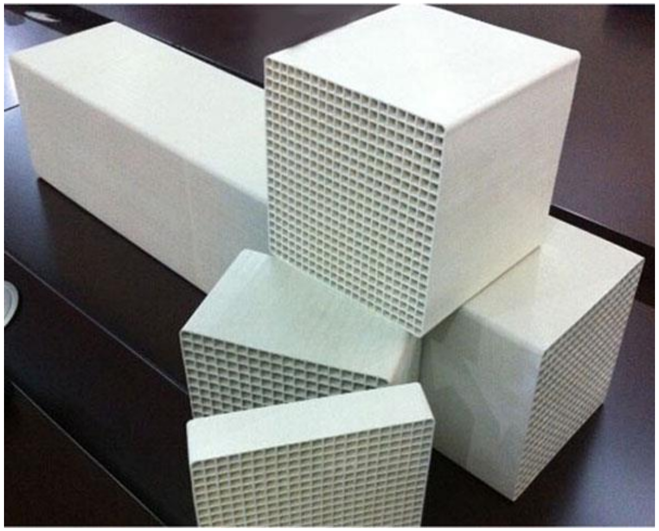
Reduction of NOx Emission in Cement Plants with the SCR Technology

(Selective Catalytic Reduction)

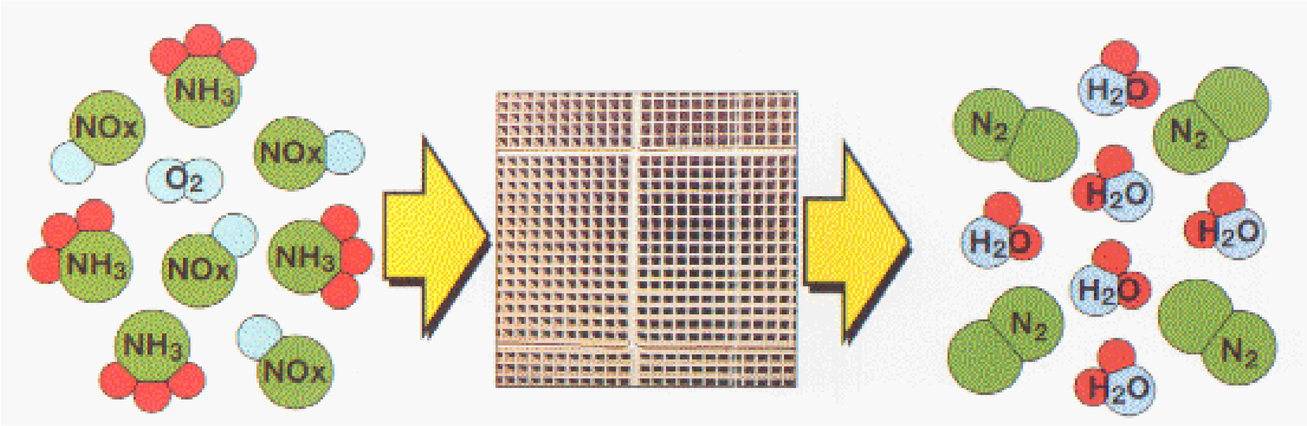


Waltisberg Consulting

Josef Waltisberg
dipl.Ing. ETH
Eichhaldenweg 23
CH-5113 Holderbank / Switzerland
josef@waltisberg.com

Selective Catalytic Reduction

1.) Reduction of Nitrogen Oxides (NOx) with the help of a Catalyst



2.) Reduction of other Exhaust Gas Components on the same Catalyst

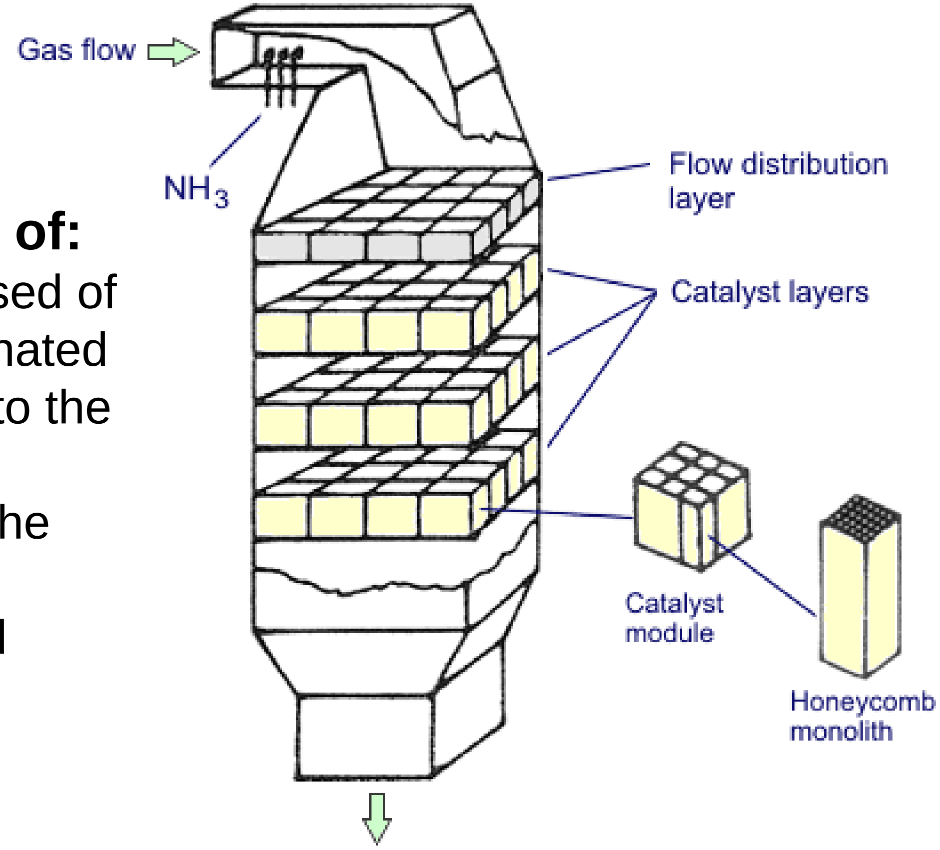
(e.g. NH_3, CO, VOC, PAH, PCB, «Dioxins»)

Waltisberg Consulting

Catalysts

The Catalyst used in SCR Applications usually consists of:

- a monolithic honeycomb composed of a ceramic substrate with impregnated catalyst homogenously mixed into the catalyst material; or
- catalyst materials deposited on the surfaces of a ceramic substrate supported on a flat or corrugated plate.



Waltisberg Consulting

Catalysts

The Metal Oxides

- The metal oxide acts as a porous base with a high surface area-to-volume ratio created by the presence of microscopic pores within the metal oxide base. On this metal oxide base, typically titanium dioxide (TiO_2), one or more metal oxide catalysts are deposited in various concentrations. In SCR applications, the active catalyst material typically consists of vanadium pentoxide (V_2O_5), tungsten trioxide (WO_3), and molybdenum trioxide (MoO_3) in various combinations.

