3rd Annual Meeting of the Task Force on Techno-Economic Issues (TFTEI) – UN-ECE Convention on Long Range Transboundary Air Pollution (LRTAP) Rome, Italy – 20 October 2017

EXPERIENCE ON NO_X EMISSION REDUCTION IN EUROPEAN CEMENT PLANTS

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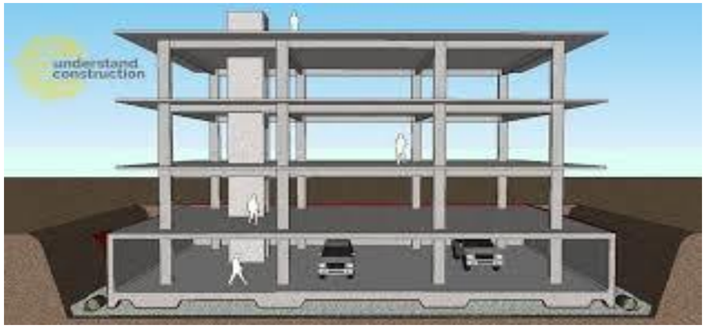
ABOUT CEMENT AND CONCRETE



- The Roman and the modern cement, patented 200 years ago, are not so different in composition and properties.
- The world production of cement is today **over 4 billion metric tons** (~50% from China).
- Cement is mainly used to produce **concrete and mortar**.

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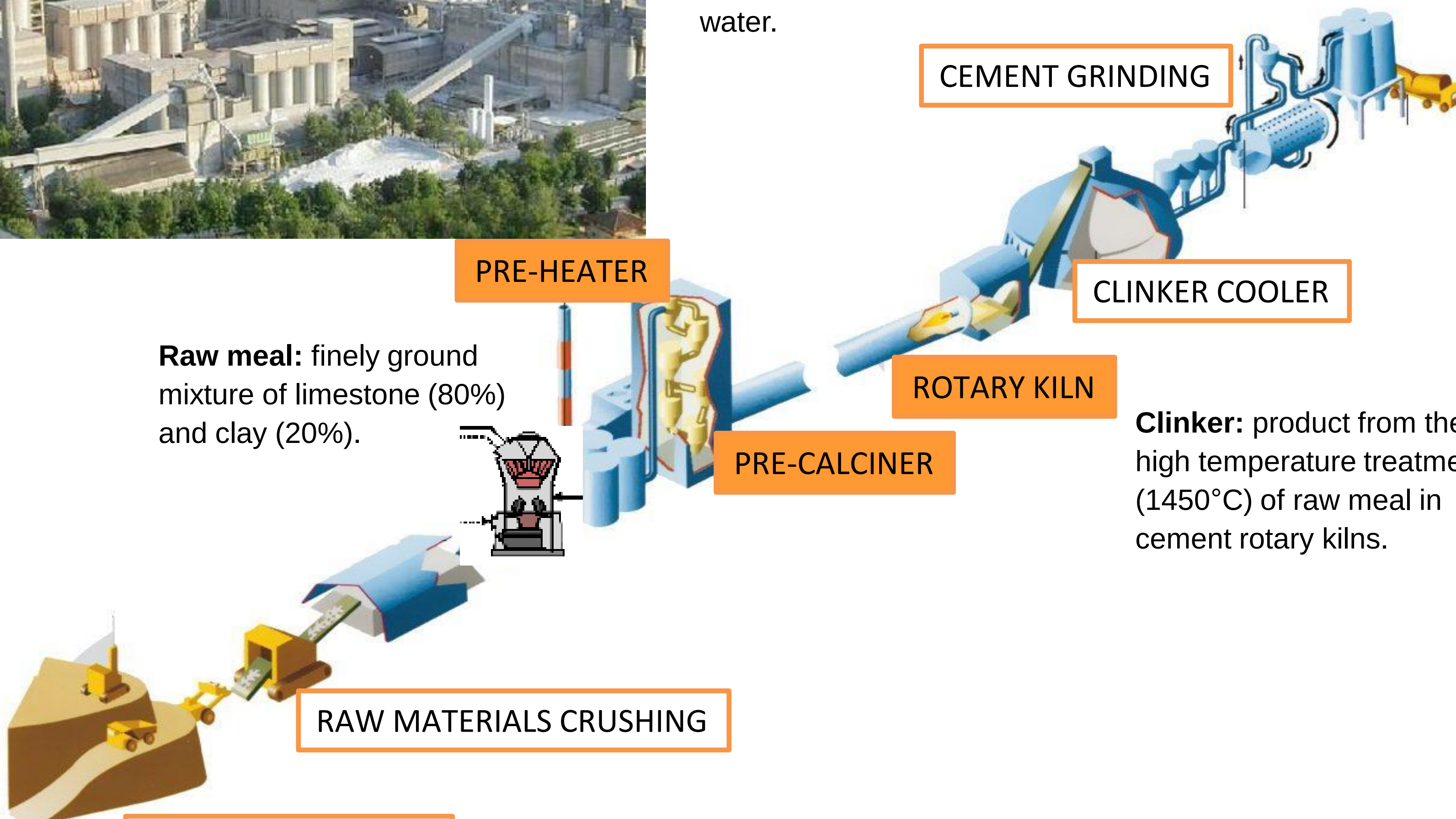
THE CEMENT PRODUCTION PROCESS

Concrete: mixture of cement, water and aggregates (sand and gravel).

Cement: fine grey powder made up of clinker, additions (e.g. blast furnace slag, fly ash) and gypsum which harden when mixed with water.



Raw meal: finely ground mixture of limestone (80%) and clay (20%).

Clinker: product from the high temperature treatment (1450°C) of raw meal in cement rotary kilns.

