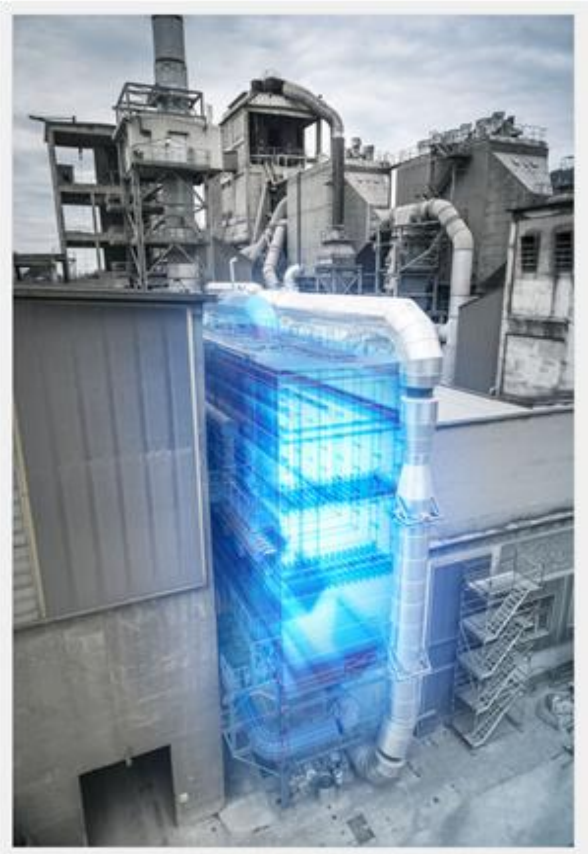
Reduction of NOx, CO and Organic Compounds in a Cement Plants with the DeCONOx Technology

Workshop: Organic Pollutants Emission Control for Co-incineration in Cement Kilns

Tsinghua University, 12.09.2019



World's first DeCONOx plant at Kirchdorfer Zement

Waltisberg Consulting

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A Brief Look to Germany

- Starting in 2019, the German government will lower the daily limit value for nitrogen oxide (NOx) to 200 [mg/m^3_N].
- Of the 35 German cement plants with clinker production
  Haegermann, B. (2018): NOx Abatement in the German Cement Industry. International VDZ Congress, Düsseldorf, 26.-28.9.2018.
  - 19 use SCR technology, with nine SCR plants already in operation and a further ten in the planning stage. Three of them are or will be equipped with DeCONOx or AutoNOx (as of March 2019).
    AutoNOx = Competitive process of DeCONOx
  - Eleven systems, eight of them with calciner, are (still) practicing SNCR.
  - The development of four plants is not (yet) known.
  - One plant relies exclusively on primary measures (no SNCR/SCR)
- Additionally emissions of organic compounds are also being discussed, especially in connection with waste-based fuels and raw materials.

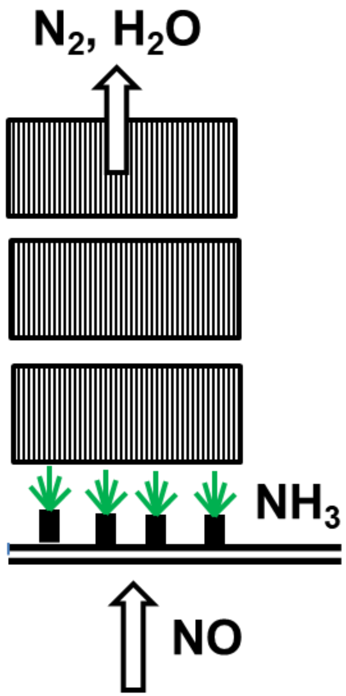
DeCONOx
→ Reduction of CO (and organic compounds) and NOx