Tailored Composition

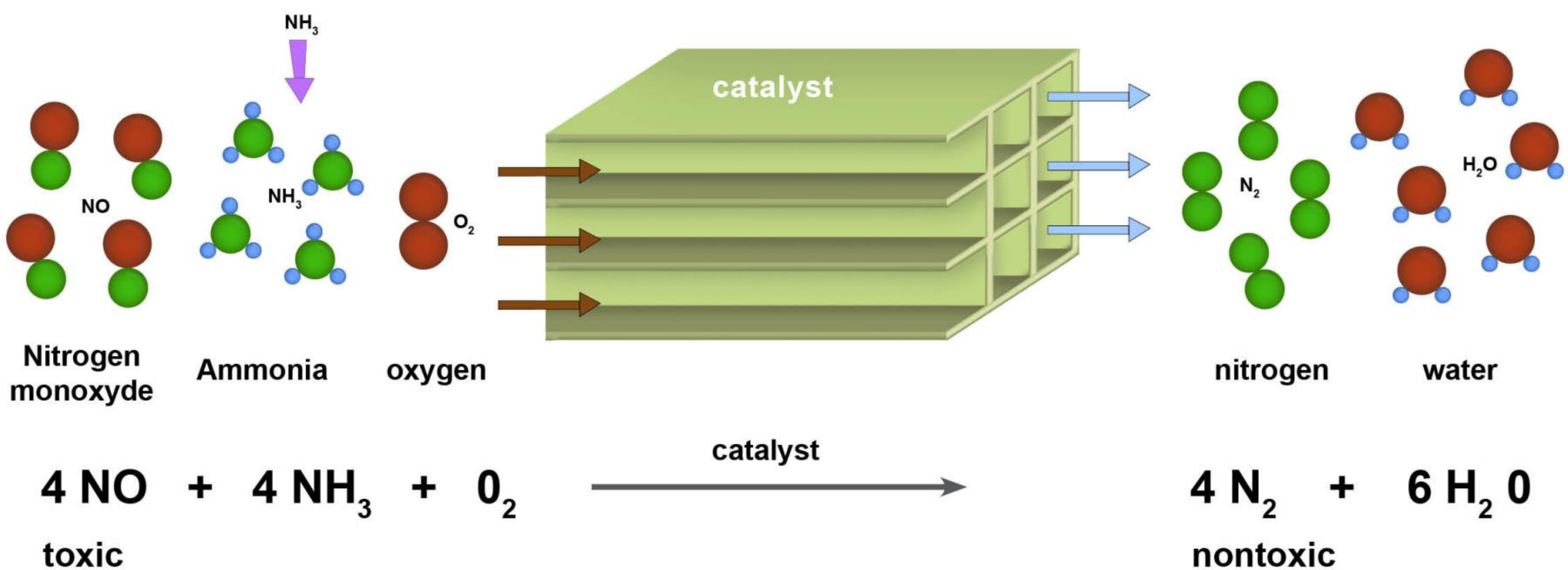
- The composition, also known as formulation, is tailored by the catalyst vendor to best suit a particular SCR application.
  - Some catalyst formulations are more reactive (typically those with higher V_2O_5contents)
  - Some limit SO_2 oxidation (typically those with higher WO_3 content and lower V_2O_5contents)

    $SO_2 + ½\ O_2 \rightarrow SO_3$
  - Some (such as those with higher MoO_3 contents) are less vulnerable to the poisoning effects of specific species (e.g. heavy metals; thallium) in the exhaust gas stream.

Waltisberg Consulting

Chemical Reactions on Catalyst

- **Main Reaction with NO (Equation 1):**
  NO and reagent ammonia (NH_3) react in the presence of a catalyst to molecular nitrogen (N_2) and water vapor (H_2O):
  $4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
  Ammonia must be stored in the micro-pores of the catalyst before NO is reduced. Since the catalyst elements store ammonia in their micro-pores to a certain extent, ammonia is not necessarily consumed immediately upon injection. Conversely the reaction can proceed for some time after discontinuing injection. The catalyst itself is not a reactant and is not consumed in the process.



Chemical Reaction on Catalyst

- **Reaction with NO_2 (Equations 2 and 3):**
  NO_2, present in very low concentration in cement exhaust gases (<< 5 [%] of NOx), is also reduced in a manner similar to the reduction of NO:
  $6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$
  $2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$

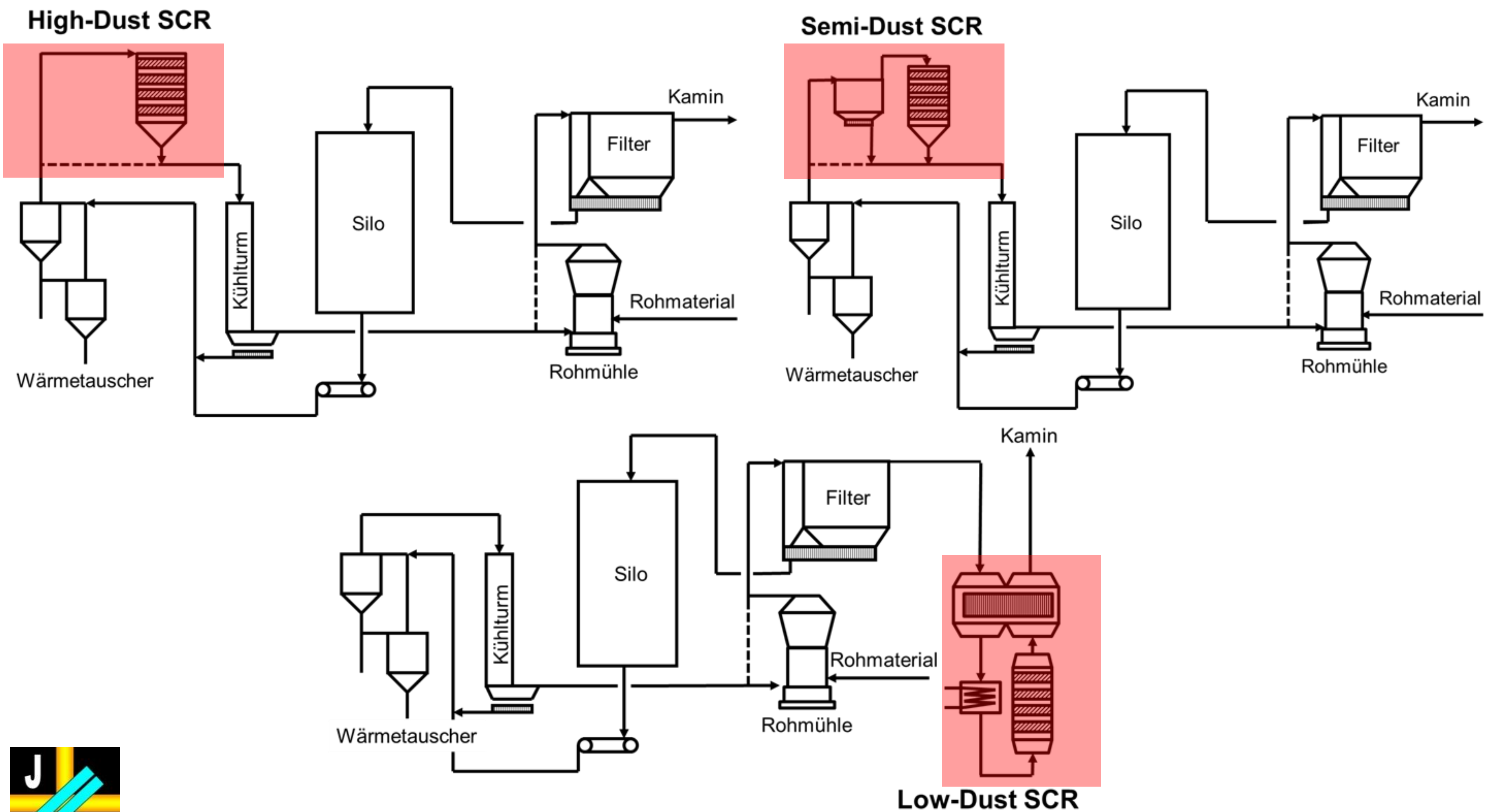
- **Reaction wit SO_2 (Equation 4):**
  Also a reaction with SO2 can occur
  $2\ SO_2 + O_2 \rightarrow 2\ SO_3$