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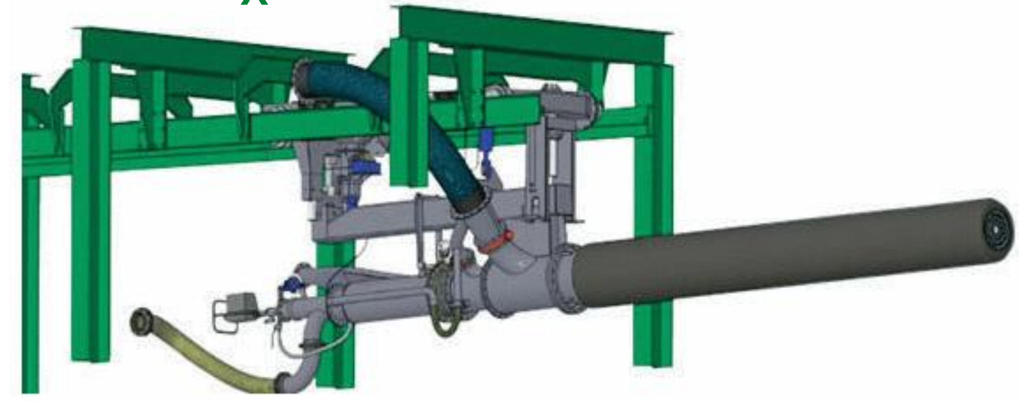
CONDITIONS THAT FAVOUR NO_X FORMATION



- The **main burner** generates a flame that can reach **2000°C** thanks to the pre-heated combustion air.
- The **excess air** (2-3%) guarantees the <u>oxidizing conditions</u> that are necessary for the good quality of the clinker produced.
- The combustion process in the **pre-calciner** at 900°C is also operated in excess air to avoid CO formation.

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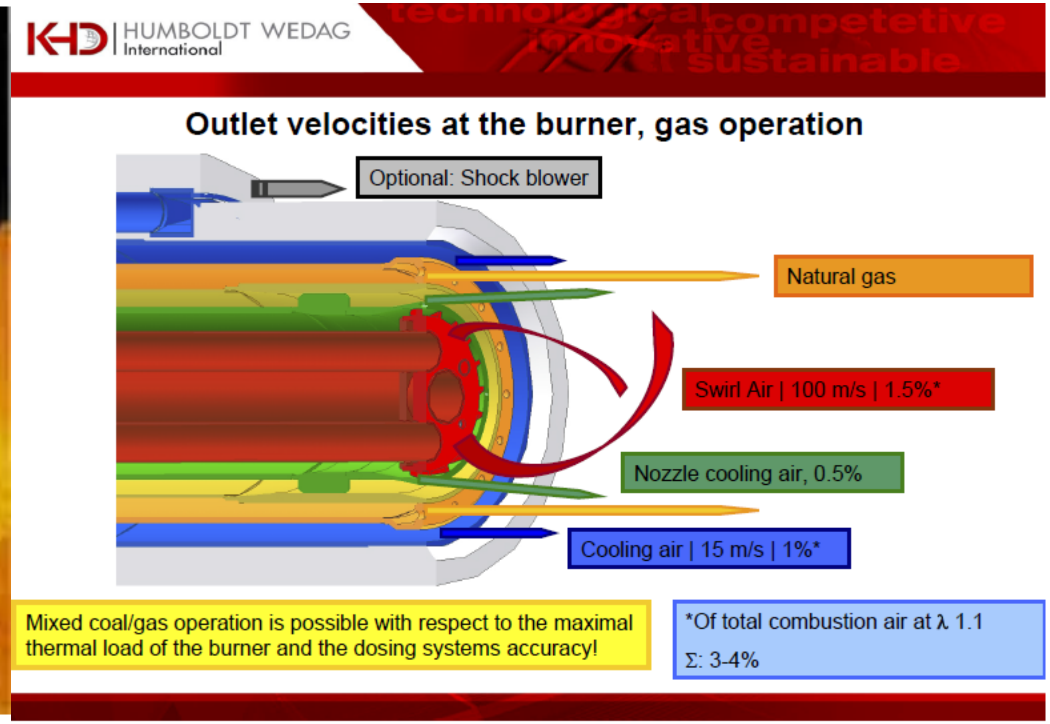
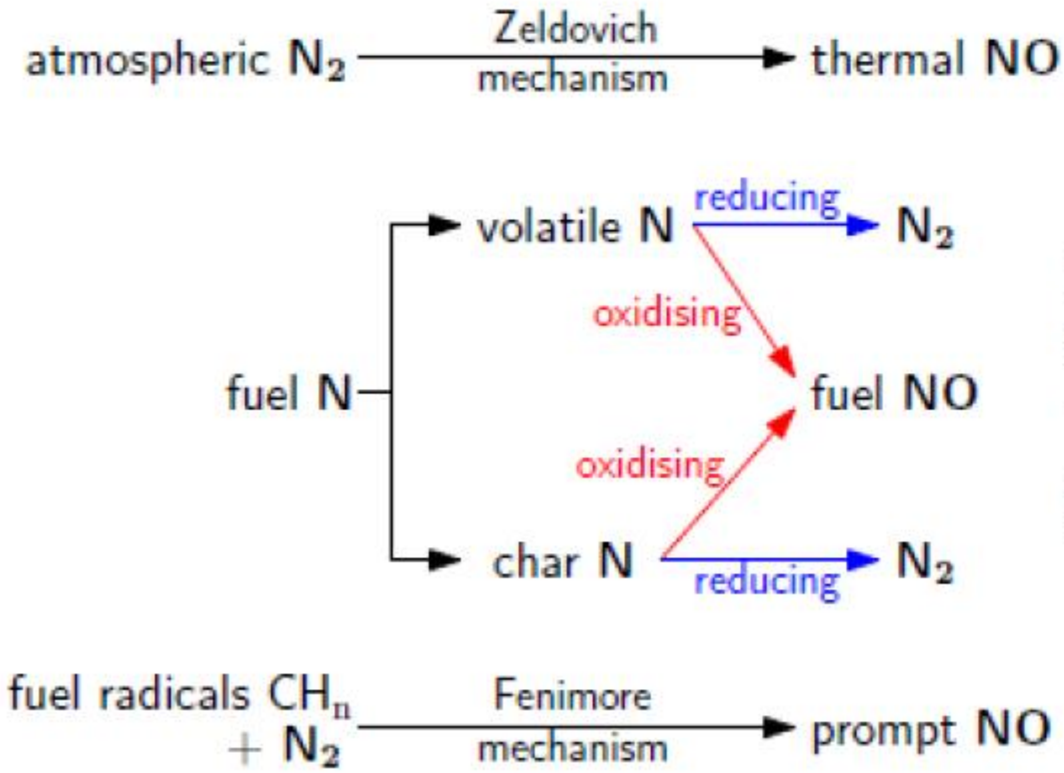
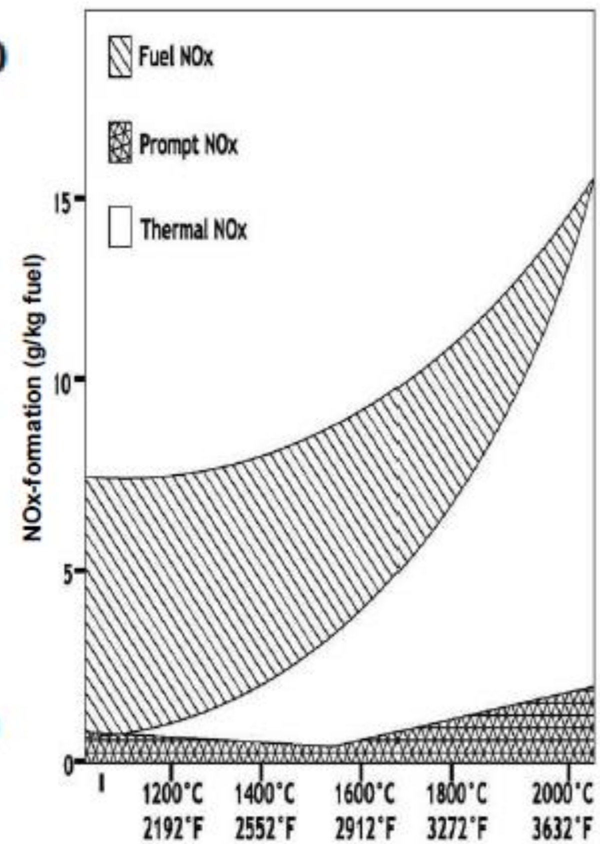
THE MAIN BURNER AND THE NITROGEN OXYDES