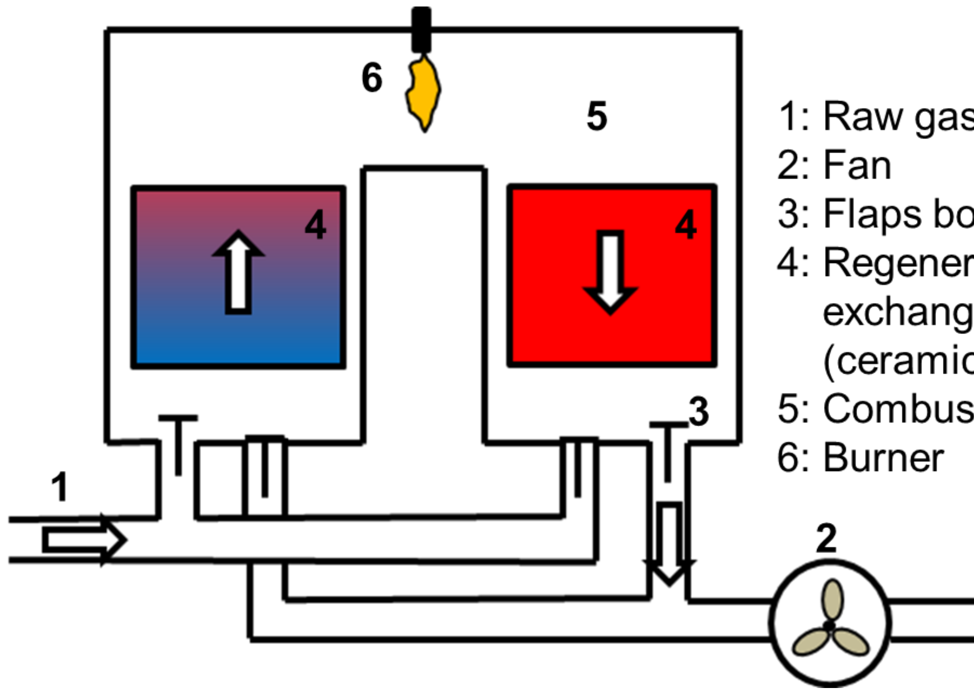
Reduction of Carbon Monoxide (CO)
and
of Organic Compounds

Reduction of Nitrogen Oxides
NOx

A combination between a **RTO** (Regenerative Thermal Oxidizer)
and
a **«Low Dust» SCR** (Selective Catalytic Reduction)

Combination SCR + RTO





1: Raw gas inlet
2: Fan
3: Flaps box with lift flaps
4: Regenerative heat exchanger beds (ceramic honeycomb)
5: Combustion chamber
6: Burner

SCR

Catalytic Reduction of NO

$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$

RTO

Heating up in Regenerator (left)

Oxidation of CO and VOC > 850 [° C]

Cooling of the gases in regenerator (right)

Reversal of the flow by flaps

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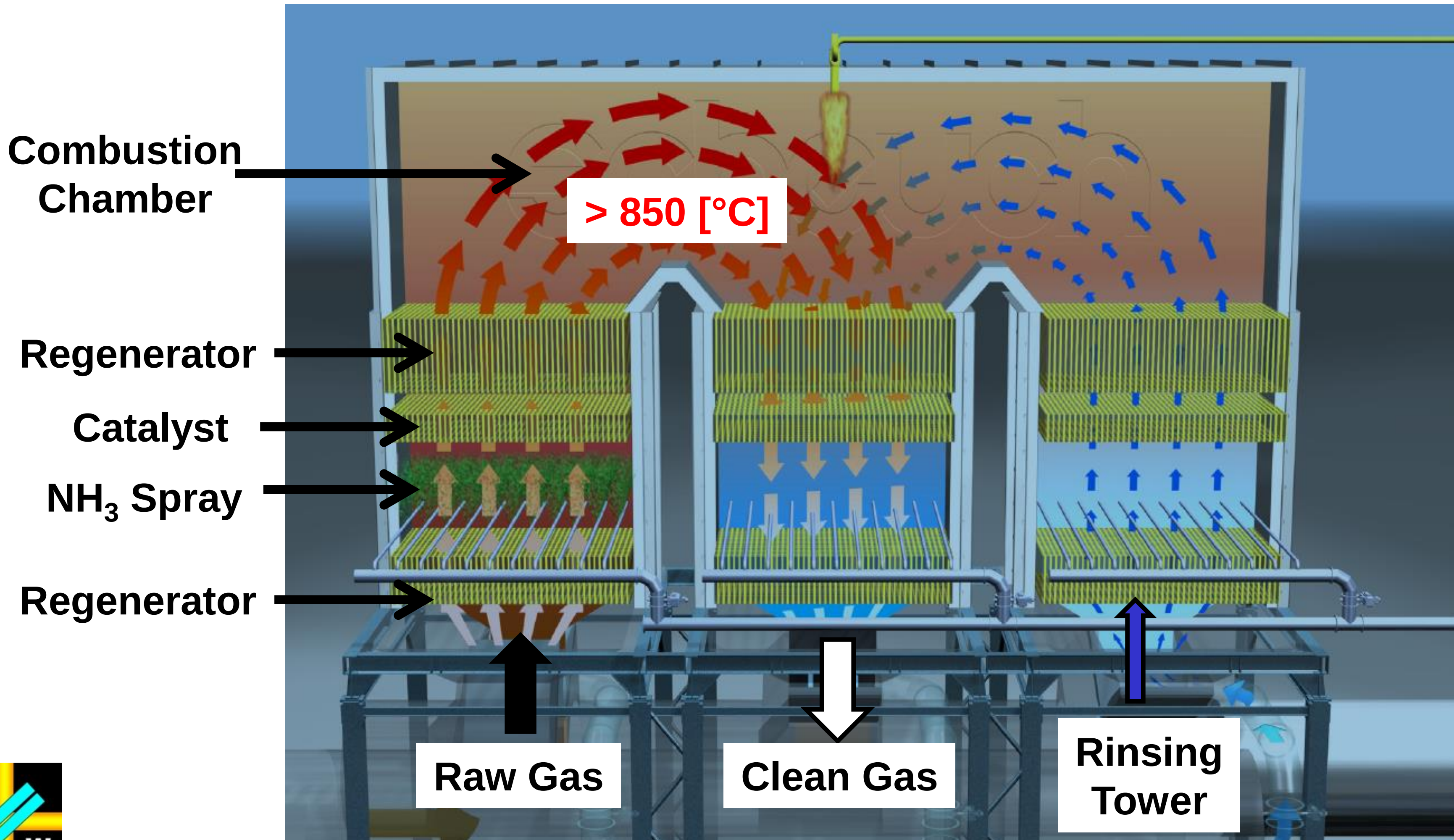
Structure of the DeCONOx System