- **Reaction with Volatile Organic Compounds VOC (Equation 5):**
  $4\ C_nH_m + (4n + m)\ O_2 \rightarrow 4n\ CO_2 + 2m\ H_2O$

- **Reaction with «Dioxins» (Equations 6 and 7):**
  $C_{12}H_nCl_{8-n}O_2 + (9 + 0.5n)\ O_2 \rightarrow (n - 4)\ H_2O + 12\ CO_2 + (8 - n)\ HCl$
  $C_{12}H_nCl_{8-n}O + (9.5 + 0.5n)\ O_2 \rightarrow (n - 4)\ H_2O + 12\ CO_2 + (8 - n)\ HCl$

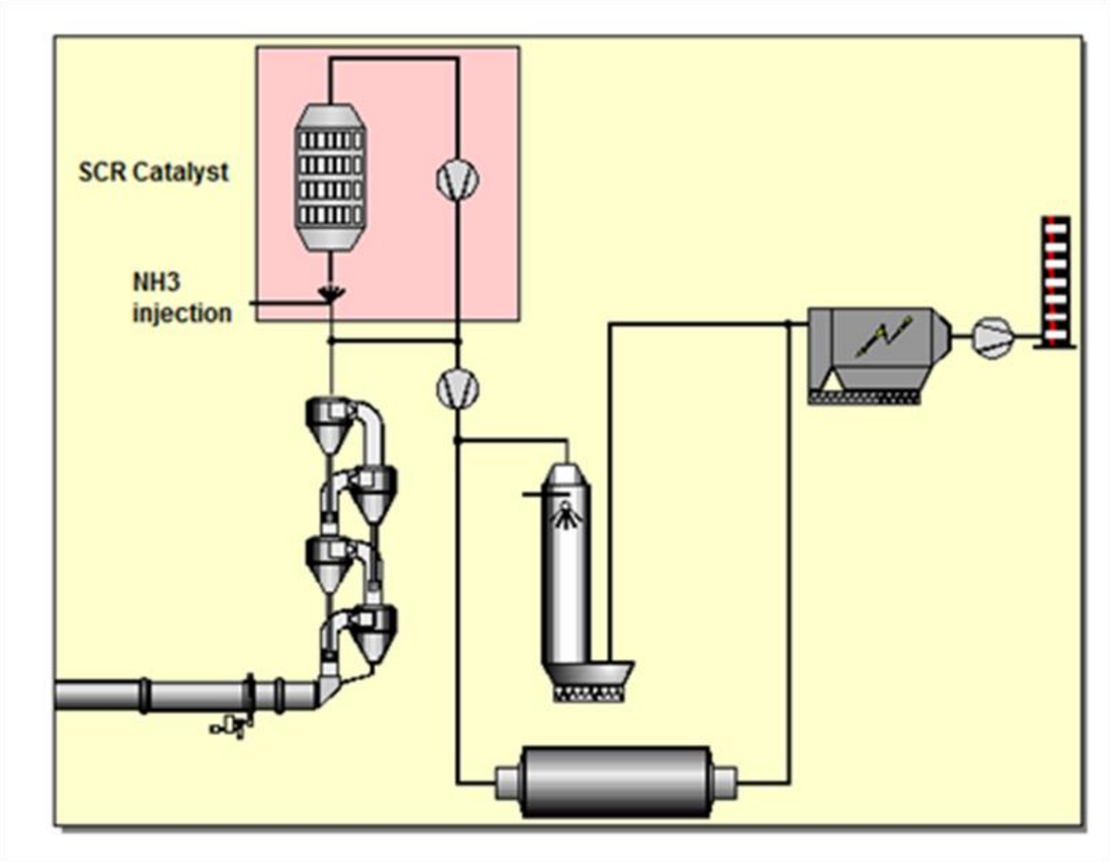
Waltisberg Consulting

Types of SCR Systems



Waltisberg Consulting

«High-Dust-» and « Semi-Dust» Solutions



Catalyst just behind the Preheater:

- High dust content (order of magnitude: 10 to 80 [g/m^3])
- Gas temperature more or less in the optimal range (300 to 350 [°C])

Examples:

- Solnhofner Portland Zement AG, Germany
- Cementeria di Mont Selice, Italy
- Schwenk Zement KG, Mergelstetten, Germany

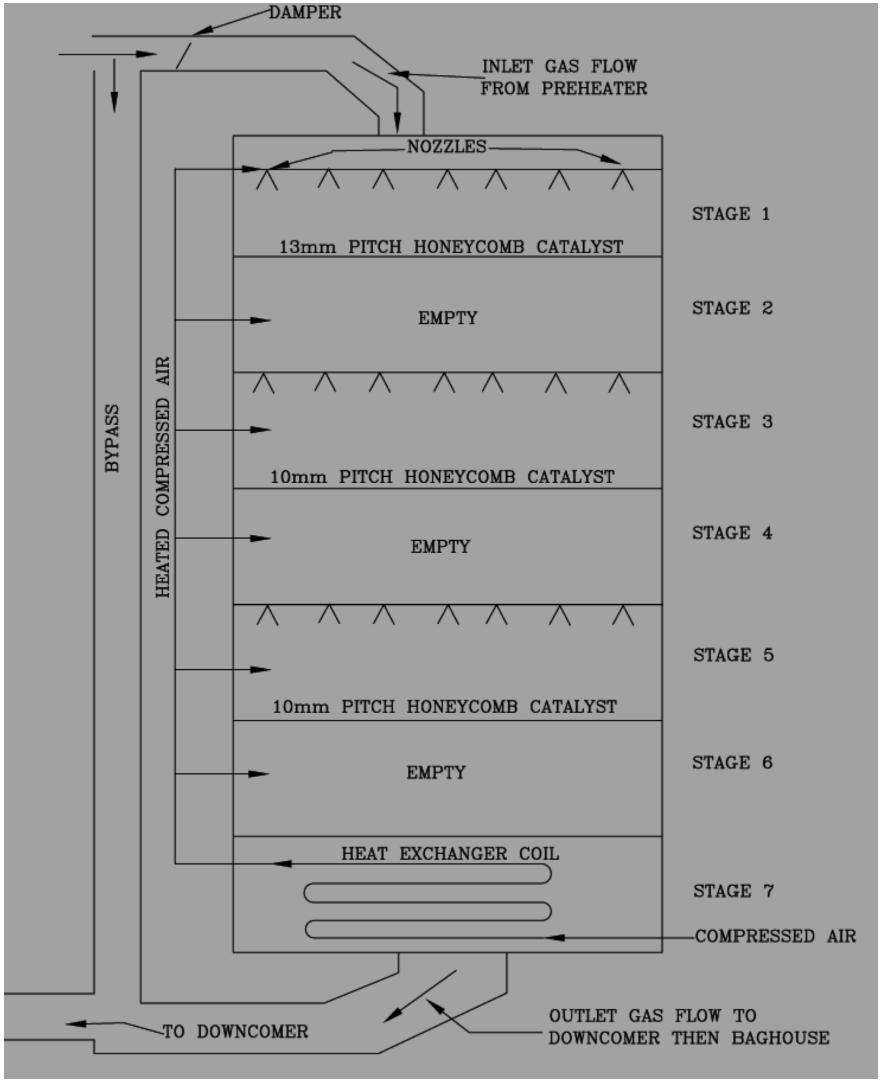
Waltisberg Consulting

« High-Dust-Solution »
Solnhofner
Portland Zement AG
Germany

Design of Catalyst Unit

Construction with 6 catalyst layers; but only 3 charged

- The first SCR layer contains honeycomb catalyst with a 13 [mm] pitch.
- The second layer is empty.
- The third layer contains honeycomb catalyst with 10 [mm] pitch.
- The fourth layer is empty.
- The fifth layer contains honeycomb catalyst with 10 [mm] pitch.
- The sixth layer is empty.