- In the **main burner**, the primary combustion air (about 10% of total combustion air) is split in at least two main flows: the **axial** air and the **swirl** air in order to control the flame shape and the burning zone position.
- **If <u>no</u> measures are adopted, nitrogen oxides (NO_x) from the combustion process can reach concentrations of 1200-1500mg/Nm^3 @ 10% O_2 at the stack.**

NO_x GENERATION MECHANISM





- **Almost all the NO_x generated is actually NO** (PM 30) and <u>not</u> NO_2 (PM 46), with an overestimation of mass concentration of 50%.

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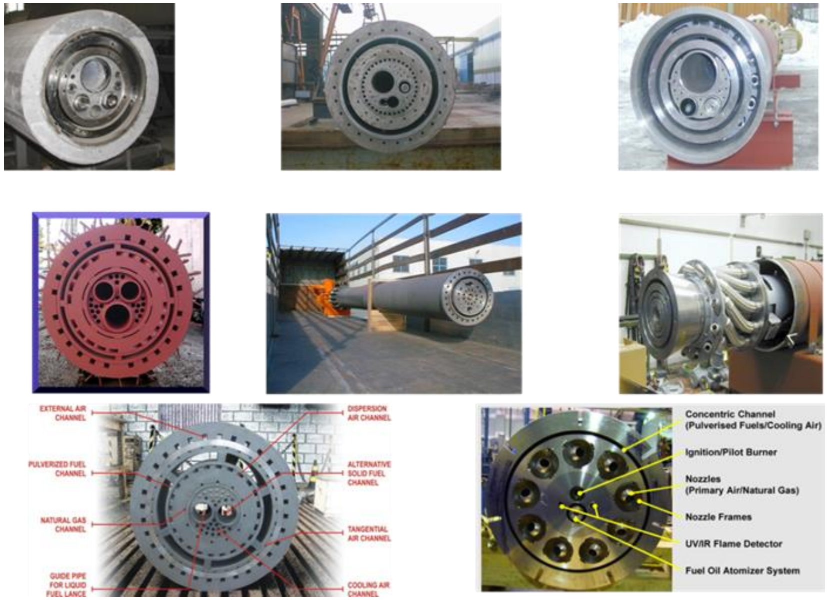
PRIMARY MEASURES TO REDUCE NO_x

Primary NO_x abatement technologies are designed to lower the peak temperatures inside the combustion zone in order to slow down the thermal NO_x formation process:

- **Flame cooling**: combustion of low-cal fuels with high water content, steam or water injection.
- **Low-NO_x burners**: flame profile is modified to lower peak temperatures inside the combustion zone.
- **Process optimisation**: stabilizing process conditions, lowering heat consumption, etc.
- **Mineralized clinker**: the use of mineralizers such as fluorine, reduces the heat needed in the sintering zone.
- **Staged combustion**: in pre-calciner kilns, fuel is injected in the pre-calciner in a reducing atmosphere. NO_x formed in the sintering section of the kiln, is reconverted into nitrogen.
- **Mid-kiln firing**: in long kilns lump fuel can be introduced half way the kiln creating a reducing atmosphere and herewith reducing NO_x formed in the main burner.