Scheuch GmbH

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First DeCONOX System Worldwide

First DeCONOX at Kirchdorfer Zement, Austria
built by Scheuch GmbH, 4971 Aurolzmünster, Austria

Design Data:

- Installation «End of Tail»
- Clinker Production: 1'500 [t/d]
- Cement Production: 500'000 [t/year]
- Flow: 151'000 [m^3_N/h]
- Alternative Fuels: 91 [%] (2016)
  (Waste tires and recovered wastes from trade and industry)
- Temperature: 120 [°C] – 220 [°C] (Exit Filter)
- Dust: < 5 [mg/m³]

Very limited
space conditions

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Kirchdorfer Zement (Austria)

Target for DeCONOx

(m^3_N: 1013 [mbar], 0 [°C], dry, 10 [%] Oxygen)

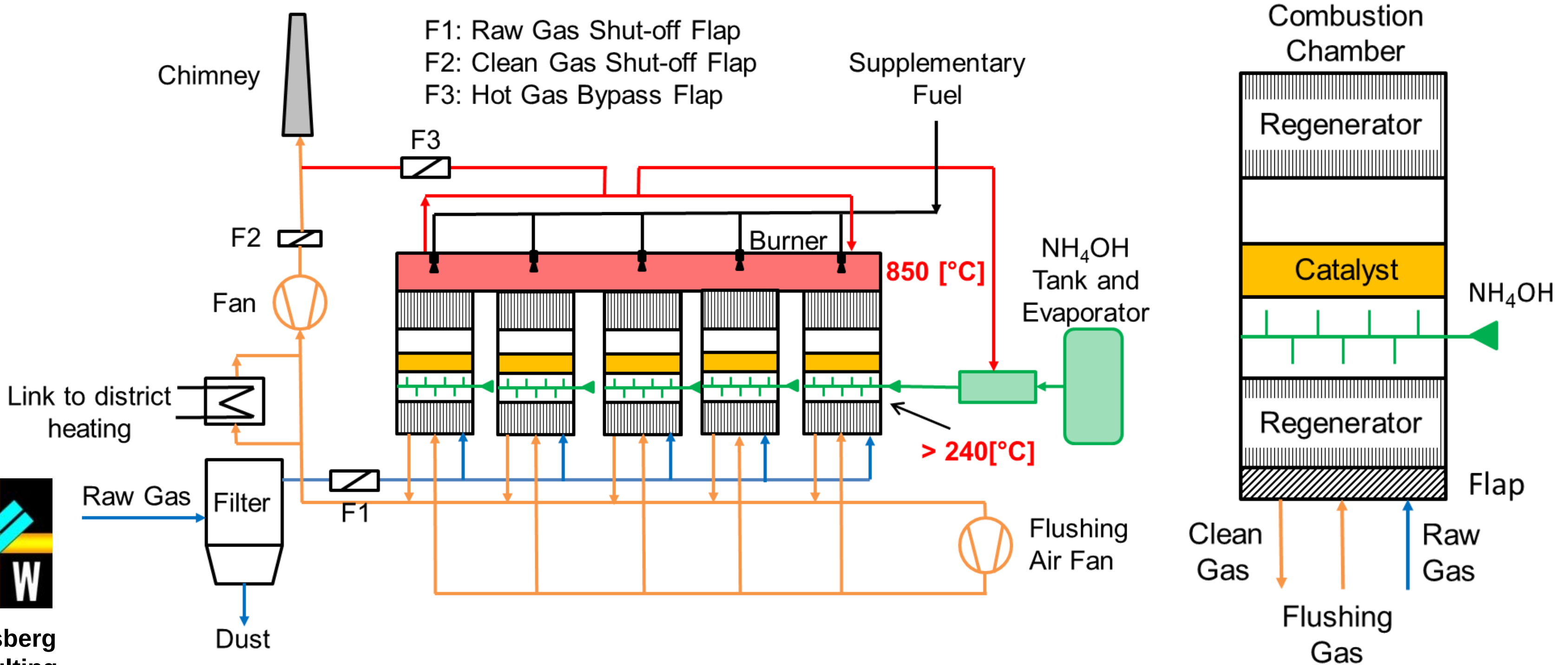
- < 200 [mg/m^3_N] NOx
- < 20 [mg/m^3_N] NH_3
- < 10 [mg/m^3_N] VOC (Volatile Organic Compounds)
- > 99% reduction of CO; max. 100 [mg/m^3_N]