Waltisberg Consulting

Technical Data

First Full-Scale-Installation in Germany

Kiln

- Normal prehater kiln without precalciner; production 1600 [t/Tag]

SCR-Installation

- Supplier: CemCat (ELEX)
- Commissioning: 2001
- Each catalyst bed contains six modules. Each of these modules contains 144 catalyst elements in a 12 x 12 arrangement. The total depth of each catalyst layer is 900 [mm].
- Catalyst produced by KWH Katalylists GmbH, 45136 Essen (Germany)
  - Guaranteed lifetime: 2 years
  - Expected lifetime: 3 - 4 years
  - After 4 ½ years (January 2006) the catalyst was replaced
  - It is assumed that the catalyst could reach a lifetime of 5 to 6 years
- **The Full-Scale SCR plant in Solnhofen was taken out of service again after a few years because of the extensive catalyst purification and the threshold value of 500 [mg/Nm^3] achievable with SNCR**

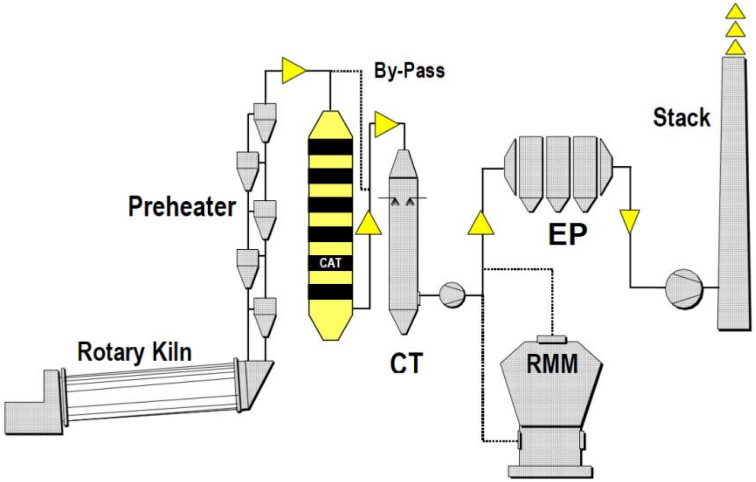
«High-Dust-Solution» Cementeria di Mont Selice (Italy)

Literature:
High Dust SCR Succeeds at Cementeria di Monselice (I)
Ulrich Leibacher, ELEX, Schwerzenbach (CH);
Clemente Bellin, Cementeria di Monselice SpA (I)
and A.A. Linero, P.E., Tallahassee, Florida (USA)
www.aramis.admin.ch/Default.aspx?DocumentID=582&Load=true

Kiln System and Catalyst Unit

Kiln system

Capacity:	2400 [t/day] (design)
	1800 [t/day] (effective)
Preheater:	5 stages without precalcination
	Exit temperature 320 – 350 [°C]
Fuels:	80 [%] petcoke + 20 [%] coal



Installation from CemCat (ELEX)

Catalyst

Layers:	6, 1 in reserve
	only 3 are loaded
	(smaller production)
Material:	V_2O_5 as active metal
	(and other metals)
	TiO_2 as ceramic base

Test Results 2006

Parameter		Design	Actual	
Kiln production	[t/Tag]	2400	1800	
Volume stream gas	[m^3/h] 1)	160000	110000	
NOx exit preheater	[mg/m^3] 2)	2260	1530	1071
Molar ratio	[NH_3]/[NO]	0.905	0.98	0.2
NOx exit catalyst	[mg/m^3] 2)	232	75	612
NOx chimney	[mg/m^3] 2)	200	50	408
NOx reduction	[%]	90	95	43
NH_3 slip	[mg/m^3] 2)	< 5	< 1	< 1
O_2 inlet catalyst	[%]	2.5	2.7	
O_2 chimney (direct)	[%]	5	7.1	
O_2 chimney (compound)	[%]		8.8	
Pressure loss	[mbar]	15	< 5	
NH_4OH (25 [%] solution)	[kg/h]	445	204	34

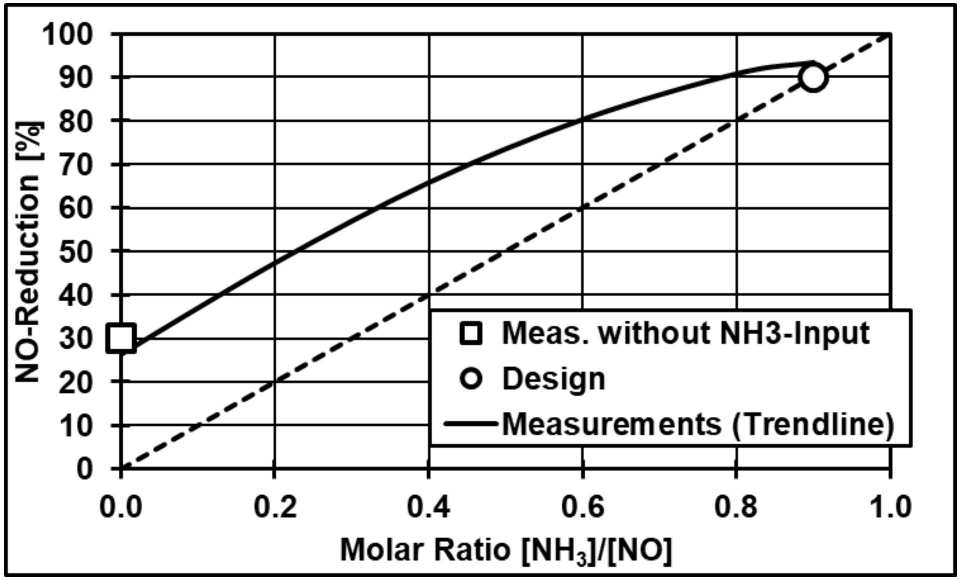
1) Standard conditions (1013 [mbar], 0 [°C] wet gas

2) Standard conditions (1013 [mbar], 0 [°C] dry gas, actual O_2 content

Results after 1 Year of Operation

▪ Operation time since March 2007:	> 7000 [h]
▪ Availability:	nearly 100 [%]
▪ NOx Reduction during test period:	up to 97 [%]
▪ NH_3 during test period:	< 1 [mg/m^3]
▪ VOC Reduction: (Volatile Organic Compounds)	75 [%]
▪ Other effect:	significantly less odor
▪ Cost for 90 [%] Reduction:	1 – 1.3 [€/t Clinker]

Results during Operation



- Measured values (Trendline) > than theoretical line (dotted line) Without NH_4OH input into SCR equipment, the reduction is the range of 30 [%] reduction
- Ammonia in exhaust gas before the installation of the SCR system was measured at 50 - 150 [mg/m^3] (odor problems round the plant). This ammonia of raw material origin is completely consumed in the SCR process thus reducing the emissions. This conveniently results in a molar ratio (injected $[NH_3]/[NO]$) less than unity.