PRIMARY MEASURES TO REDUCE NO_x

- The primary measures techniques have strongly affected the **design of the main burner**.
- Also the **design of the pre-calciner** has been developed in order to minimize the NO_x formation with local reducing conditions, splitting the combustion air, the fuel and the raw feed.
- In many cases the best primary measure is the **use of alternative fuels**, mainly chopped tires.



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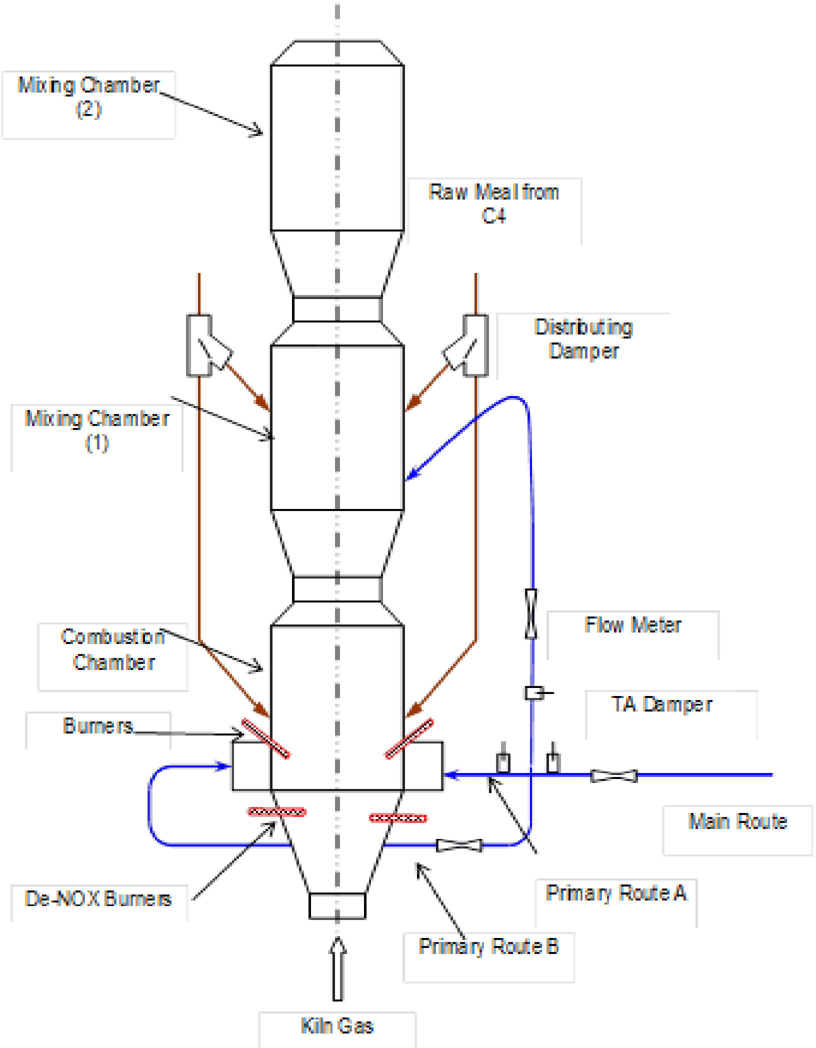
PRIMARY MEASURES AND THEIR LIMITS

- **The optimum conditions for NO_x prevention are frequently in conflict with the best setting for the kiln operations**.
- There are also limits to this approach mainly due to the formation of CO and SO_2 emissions.
- As a general rule, primary measures **cannot** guarantee the attainement of emission limits as low as $500 mg/Nm^3$ @10% O_2, daily average.



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SECONDARY MEASURES TO REDUCE NO_x

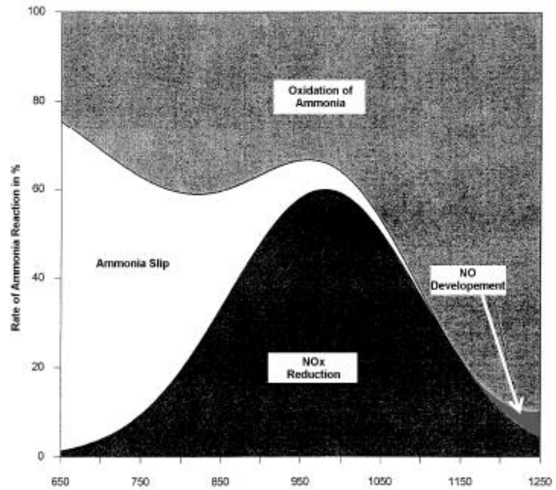
Secondary technologies are based on injection of a reducing agent (ammonia/urea) promoting NO_x destruction into nitrogen and water. This reaction can take place spontaneously at around 900°C, or at 300-350°C catalyzed by Ti and V oxides.

- SNCR (selective non-catalytic reduction): ammonia or urea is injected at temperatures zones inside the kiln of 900-1100°C, reducing NO_x without the help of a catalyst

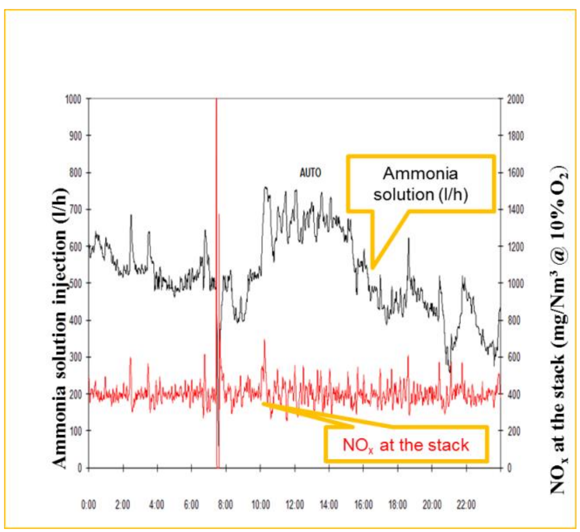
- SCR (selective catalytic reduction): NO_x reduction over a catalyst using ammonia or urea as reducing agent at kiln temperatures of 200-400°C

SECONDARY MEASURES: SNCR

- SNCR: 850 – 1.000°C



- residence time: > 2 sec.