Special Carbon Monoxide Situation

- 2006: Installation of an inline calciner with tertiary air
  Reason: Increase in clinker production and increase in alternative fuels
  Problem: Carbon monoxide (CO) increases to 6'000 - 8'000 [mg/m^3] and the volatile organic compound (VOC) up to 60/70 [mg/m^3]
  My opinion: The calciner is a faulty construction and can burn the required amounts of alternative fuels only insufficient.
- 2007: Begin of test with DeCONOx-pilot plant
- 2014: Installation of a full-scale DECONOx plant by Scheuch

The Installation in Kirchdorf

- The plant has five reactors, two with raw gas and two with clean gas. In order to avoid the peaks in raw gas concentration that occur during the switching cycles, the fifth reactor is flushed with air and the incompletely converted waste gas is transported to the combustion chamber where it is burnt.
- The plant is operated under negative pressure.



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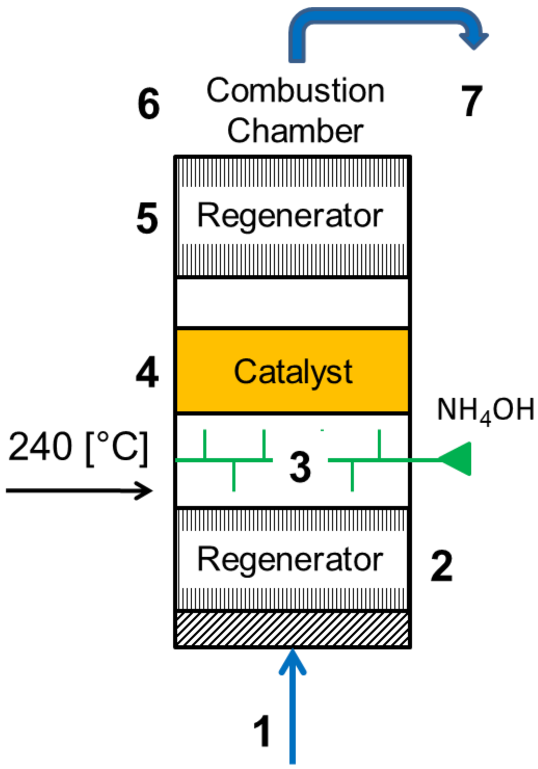
The Installation in Kirchdorf