Waltisberg Consulting

«High-Dust-Solution» Schwenk, Mergelstetten (Germany)

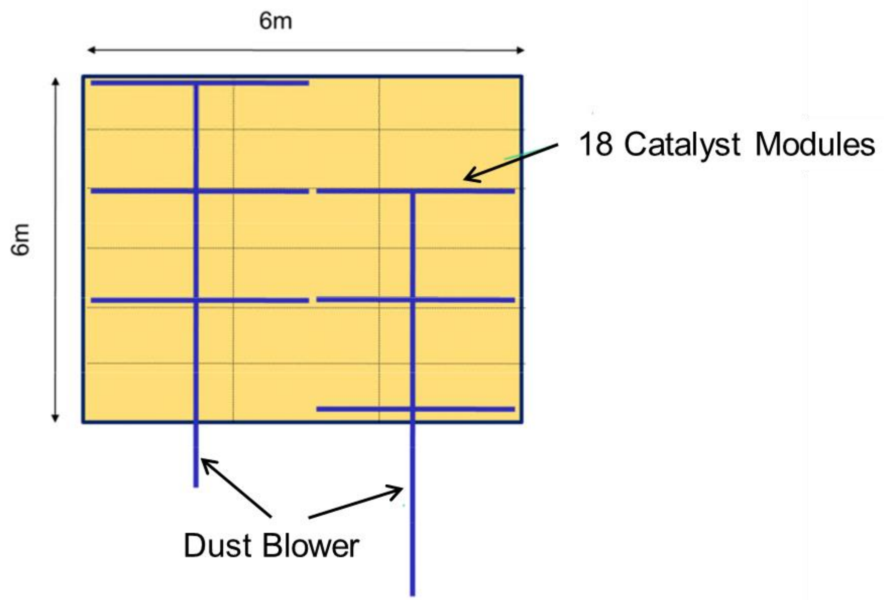
Literature:
BMU-Umweltinnovationsprogramm; Abschlussbericht zum Vorhaben Minderung von NOx-Emissionen in einer Drehofenanlage mittels SCR-Technologie
Detlef Edelkott und Jürgen Thormann, Schwenk Zement
Volker Hoenig, Helmut Hoppe, Martin Oerter, Cornelia Seiler. Verein deutscher Zementwerke (VDZ)
KfW-Aktenzeichen MB e1-001599
www.umweltinnovationsprogramm.de/sites/default/files/benutzer/36/dokumente/zement_schwenk_ab_scr_high_dust_2014.pdf

SCR Unit

▪ Supplier:	Cemcat / ELEX
▪ Commissioning:	Mid 2011
▪ Type:	«High Dust» (behind preheater)
▪ Dimension:	Height 42 [m], with 6[m]
▪ Flow:	Vertically from top to bottom
▪ Raw Gas:	360 – 420 [°C] maximum 220'000 [m^3_N/h] (normal, wet)
▪ Reducing Agent:	25 [%] NH_3 solution or 40 [%] urea solution Before the top cyclone stage or on stage 6 of the heat exchanger tower
▪ Quantity:	Maximum 1'200 [l/h]; 2 Lances
▪ Regulation:	Dynamic (via NO signal clean gas) and manual
▪ SNCR:	SNCR installation was not eliminated. Combination SNCR + SCR

Catalyst

- Manufacturer: CERAM Frauental (D)
- Dimensions per layer: 6 x 6 [m] (18 modules per layer / 72 elements per module)

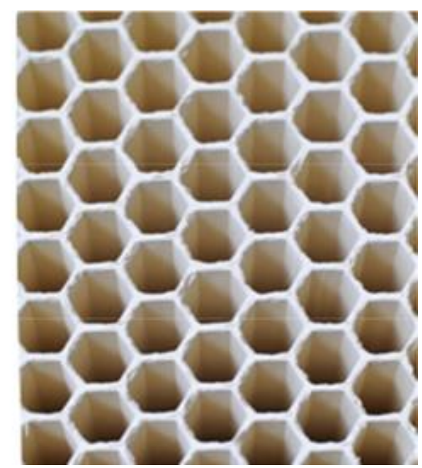


- Cleaning: 3 air compressors (2 - 3 [bar], 120/130 [kW]
  Compressed air quantity: 3000- 5000 [m^3_N/h]
  2 hot air blowers per layer

Waltisberg Consulting

Catalyst

- Type: honeycomb catalyst (hexagonal honeycomb)
  lowest level 4 since 02/2011:
  square honeycomb
- Pitch: 13.6 [mm] Hexagonal honeycomb / initial configuration
  11.3 [mm] Square honeycomb
- Composition: Titan dioxide (TiO_2) / tungsten trioxide (WO_3)
  ~ 4.5 – 4.7 [%]
  Vanadium pentoxide (V_2O_5) ~ 2 [%]

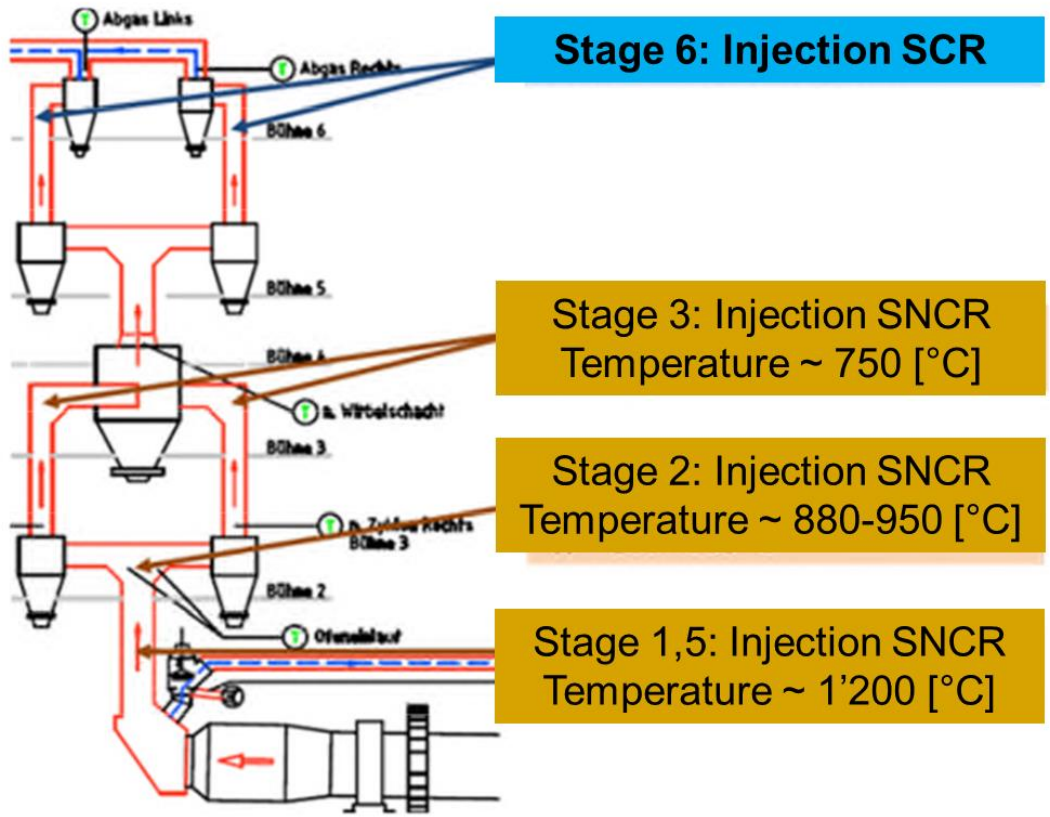


Waltisberg Consulting

Injection Points SCR + SNCR

Combination SNCR + SCR

- More flexibility
- Catalyst gets smaller
- More consumption of ammonia or urea as pure SCR