- SNCR has been applied to almost all kinds of cement kilns, by injecting urea or ammonia solution where the best temperature window is located.
- The application of SNCR to the pre-calciner produces rather good results, provided that an even distribution of the reagent is realized and oxidizing conditions are guaranteed. In this case, ammonia performs better than urea.
- Levels below 350mg/Nm³ daily average can be attained. Values around 200mg/Nm³ have been reported in favorable conditions.

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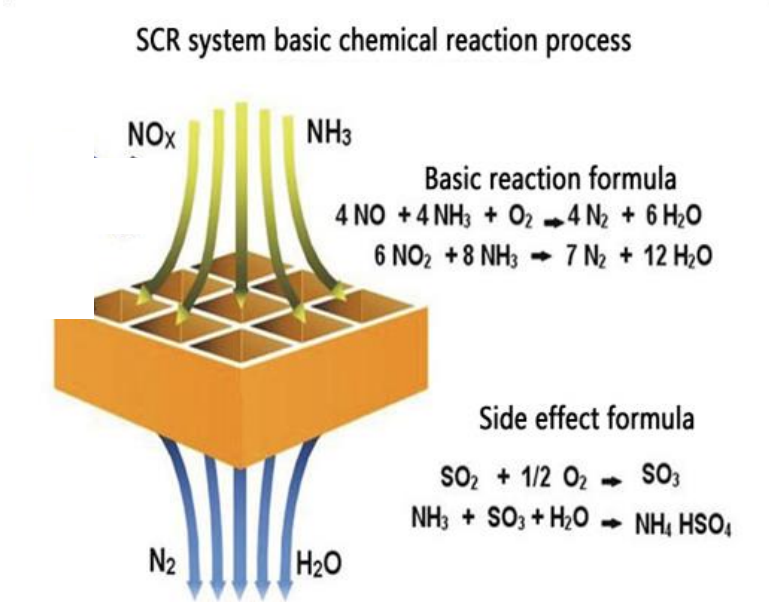
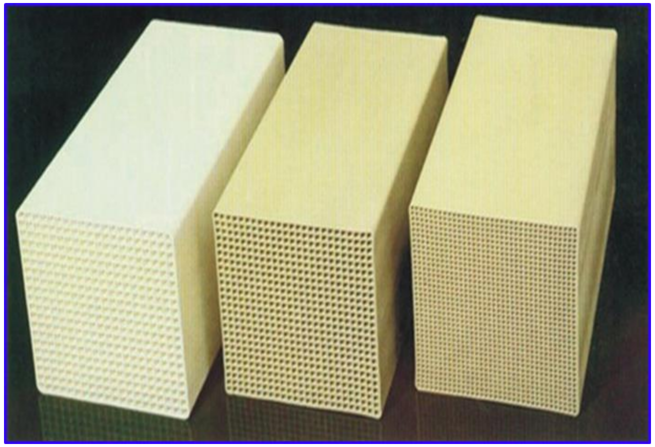
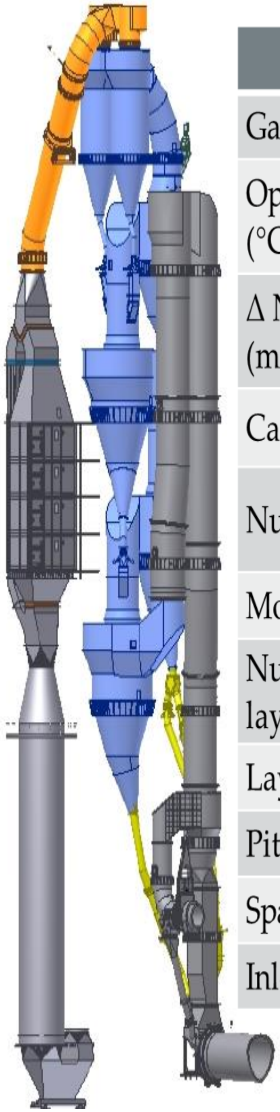
SECONDARY MEASURES: SCR



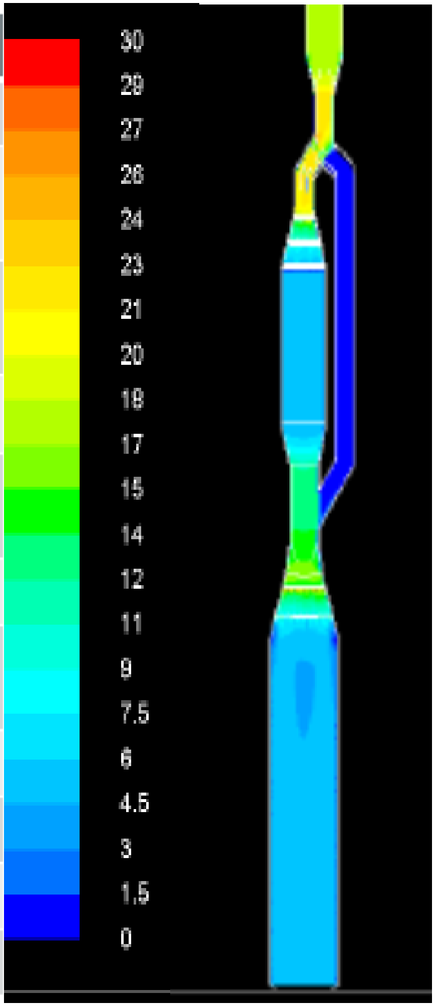


- Proven for other industrial sectors, SCR technology has very few applications in the clinker burning process in EU cement plants.
- TiO_2 and V_2O_5 catalyst bricks are put in contact with the kiln gases at ~300°C in which ammonia solution has been evaporated. Two or more layers of catalyst bricks are located after the pre-heater outlet (high-dust) or as a tail-end system after the process filter (low-dust).
- To prevent catalyst deactivation SO_2 concentration must be kept as low as possible.
- The catalyst life within 3-to-4 years or more, depending on local situations.