1. A fan with about 700 [kW] draws the exhaust gas (150'000 [m^3/h] through the DeCONOx plant; Inlet temperature: ~ 130 [°C]
   Each individual reactor has pneumatically operating flaps
2. The raw gas first flows through the lower regenerator layer and is heated up to the catalyst inlet temperature of 240 [°C]
3. Intermediate Space: Input of ammonia water; 25 [%], 30-300 [l/h] (Pre-evaporation of the NH_3 solution with heat from the combustion chamber, mixture reached optimal temperature of ~ 400 [°C])
4. SCR-Catalyst → Reduction of NOx
   Catalyst: TiO_2 matrix with V_2O_5 and WO_3, 50 [m^3] in 5 towers, Free space ~ 63 [%]

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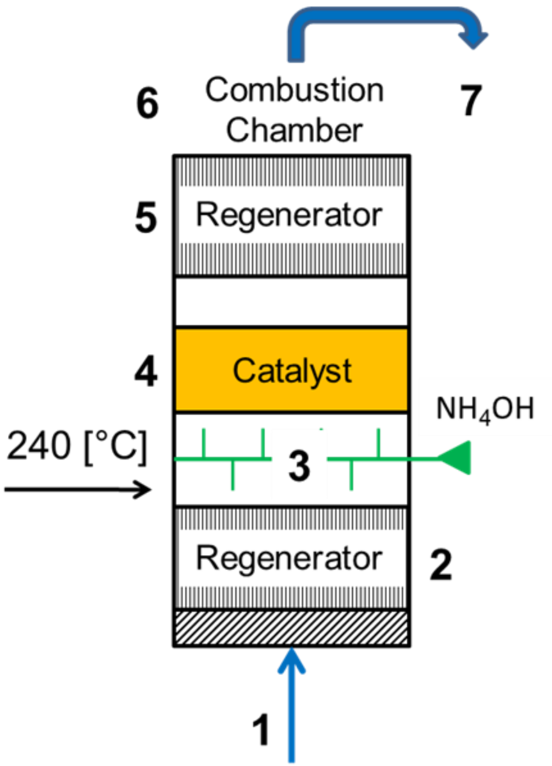
The Installation in Kirchdorf



5. Intermediate layer and upper regenerator: Raises the gas temperature up to 850 [°C]
6. Combustion chamber located above the five towers; temperature at least 850 [°C] → , fullest possible oxidation of CO and organic compounds
7. Heat dissipation in neighboring tower and heat-up of this tower.
   The clean gas leaves the DeCONOx plant with a temperature of ~160 °C and is therefore ~ 30 [°C] warmer as the raw gas flowing into the DeCONOx.
   The clean gas is now fed to a tube bundle heat exchanger with a capacity of 5.3 [MW] → Exit temperature 110 [°C].

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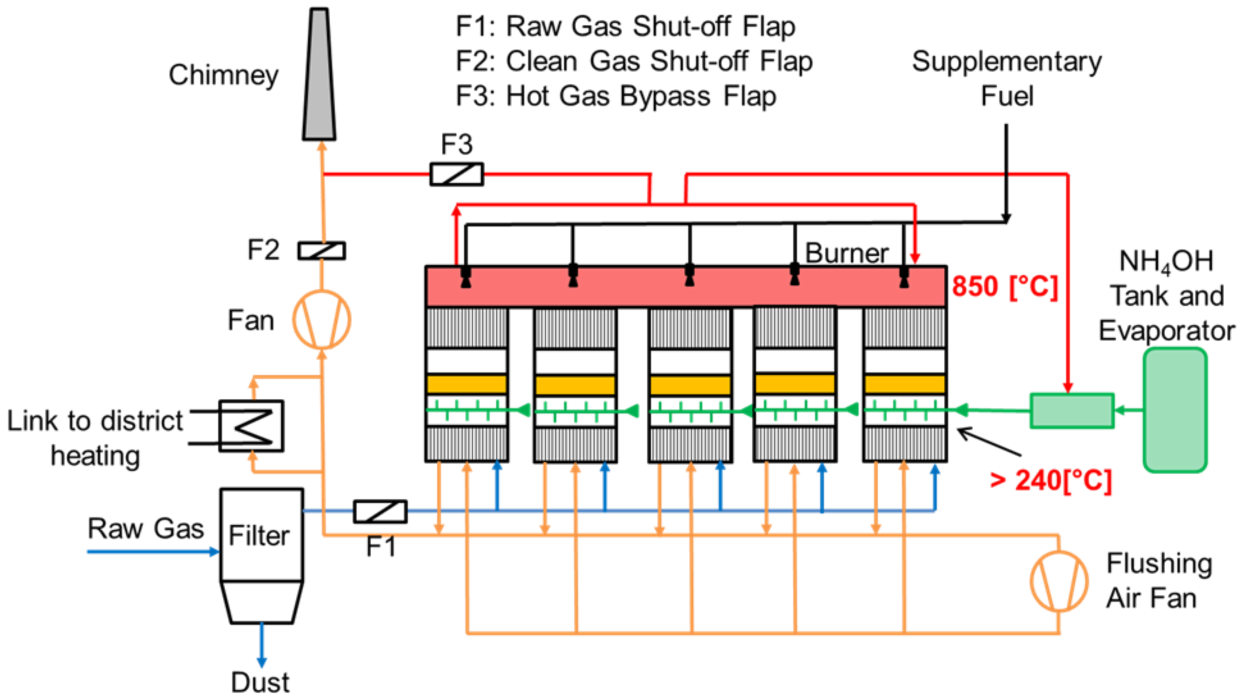
The Installation in Kirchdorf

