambers are used for the destruction of PAHs and POPs, a water quench is used immediately after the high-temperature chamber to cool the exhaust gases in order to allow the temperature window for the de novo synthesis of dioxins and furans to pass through as quickly as possible from 650 °C to $<200\text{ °C}$, thereby preventing de novo synthesis of dioxins and furans.

Nevertheless, the use of DeCONOX technology can ensure long-term compliance with the strict emission limit value for ultra-toxic substances (dioxins and furans) of $0.1\text{ ng}_{\text{TE}}/\text{m}^3(\text{Vn})$ (10 vol.-% O_2), provided that the use of substitutes contaminated with ultra-toxic substances (- these substances can be found in some hazardous materials -) is strictly avoided, which is the case for Anhovo cement plant.

No reliable results are yet available on the ageing of the catalyst material in DeCONOX plants. However, the service life is likely to be several years.

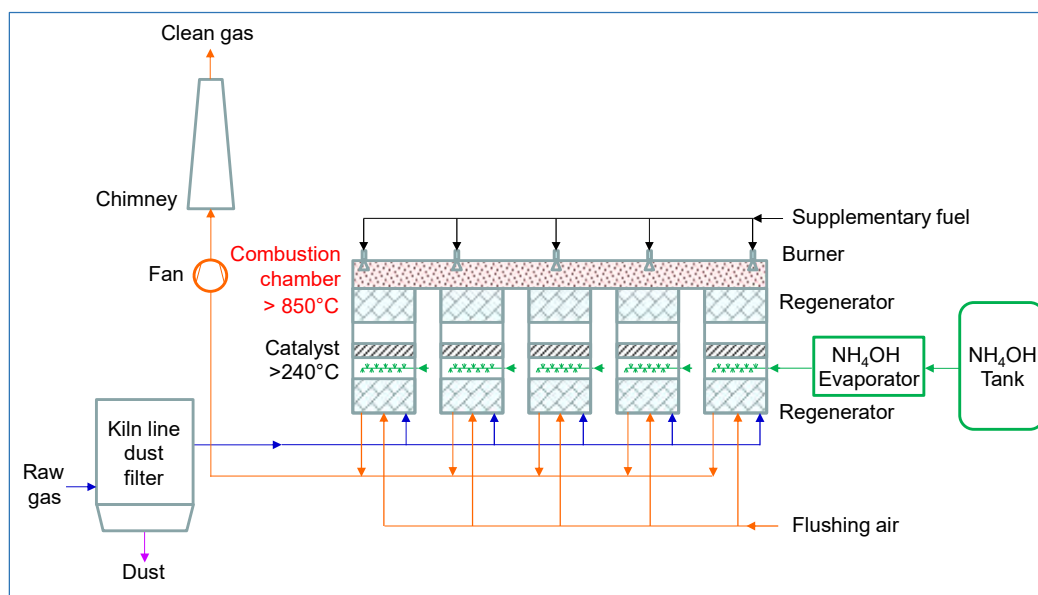


Figure 5: Simplified flow diagram of a DeCONOX plant with five reactors

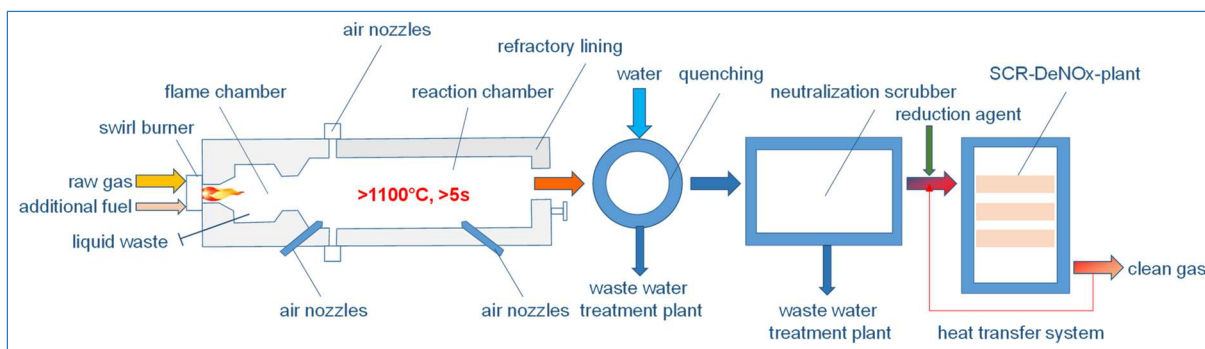


Figure 6: Simplified flow sheet of a high-temperature post-combustion chamber

3.4 Measures to reduce mercury emissions

This heavy metal enters the cement clinker production process via input mass flows through the use of mercury-containing raw materials (e.g. clays contaminated with cinnabar), the combustion of mercury-containing solid conventional fuels, and the use of substitute raw materials and fuels contaminated with mercury (Hg) [8].

A primary measure to reduce mercury input into the furnace system is extensive deposit exploration, which, where applicable, involves identifying deposit areas with increased mercury compounds (cinnabar (HgS)) at an early stage and, if possible, excluding them from excavation. The selection of mercury-containing substitutes must be limited in any case in order to keep the mercury input into the cement production process low. Even if the mercury content in the input materials varies greatly, it can be assumed that approx. 60 % of the mercury input comes from raw materials and approx. 