SECONDARY MEASURES: HIGH-DUST SCR



PARAMETER	VALUE
Gas Flowrate (Nm^3/h)	220.000
Operating Temperature (°C)	295
Δ NOx Inlet- Outlet (mg/Nm^3, dry 10% O_2)	1.000
Catalyst Volume (m^3)	119
Number of layers	3 (active) + 1 (spare)
Module size (mm x mm)	1.930 x 960
Number of modules per layer	16
Layer Heigth (mm)	1.300
Pitch size (mm)	11,4
Space velocity (h^{-1})	1849
Inlet buffle plates	YES



- In Rezzato cement plant (Italy) a high dust configuration has started with a new kiln line of 3000 tons per day.
- After 2.5 years of operation the efficiency remains unchanged.
- NO_x emission limit of 200mg/Nm^3 @10% O_2 daily average can be attained.

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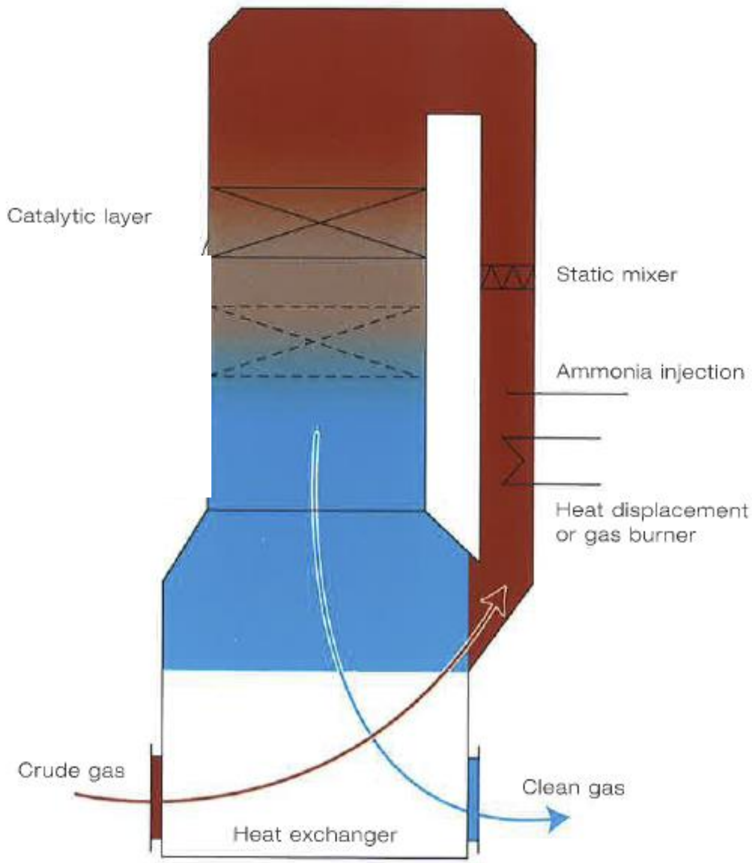
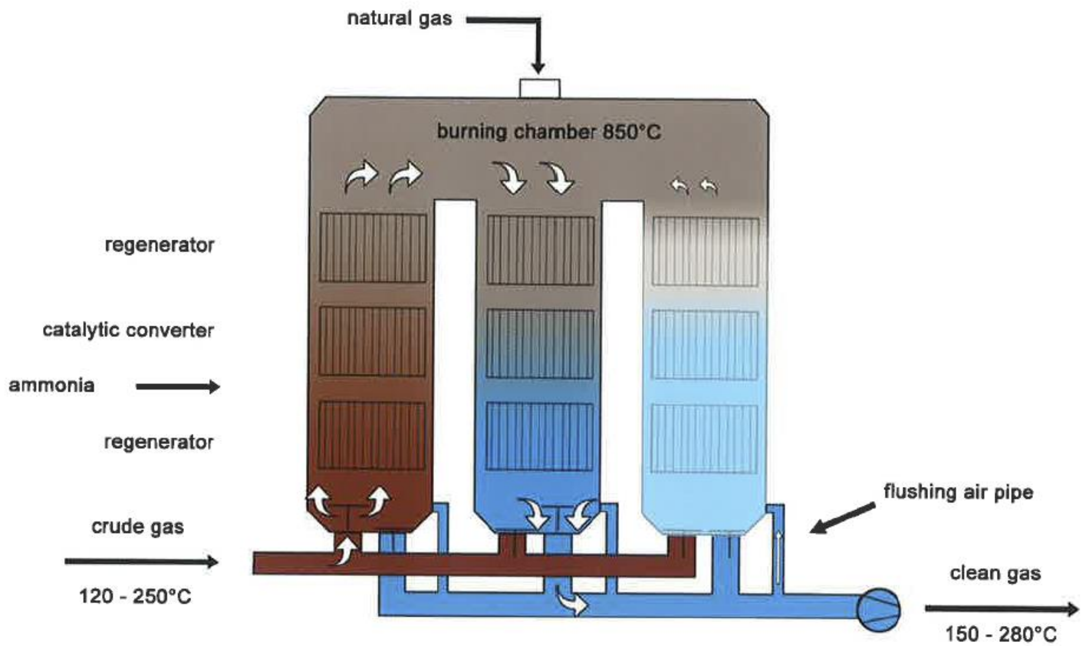
SECONDARY MEASURES: LOW-DUST SCR



Source: Scheuch

- In low-dust SCR the gas stream has to be reheated with a heat exchanger where in a first passage the temperature is increased to 300°C, and then, in a second passage in the same heat exchanger, the heat is given back to the incoming gas.
- The thermal energy losses are compensated recovering heat from the pre-heater gases, or from cooler vent air, or from a dedicated burner, using gas.
- The efficiency of the system is the same as for high-dust SCR, with the important advantage to prevent any possible risk of plugging the catalyst.
- A longer catalyst life is also expected. The total investment is quite higher.