- Start-up: Natural gas and fresh air; 6 to 12 [h] to heat up; maximum heat-up rate of 6 [°C/min]
- An auto thermal operation of the DeCONOx system without additional fuels is possible under the given plant conditions a CO concentration in the exhaust gas of about 6'000 [mg/m^3] (normal conditions, actual oxygen) to be treated.



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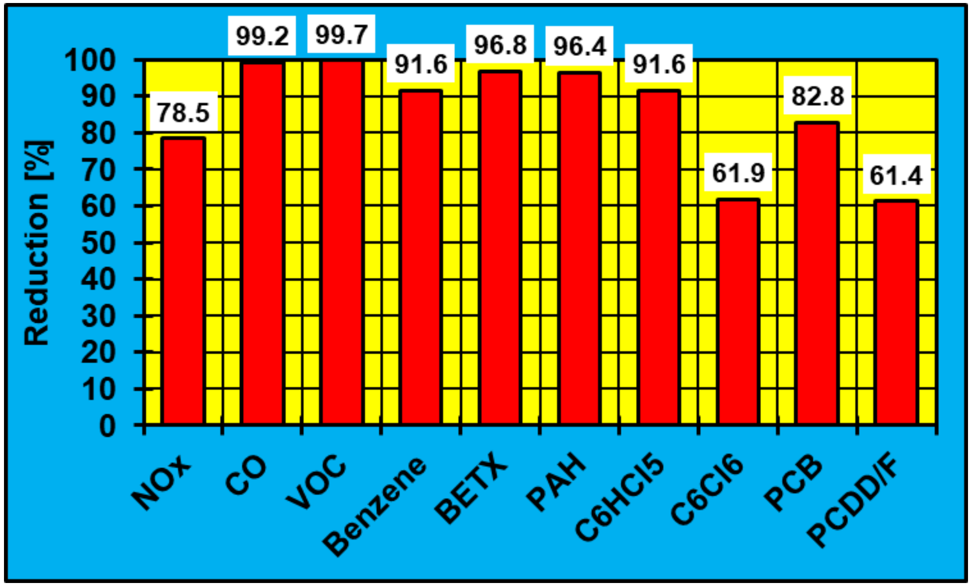
Emissions 2017

- Values = Yearly average 2017 in [mg/m³] (1013 [mbar], 0 [°C], dry, 10 [%] oxygen)
- Limits = Daily Averages; 389th Ordinance: Waste Incineration - Collective Ordinance of October 25, 2002 or Approval Notice: AUWR-2006- 7/936-Wi and AUWR-2006-7/689-Wi

	Limit	Average 2017	Remark
Dust	15	0.7	Fabric Filter
NOx	400	149	
SO_2	180	1	No influence from DeCONOx
NH_3	30	4	
VOC	50	0	Below detection limit (1 [mg/m³])
Benzene	?	< 0.2	Calculated from reduction rate
CO	---	63	04.03.2016 – 31.07.2017
PCDD/F	0.1	0.0006	in [ngTE/m³]

Reduction of NOx, CO and Aromatic Compound

- NOx, CO and VOC: Average of continuous measurement between the 04th March 2016 and the 31st July 2017
  Other compounds: Average of three measurements
- The concentration of the components of the components PAH, C_6HCl_5, C_6Cl_6, PCD and PCDD/F is therefore low and their measurement has a greater uncertainty. In any case the reduction rate is in any case > 60 to 70 [%].