40 % from combusted fuels. However, it should be noted that the mercury content in natural raw materials and conventional fuels can sometimes be higher than the mercury content in substitutes. Due to the high flame temperatures of the main burner ($>2000\text{ }^{\circ}\text{C}$), the mercury from mercury-containing fuels is present as elemental (metallic) mercury (Hg^0) after combustion. The mercury from mercury-containing raw materials is converted in the temperature range of the cyclone preheater ($250\text{ }^{\circ}\text{C}$ to $850\text{ }^{\circ}\text{C}$) after the $\text{Hg}^{(+I)}$ has been converted to ionic mercury compounds $\text{Hg}^{(+II)}$ and metallic Hg^0 (disproportioning). The $\text{Hg}^{(+II)}$ can be present as mercury halides, as HgS or as HgSO_4 or as HgO [9].

Due to the relatively high vapour pressure of mercury, increased mercury emissions from cement industry plants may occur. It can be assumed that at temperatures of approx. $140\text{ }^{\circ}\text{C}$, depending on the dust concentration and particle size distribution in the exhaust gas, between 15 % and 75 % of the metallic mercury and its compounds are present in an adsorbed form. Mercury element cycles form between the raw mill, kiln filter and cyclone preheater. In combined operation, when the raw mill is in operation, mercury emissions at the chimney are reduced due to increased mercury adsorption on raw meal particles.

Stricter Hg emission limits (*Minamata Convention*) will make it necessary in future to use more secondary flue gas cleaning technologies in order to comply with stricter Hg emission limits on a permanent basis. The ExMercury process or a dry additive process can be used as emission reduction techniques for this purpose.

3.4.1 Description of the ExMercury process

Due to the vapour pressure behaviour of mercury, this metallic trace element partially accumulates in the external element cycle of the kiln/preheater/filer system, with higher Hg concentrations being found primarily in the dust of the kiln filter. Nevertheless, it is precisely the high volatility of this heavy metal that can lead to increased Hg emissions into the atmosphere.

The ExMercury process (Figure 7) is designed to thermally remove mercury from these furnace filter dusts, adsorb the Hg and then extract the Hg-contaminated residue and dispose of it properly [10]. This effectively removes mercury from the furnace system, significantly reducing Hg emissions from cement industry plants.