SCR AND REGENERATIVE THERMAL OXIDIZERS (RTO)



Source: Scheuch

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- When NO_x is associated with high emissions of CO and organics it is possible to operate the reduction of both in a system which substantially put together the low-dust SCR and the RTO technologies in a system where the gas is heated first up to 350°C for the abatement of NO_x, and then to 850°C to oxidize CO and organics.
- The sensible heat is recovered in a regenerator before the gas leaves the system. Then the gas flow is inverted. When the concentration of CO and organics is higher than 4000 ppm the generated heat is enough to compensate the heat loss and the system is self-sustaining.

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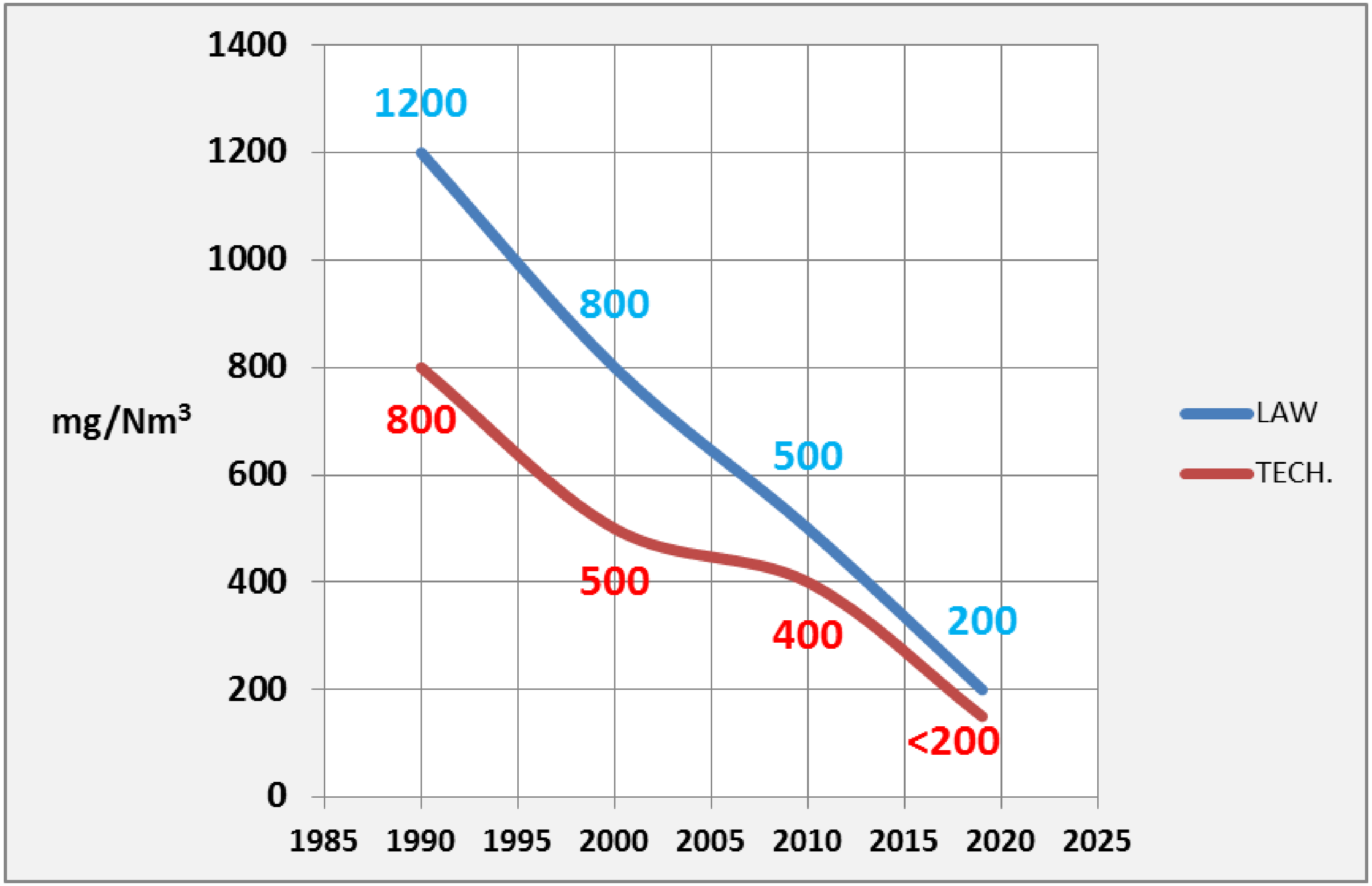
TECHNOLOGY PERFORMANCE AND LAW REQUIREMENTS FOR NO_X



ABATEMENT POTENTIALS AND COSTS OF BAT IMPLEMENTATION

- The full BAT abatement potential of NO_x is about 250 kton compared to current emissions levels of approximately 400 kton.
- The current abatement cost of NO_x in the cement sector is, on average, 0.3 €/ton-clinker.
- Full enforcement of ‘upper-limit’ BAT will increase the average abatement costs to 0.7 €/ton-clinker.
- Further enforcement to ‘lower limit’ BAT will increase the average abatement costs to 0.9 €/ton-clinker.