VOC	Volatile Organic Compounds
BETX	Benzene, Ethyl Benzene, Toluene, Xylene
PAH	Polycyclic aromatic hydrocarbons
C_6HCl_5	Pentachlorobenzene
C_6Cl_6	Hexachlorobenzene
PCB	Polychlorinated biphenyls
PCDD/F	«Dioxins and Furans» Dibenzo-p-dioxins and Dibenzofurans

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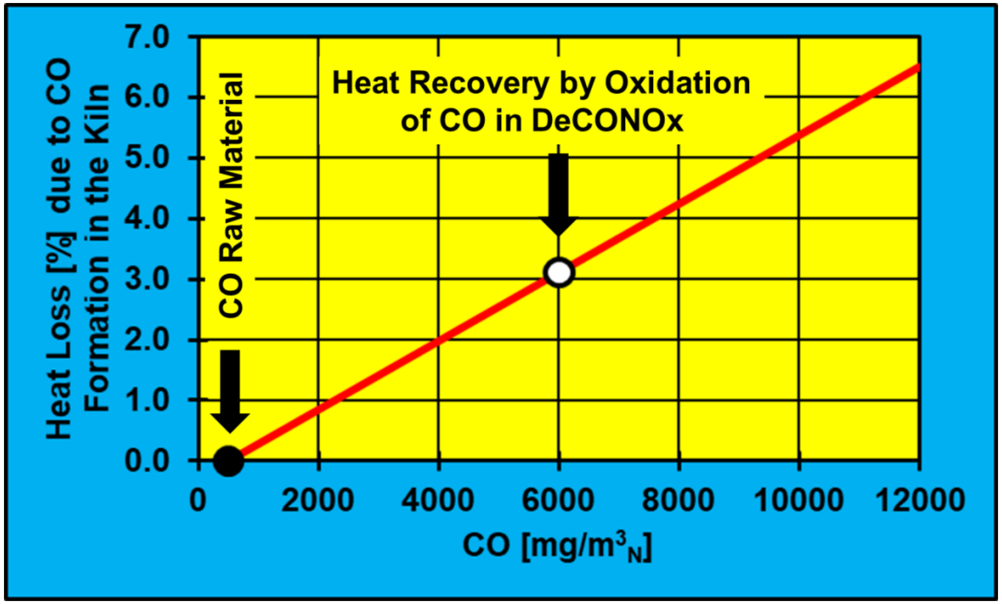
Auto Thermal Operation

Auto thermal operation from 6’000 [mg/m^3] CO on (Normal conditions, wet, actual oxygen)

- This CO content must at least be produced in the kiln, otherwise heat must be supplied to the DeCONOx system
- Calculation for a CO input of 6’000 [mg/m^3] at inlet DeCONOx required fuel
  - Assumptions for the calculations:
    (Detailed data of the Kirchdorf kiln are unknown)
    - Production: 1’500[t Clinker/day]
    - Heat consumption of the kiln: 3.9 [MJ/kg Clinker]
      (Average of German kilns 2017, value of Kirchdorf kiln: unknown)
    - The origin of 500 [mg/m^3] CO is the raw material (assumption) and not the fuel(s). The rest is produced from fuel(s) secondarily in the calciner (incomplete combustion).

Heat Loss by CO in the Combustion

- The incomplete combustion increases the total heat consumption of the kiln.
- CO from the raw material (here 500 [mg/m^3_N]) has no influence on heat consumption of the kiln.
- DeCONOx: Heat recovery by oxidation of CO (~ 3.1 [%]) of total heat consumption. CO will be completely oxidized
- CO will be completely oxidized
  - CO > 6000 [mg/m^3_N] → Some heat must be dissipated
  - CO < 6000 [mg/m^3_N] → Some heat must be added