Mercury-enriched kiln filter dust is fed into the ExMercury system, where it is passed in counterflow to hot kiln gas and heated to approx. 400 °C. The hot furnace gas volume flow required for this is usually taken from the top stage of the cyclone preheater. As a result of the heating, the filter dust to be treated releases approx. 90 % to 95 % of its mercury load into the carrier gas stream. The mercury-containing furnace gas loaded with fine dust particles leaves the top cyclone stage of the ExMercury system and enters a downstream hot gas dust collector (approx. 360 °C). There, the dust concentration is further reduced with the aid of high-temperature-resistant ceramic filter cartridges. The dust separated in the cyclone preheater of the ExMercury system and the dust cleaned by pulse jet in the hot gas dedusting system are collected and returned to the cyclone preheater. The dedusted, mercury-containing carrier gas is then rapidly cooled to approx. 100 °C to 120 °C with water in a spray tower. Fine-grained adsorbent (e.g. brown coal activated coke, activated carbon, brominated activated carbon) is then injected into the cooled gas flow, which adsorbs the gaseous mercury. The mercury-laden sorbent is then separated from the carrier gas stream using a filter separator equipped with high-performance textile filter media and disposed of as hazardous waste in accordance with all occupational health and safety regulations for operating personnel (e.g. safety clothing, respiratory masks, airlock systems). In order to ensure that the adsorbent is as fully loaded as possible and thus to save operating costs, the adsorbent is recycled until it reaches Hg saturation.

The ExMercury process achieves mercury reduction in the cement process by removing Hg-contaminated dust and disposing of it as hazardous waste.

Operation experience shows that when the ExMercury process is used in plants in the cement industry, Hg emission limits of 25 µg/m³(Vn) (monthly average) at 10 vol.% reference oxygen concentration in the clean gas can be maintained on a permanent basis.

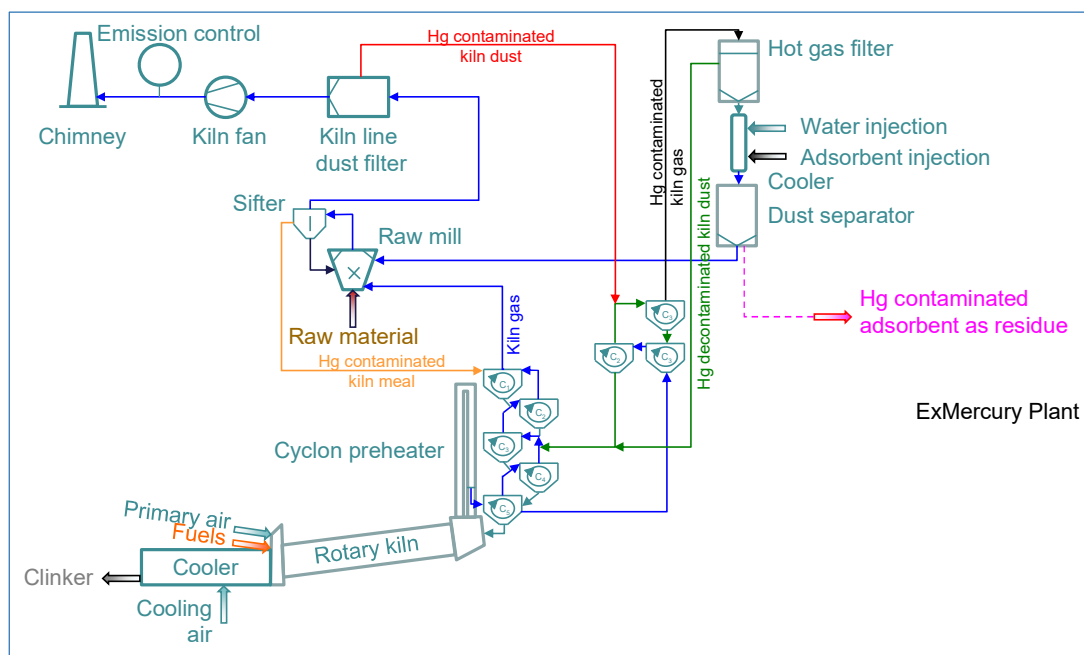


Figure 7: Simplified flow sheet of an ExMercury system implemented in the cyclone preheater process