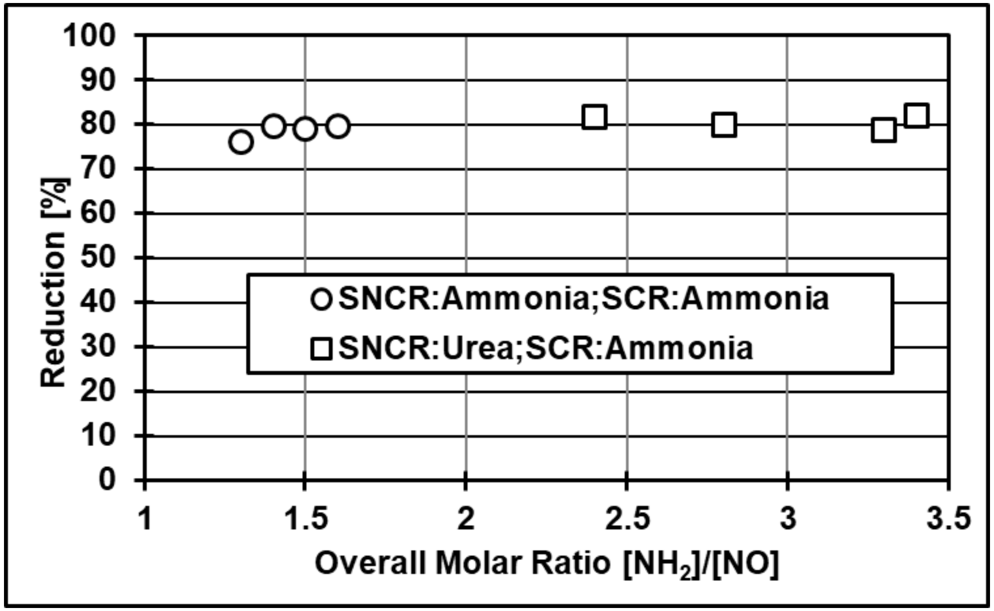


Waltisberg Consulting

Combination SNCR/SCR

Trial with combination SNCR / SCR

1. SCR system works with ammonia solution (0, 50, 100, 150 [l / h])
2. SNCR plant is regulated to a total reduction of 80 [%]
3. SNCR is operated with ammonia solution or with urea solution, SCR with ammonia solution only



Causes:

- ○ NH_3-slip in the SNCR zone
- □ Incomplete decomposition of urea because of too low temperature $CO(NH_2)_2 \rightarrow NH_2 + CONH_2$

Waltisberg Consulting

Emission between 2010 and 2018

2010/2011 Trial operation
Yearly averages (1013 [mbar], 0 [°C], dry, 10 [%] O_2)
*) Personal information

Year	NOx [mg/m³]	NH_3 [mg/m³]	Availability SCR
2010	254	9	60
2011	231	12	75
2012	196	9	93
2013	192	8	93
2014	185	3	95+
2015-2018 *)	< 200	?	95+

Reduction of Carbon Monoxide (CO) and of Organic Compounds

Carbon Monoxide

- No reduction effect in the SCR Installation

Volatile Organic Compound (Total organic Carbon)

- 10 – 20 [mgC/m^3] reduced by approximately 70 [%]
- Smaller reduction of short-chain compounds (C_1 and C_2)

Benzene (carcinogenic substance)

- From < 2 [mg/m^3] before the SCR to < 0.6 [mg/m^3] at the stack

Waltisberg Consulting

Reduction of Organic Compounds

Polycyclic Aromatic Compounds (PAHs according to EPA 610)

- From 70 to 90 [µg/m^3] before the SCR to < 5 [µg/m^3] at the stack

Polychlorinated Biphenyls (Sum of PCBs according WHO)

- Very low concentration before the SCR plant (<0.02 [ng/m^3])
- Reduction in the SCR system, but not exactly determinable
- Reduction rate between < 10 and > 30 [%]

«Dioxins and Furans» - Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/PCDF)

- Reduction rate approximately 50 to 60 [%]
- Emission at the stack < 0.001 [ngTE/m^3]

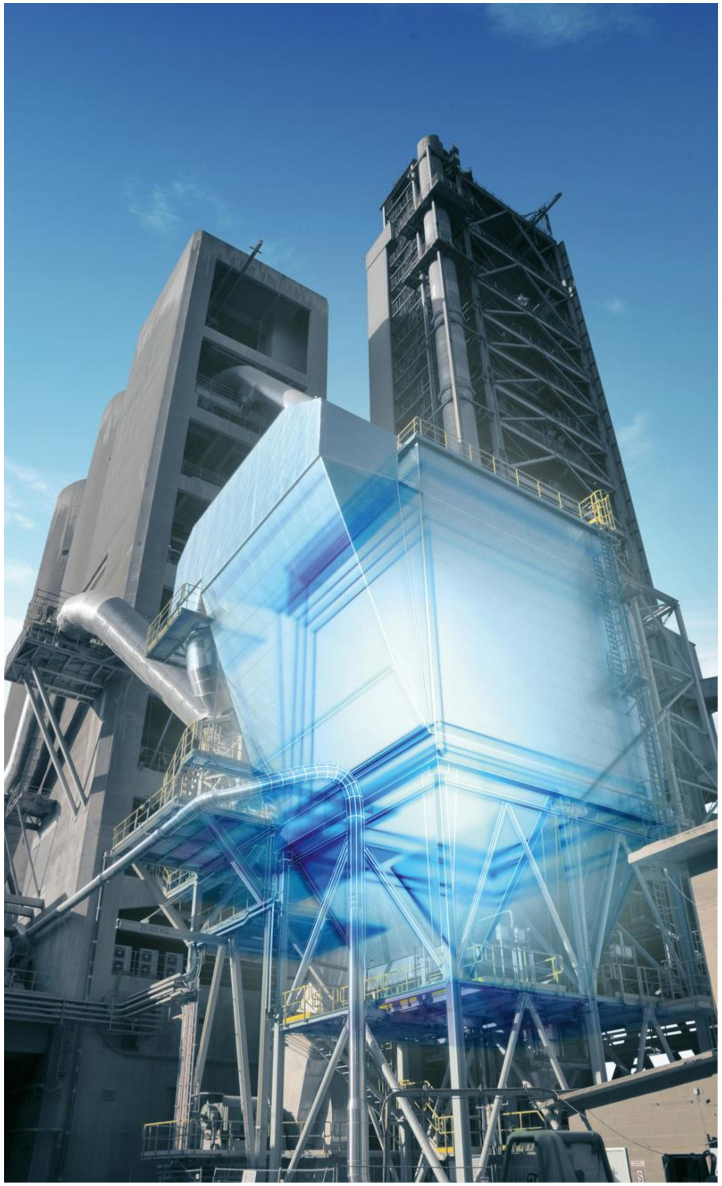
Operating Cost

Resources	Determined Need	Specific Operating Costs
Catalyst	1 layer per year	0.30 [€/t Clinker]
Electrical power	5.0 [kWh/t Clinker]	0.40 [€/t Clinker]
Reducing agent	3.5 [kg/t Clinker]	0.42 [€/t Clinker]
Sum		**1.12 [€/t Clinker]**

Waltisberg Consulting

«Semi-Dust-Solution»
Lafarge Perlmooser GmbH in Mannersdorf (Austria)

Scheuch – Technology for Clean Air
Innovative SCR Technologies for NOx-VOC-CO-Odor-Reduction
April 2016