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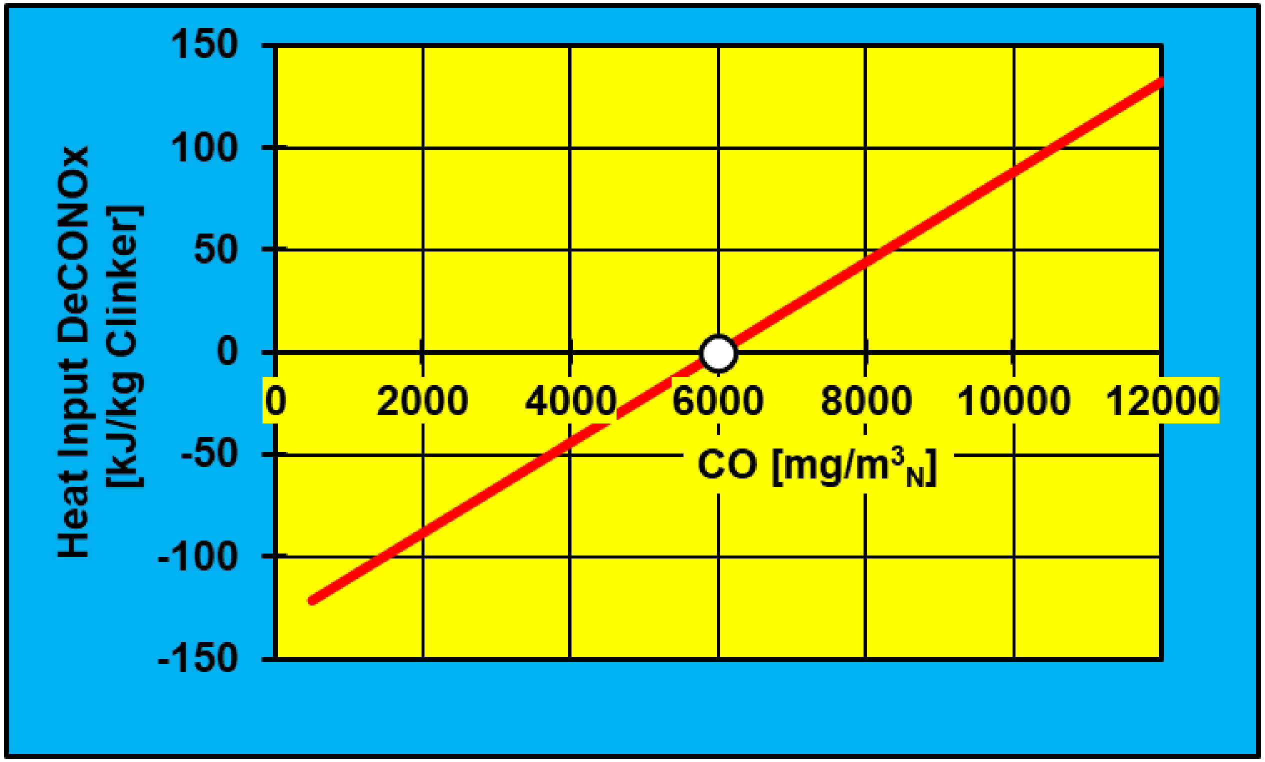
Operation of DeCONOx



Heat surplus due to CO oxidation
(Heat must be dissipated)

Heat deficit due to CO oxidation
(“Clean" fuel must be added)

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Some Additional Information

- Acquisition costs: 7.3 million Euros
- Additional electrical energy requirement: 8 [kWh/t Clinker].
- Information from the plant: Additional heat (“clean” fuel, gas) negligible
  (Remark. CO content of gas from the kiln exceeds 6000 [mg/m^3_N])
- NOx reduction: 80 [l/h] aqueous ammonia solution for a reduction from 600 to 140 [mg/m^3_N]
  (1013 [mbar], 0 [°C], dry, 10 [%] oxygen)

My Statement to this System

- Advantage of DeCONOx against a pure SCR Systems:
  - SCR systems partially reduce organic compounds, but the efficiency is lower. This is the big advantage of this system. It reduces these compounds thermally almost completely, i.e. down to the trace level.
  - A pure SCR system do not reduce carbon monoxide (CO).

- Waste-based Fuels
  - Organic emissions of waste-based fuels are eliminated in the DeCONOx system and even raw materials with organic compounds can be used.
  - The “poor combustion" of waste-based fuels can be lucrative, because more cheap fuels or even fuels for which one still receives disposal fees can be used.
  - A poor combustion in secondary firing can also have negative effects. For example, sulfur may have a higher volatility in the secondary combustion area, leading to additional emissions from this area and problems in the catalytic converters. In Kirchdorf it seems that sulfur is not a problem, but in other places it can lead to problems.
  - With such a plant one must consider therefore exactly whether one wants to operate auto thermally, i.e. with CO generation by the combustion, or with “clean” fuel.

Literature

The information contained in this presentation can be found in the literature references listed below.

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Kirchdorf Cement – The cement plant with the lowest emissions in the world
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Innovative SCR Technologies for NOx – VOC – CO – ODOR – Reduction
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