3.4.2 Description of the dry additive process

Another method for reducing mercury emissions from cement industry plants is the use of the dry additive process. In this process, conventionally activated carbon, brominated activated carbon, activated coke or calcium hydroxide is injected into the exhaust gas stream of cement plants as an adsorbent to immobilize vapour-phase mercury and its compounds, whereby both physical adsorption and chemical adsorption can take place. Due to the relatively high Hg vapour pressure, it is understandable that this technique can only be successfully implemented if the exhaust gas temperature is as low as possible (120 °C to 140 °C). However, the dew point must not be exceeded under any circumstances. Cooling followed by reheating of the exhaust gas stream is not practical for economic reasons. The use of activated carbon also offers the advantage of separating traces of other moderately to relatively volatile metallic elements and their compounds, as well as residues of halogen compounds, hydrocarbon compounds (including ultra-toxic substances) and more. As a tail-end technology, it should be used in the immediate vicinity of the chimney, where the lowest exhaust gas temperatures can be detected. The contaminated activated carbon particles must be removed from the flue gas stream using filter dust separators. This produces a powdery residue which must be disposed of as hazardous waste. This procedure places additional demands on operating personnel (including the wearing of protective clothing and respiratory protection, and the installation of airlock systems at the extraction point). The activated carbons used require careful material selection to prevent corrosion. Attention must be paid to the formation of explosive atmospheric mixtures. The grinding of contaminated carbons into product streams must be questioned due to the possible mobilisation of pollutants during heat development during cement grinding. The possible elution behaviour of pollutants from cement products (concrete blocks) containing heavy metal-contaminated activated carbon must be investigated in more detail. There is a fundamental difference between the permanent incorporation of heavy metals into the glass phase of cement clinker and the incorporation of heavy metals into the sol/gel matrix of cement products. In addition, sorbents added to cement can influence the colour of cement products and change their porosity.

When assessing the effectiveness of emission reduction techniques for mercury through secondary emission reduction measures such as the ExMercury technique or the dry additive technique, the initial value of the Hg emissions to be reduced must be taken into account. If the mercury input into the furnace system can be kept low by using Hg low natural raw materials and Hg low fuels, secondary Hg-emission reduction processes are not necessary.

Through the specific selection of raw materials with low Hg content (e.g. mining exploration techniques) and strict limits on mercury in all input mass flows, as well as the implementation of a quality assurance system to monitor the properties of all materials used, the Anhovo cement plant should be able to reliably comply with Hg emission limits of 25 µg/m³ (Vn) (monthly average). These measures should be supported by the installation of a tail-end high-pressure water injection system to reduce the exhaust gas temperature to 130 °C, in order to improve Hg sorption on the dust particles to be almost completely separated.

If alternative materials (e.g. substitute fuels, secondary substitutes) are used, Hg emissions should be monitored continuously. This also facilitates monitoring of the Hg input mass flows into the furnace system.

4 Summary and concluding remarks

The installation of a DeCONOX system at the Alpacem cement plant in Anhovo would be a decisive and state-of-the-art step towards mitigating gaseous emissions. This technology is considered groundbreaking in the European cement industry, particularly with regard to significantly mitigating NO_x- and NH₃-emission levels and achieving particularly low emission levels for CO and TOC.

Based on experience gained during the operation of existing full-scale reference plants, I can conclude that, following an optimisation phase after commissioning as part of a longer-term trial operation, this technology has the potential to achieve very low average emission levels for NO_x, NH₃, CO and TOC.

Based on the knowledge in air pollution control techniques for cement industry plants,

- as a consultant to the "Advisory Board for Environmental Protection and Technology" of the Austrian cement industry,
- as data trustee for the Austrian cement industry and as author of the annual emission inventories for the Austrian cement industry since 1995,
- as a member of the project working committee of the UBA Berlin Dessau "Pure gas SCR in Rohdort cement plant" (Südbayerisches Portland-Zementwerk Gebr. Wiesböck & Co. GmbH, Germany),
- as a member of the project working committee of the VÖZ "Pilot tests for the catalytic reduction of nitrogen oxides in exhaust gases from Austrian cement plants",
- as consultant to Kirchdorfer Zementwerk Hofmann Ges.m.b.H., Kirchdorf/Krems, Austria, for the initial implementation of the DeCONOX process in the cement industry,
- as a member of the project working committee "Exhaust gas purification SCHWENK Allmendingen" (Schwenk Zement GmbH & Co. KG, Germany)",
- as a member of the VDI guidelines committee VDI 2094 "Emissions reduction in cement plants",
- as Chairman of the VDI Guidelines Committee VDI 3677 "Filtering Separators – Hot Gas Filtration",
- as a member of the project working committee "Exhaust gas cleaning OTTERBEIN Großenlütder-Müs" (OTTERBEIN cement and lime works, Germany)