Waltisberg Consulting

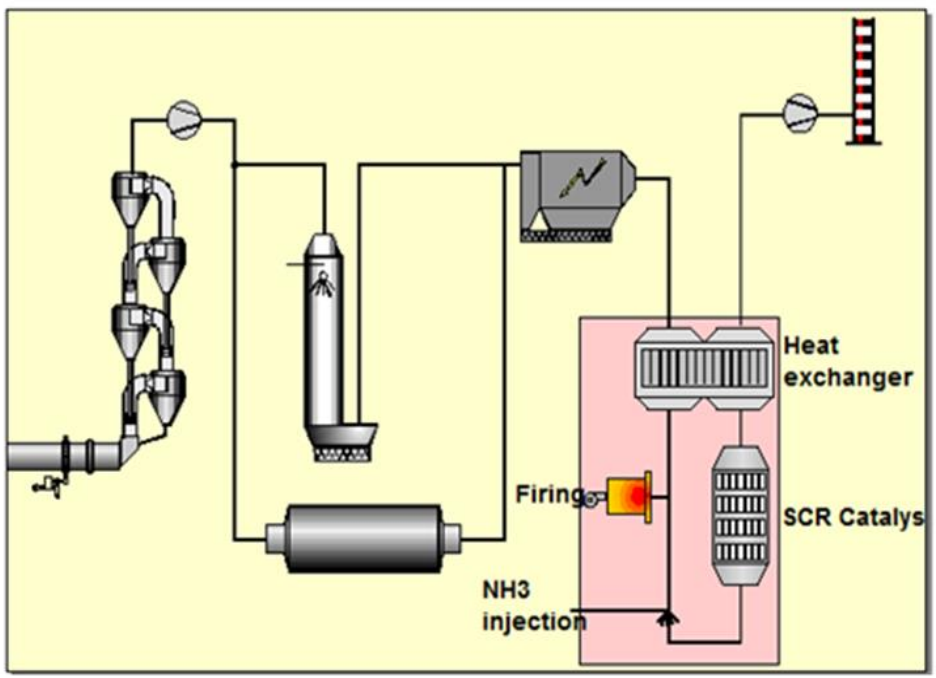
Semi Dust SCR

1st Semi-Dust SCR worldwide at Lafarge Mannersdorf, Austria

- Design Data:
  - 2500 [t/d]
  - Flow:180,000 Nm³/h
  - Temp:290°C –350°C
  - Dust:180 [g/m³] (before Hot Gas Filter; Electrostatic Precipitator)
  - < 2 [g/m³] (after ESP)
- Target:
  - < 200 [mg/m³] NOx (at the main stack)
  - < 20 [mg/Nm³] NH_3
- TÜV Measuring Campaign June 2012

[mg/m³]	NOx	NH_3	VOC
Bevor SCR	837	235	25
After First Layer	273	21	13
Exit SCR (Stack)	158	2	8

«Low-Dust-Solution»



Catalyst behind the Dust Filter, just in front of the Chimney («Tail End»)

- Low dust content (in general < 10 [mg/m³])
- Gas temperature must be increased to optimal reaction temperature (heat exchanger, additional firing or heat from the clinker cooler)

Example:

- Rohrdorfer Zement
  Südbayerisches Portland-Zementwerk
  Gebr. Wiesböck & Co. GmbH; Germany

Waltisberg Consulting

«Low-Dust-Solution» Rohrdorfer Zement (Germany)

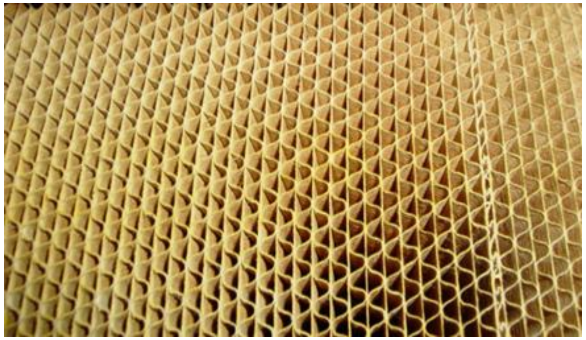
Literature:

Abschlussbericht zum Vorhaben Katalytische Low-Dust-Entstickung des Abgases an einer Drehofenanlage der Zementindustrie (Reingas – SCR)
Dipl.-Ing. Katharina Rechberger, Gebr. Wiesböck & Co. GmbH
Dr.-Ing. Nils Bodendiek, Forschungsinstitut der Zementindustrie GmbH
KfW-Aktenzeichen NKa3 – 001706
www.umweltinnovationsprogramm.de/sites/default/files/benutzer/36/dokumente/abschlussbericht_rohrdorf_final.pdf