Source: 2009 Ecofys/Emission Care - The ETS paradox Emissions trading for industrial NO_x and SO_2 in the EU: consequences for the European cement sector

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ABATEMENT COSTS SHOW A SUBSTANTIAL SPREAD AMONG INDIVIDUAL INSTALLATIONS

Table. NO_x abatement costs in the EU cement sector

Abatement cost at various emission levels	NO_x [€/ton clinker]
Current emission level	0,3 (0,1 – 1,7)
Upper BAT emission level	0,7 (0,1 – 2,9)
Lower BAT emission level	0,9 (0,2 – 3,7)

Numbers between brackets indicate cost range at the individual plant level.

Note: It should be noted, that in the investment practice of cement firms, shorter depreciation periods and higher discount rates may be used instead of the ones applied here. This would result in higher cost estimates at the individual plant level than shown in the Table.

<u>Source</u>: 2009 Ecofys/Emission Care - The ETS paradox Emissions trading for industrial NO_x and SO_2 in the EU: consequences for the European cement sector

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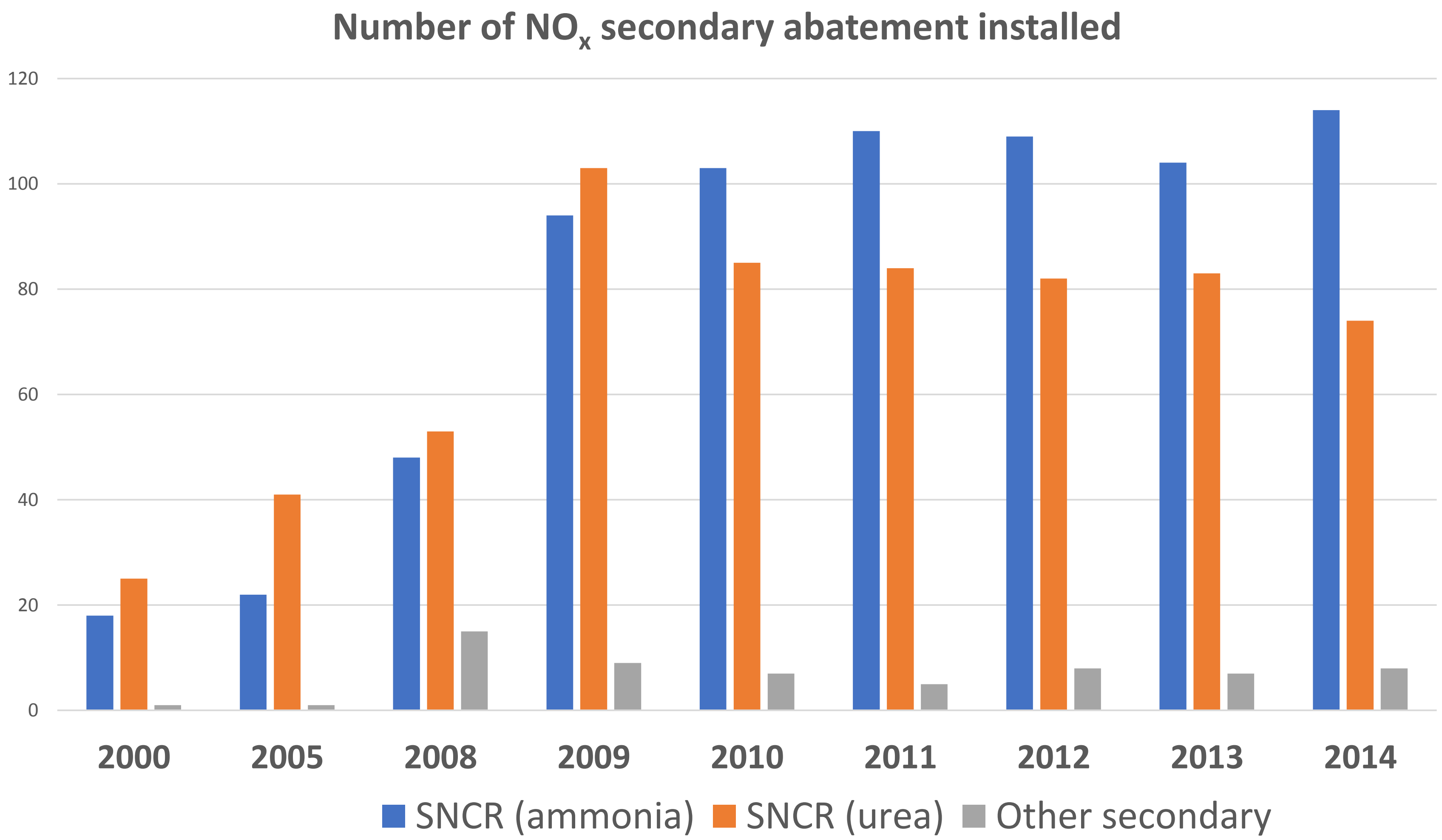
NO_x secondary abatement in the EU cement sector



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FINAL CONSIDERATIONS

- The progress in the emission control technologies is continuous and relevant, sometimes in terms of reliability and cost reduction, sometimes in terms of higher efficiency in the pollutants abatement.
- The main driver of this trend is the commitment of the whole cement sector for the reduction of the environmental footprint, not only in the most industrialized countries but also – and mainly – in developing countries, transferring the most modern technologies for environmental protection.
- Under the increasing demand for efficiency (low heat and energy consumption, high substitution rate of conventional fuels and raw materials) as well as the progressive reduction of the emission limits, now very close to BAT, the old burning lines will be replaced (and more and more in the near future) by new modern units, maybe opening the way to Carbon Capture technologies.

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