and after reviewing all reports and emission data available, the following limit values for air pollutants from cement plants, using the cyclone preheater process and state of the art technology, can be permanently complied with (see Table 3):

air pollutant	emission limit	unit	reference O ₂ concentration	comments
total suspended particulate matter (TSP)	5	mg/m ³ (Vn)	10.0 Vol.-%	bag house filter, only kiln line, daily average
total suspended particulate matter (TSP)	10	mg/m ³ (Vn)	10.0 Vol.-%	electrostatic precipitator, only kiln line, daily average
nitrogen oxides (calculated as NO ₂)	150	mg/m ³ (Vn)	10.0 Vol.-%	calculated as NO ₂ , daily average
sulfur dioxide (SO ₂)	20	mg/m ³ (Vn)	10.0 Vol.-%	daily average, without sulfur compounds in raw material
sulfur dioxide (SO ₂)	<400	mg/m ³ (Vn)	10.0 Vol.-%	daily average, with sulfur compounds in raw material
hydrogen chloride (HCl)	20	mg/m ³ (Vn)	10.0 Vol.-%	daily average
total organic carbon (TOC)	20	mg/m ³ (Vn)	10.0 Vol.-%	daily average
carbon monoxide (CO)	100	mg/m ³ (Vn)	10.0 Vol.-%	daily average
ammonia (NH ₃)	20	mg/m ³ (Vn)	10.0 Vol.-%	daily average
mercury (Hg) (gaseous and particle bound)	0.025	mg/m ³ (Vn)	10.0 Vol.-%	monthly average, continuous measurement data acquisition
dioxins and furans	0.1	ng _{TE} /m ³ (Vn)	10.0 Vol.-%	average value over a period of 6 to 8 hours

Table 3: Potentially achievable emission values for cement plants using a cyclone preheater process under optimised conditions after several years of operation

It should be emphasized that the figures presented in Table 3 represent indicative lower limits that can be achieved only after an extended period of operational optimisation and under favourable process and raw material conditions. Particularly for nitrogen compounds (NO_x and NH_3), these values are stricter than the limits currently prescribed for cement plants even in countries such as *Austria* or *Germany*.

In the specific case of the new *Slovenian* regulation, which defines emission limit values for cement plants, the final emission limits are set in advance and fixed, rather than being established based on actual performance results obtained during trial operation of new abatement systems. Moreover, the timeframe granted to cement plants to adapt to these new and very stringent limits is relatively short - only four years are available for the planning, construction, commissioning and optimisation of the new emission reduction technologies. This is especially critical for NO_x and NH_3 emission mitigation, as their optimisation is typically more complex and time intensive.

It should be noted that the implementation of the SCR De NO_x techniques and the DeCON O_x process in cement plants over the last 15 years has shown that plant operators are well advised to carry out on-site pilot tests before constructing a large-scale plant in order to verify the effects of the original flue gas on the planned NO_x emission mitigation technology. This is particularly necessary when catalytically active materials are used in the reactors to ensure that the catalytically active material is not deactivated too quickly.

Given these circumstances, the emission limits shown in Table 4 represent the strictest field-proven international NO_x and NH_3 emission limits for cement plants with kiln operation in Europe. They reflect emission levels that can be reliably achieved under real operating conditions, based on long-term experience with high-performance installations.

air pollutant	emission limit	unit	reference O_2 concentration	comments
nitrogen oxides (calculated as NO_2)	200	$\text{mg/m}^3(\text{Vn})$	10.0 Vol.-%	
ammonia (NH_3)	30	$\text{mg/m}^3(\text{Vn})$	10.0 Vol.-%	total ammonia (NH_3 slip + ammonia from raw materials)

Table 4: The strictest field proven emission limits for NO_x and NH_3 prescribed for cement plants in Europe



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