Waltisberg Consulting

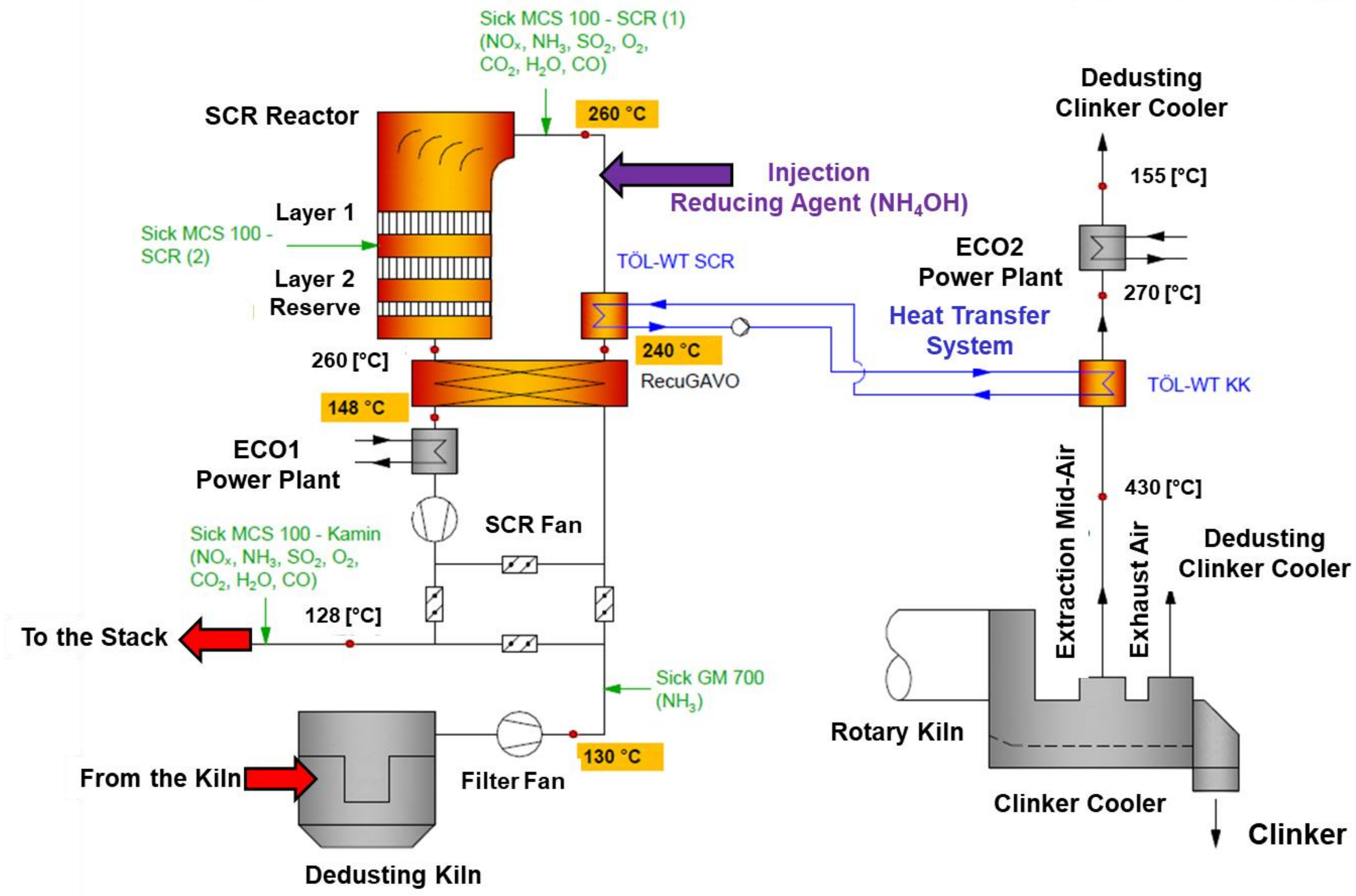
SCR Unit

- Supplier: GEA Bischoff
- Commissioning: Mid 2011
- Type: «Low Dust» (just behind filter system; heat exchanger; additional heat from clinker cooler)
- Gas temperature: 250 [°C]
- Catalyst: Sinusoidal Titanium dioxide (TiO_2) honeycomb body on a glass fiber matrix, impregnated with around 3 [%] of the active substance Vanadium pentoxide (V_2O_5). To reduce the SO_2/SO_3 conversion rate about 3 [%] tungsten trioxide (WO_3) was also added.



Waltisberg Consulting

Design of the «Low-Dust-Installation»

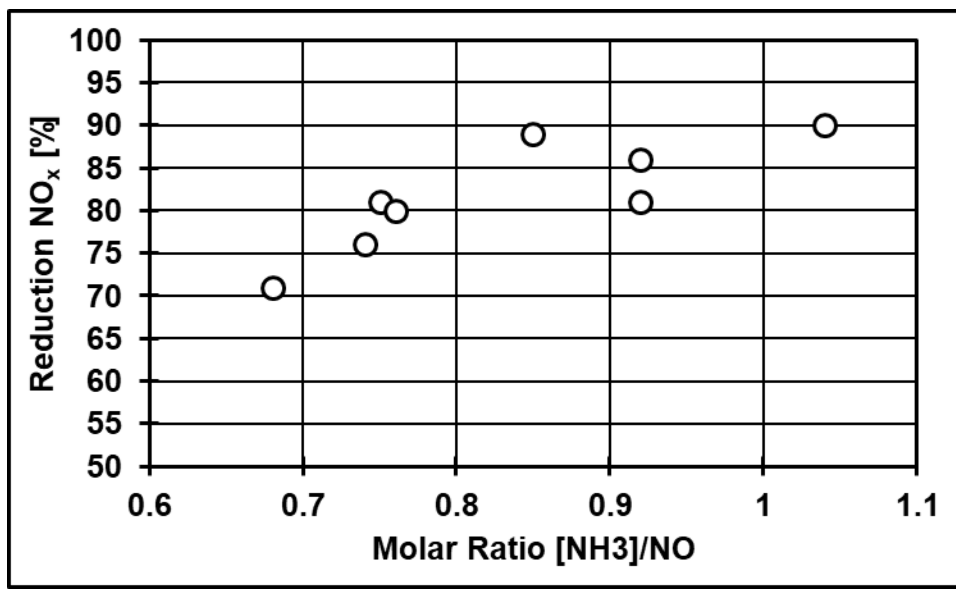


Waltisberg
Consulting

Result of different Tests

Campagne		SCR-I		SCR-II		SCR-IV		SCR-V	
Date		Sep 11		Mai 12		Mai 13		Oct 2013	
Operation		C	D	C	D	C	D	C	D
NOx before SCR	[mg/m^3] *)	501	485	671	568	503	586	408	464
NOx after SCR	[mg/m^3] *)	55	68	127	57	121	111	118	93
NOx-Reduction	[%]	**89**	**86**	**81**	**90**	**76**	**81**	**71**	**80**
Molar Ratio [NH_3]/NO	[--]	**0.85**	**0.92**	**0.92**	**1.04**	**0.74**	**0.75**	**0.68**	**0.76**
NH_3 after SCR	[mg/m^3] *)	1	18	1	10	1	0	0	0

C = Compound Operation
D = Direct Operation
*) Normal, dry, 10 [%] O_2



Availability and Bypass of SCR

Bypass of SCR

1. Below the required minimum temperature of 248 [°C] at the catalyst outlet
2. Exceeding the maximum permitted SO_2 concentration of the exhaust gas of 75 [mg/m³] (Normal, dry, 10 [%] O_2) at the stack
3. Exceeding the maximum permissible dust content of the exhaust gas of 10 [mg/m³] (Normal, dry, 10 [%] O_2) at the stack

Availability of SCR

2013 – today: > 95 [%]

Reduction of Carbon Monoxide (CO) and of Organic Compounds

Carbon Monoxide and Volatile Organic Compound (Total organic Carbon)

- The increase in CO concentration was on average around 15 [%], so that the average emission level after the SCR plant was 480 [mg/m^3].
- The organic compounds were reduced from 40 to 60 [mgC/m^3] to an average of 16 [mgC/m^3], reduction around 60 to 70 [%]
- Assuming complete conversion of Volatile Organic Compounds to CO, this equates to a CO increase of about 15 [%]
- Short-chain C_1/C_2 compounds (Methane, ethane, ethene and ethyne) are reduced mostly only to 10 to 30 [%]. Especially for methane no significant decrease was found.

Benzene (carcinogenic substance)

- Average reduction around 40 [%];
  Average emission level: 1.4 mg/m^3]

Remark: All values Normal, dry, 10 [%] O_2

Reduction of Organic Compounds

Polycyclic Aromatic Compounds (PAHs according to EPA 610)

- Reduction rate of 95 [%], whereas the reduction in the first layer was already 85 [%]
- Average emission around 2.5 [$\mu g/m^3$] (including naphthalene)
- The emission of benzo(a)pyrene was below the detection limit.

Polychlorinated biphenyls (Sum of PCBs according WHO2005)

- Reduction rate of 75 to 95 [%], whereas in average 75 [%] were reduced in the first layer
- Average emission level: 0.0008 [ng TE/m^3]

«Dioxins and Furans» - Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/PCDF)

- Reduction rate of 80 to 95 [%], whereas in average 85 [%] were reduced in the first layer
- Average emission level: 0.003 [ngTE/m^3]

Remark: All values Normal, dry, 10 [%] O_2

Behavior of other Compounds

Formaldehyde

- Neither a formation nor reduction of formaldehyde took place in the SCR.
- All measured values were below 1 [mg/m^3]

Mercury

- The measurements carried out showed that the SCR catalyst influences the oxidation state of the mercury contained in the exhaust gas.

Operation	Measuring Point	Ionic Hg [%]	Elementary Hg [%]
Compound	Before SCR	44	56
	After Layer 1	76	24
	After SCR	93	7
Direct	Before SCR	8	92
	After Layer 1	69	31
	After SCR	69	31

Remark: All values Normal, dry, 10 [%] O_2

Operating Cost

Resources	Determined Need	Assumption for Costs	Specific Operating Costs
Catalyst	10 years	49’000 [€/year]	0.05 [€/t Clinker]
Electrical power	5.6 [kWh/t Clinker]	0.07 [€/kWh]	0.39 [€/t Clinker]
Reducing agent	0.4 [l/t Clinker]	0.16 [€/l]	0.06 [€/t Clinker]
Sum			**0.50 [€/t Clinker]**

Thank you for your attention!