High Dust SCR Succeeds at Cementeria di Monselice

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ABSTRACT

Nitrogen oxides (NO_X, an ozone/smog precursor) control requirements for portland cement manufacturing facilities are becoming progressively stricter. As the practical and economic limitations of existing control measures for controlling NO_X are reached, the cement manufacturer is faced with the need to further control NO_X, while continuing to improve the control of other pollutants. Selective catalytic reduction (SCR) is a technology that can complement or be used in lieu of the better known techniques such as staged combustion in the calciner (SCC) and selective non-catalytic reduction (SNCR). Since mid-2006, the second-of-its-kind "high-dust" SCR installation has proved successful at the Cementeria di Monselice in Padova Province, Italy. The system demonstrated the ability to achieve significantly less than 200 milligrams per normal cubic meter (mg NO_X/Nm^3) equivalent to less than 0.58 lb NO_X per ton clinker (lb/ton). Furthermore, emissions of volatile organic compounds (VOC another ozone smog precursor) and ammonia (NH_3, a fine particulate precursor) were reduced or minimized. High dust SCR is a proven and cost-effective multi-pollutant control strategy.

Figure 1. SCR reactor at Cementeria di Monselice

INTRODUCTION

A great deal of information exists regarding air pollution control in the cement industry in general and NO_X control in particular. One of the finest documents for overall air pollution control from the cement industry is the Reference Document on Best Available Techniques in the Cement and Lime Industry by the European Commission (2000) that is presently being updated.[1] The Italian language counterpart is Linee Guida Per l'individuazione e l'Utilizzazione delle Migliori Tecniche Disponibile – Produzione di Cemento (2004).[2] The reader is referred to those documents and the updates for discussions on:

- Formation of thermal and fuel NO_X;
- Primary measures to reduce NO_X formation such as flame cooling and Low NO_X kiln burners;
- Secondary measures including staged combustion in the calciner in a reducing atmosphere; and
- Add-on control technologies, including SNCR.

The purpose of the present discussion is not to debate the merits of SCR versus the mentioned primary, secondary and add-on technologies. Rather it is to present the results of the high dust SCR installation at a cement plant that represents an important update to what was known when the mentioned documents were prepared.

LOCATION OF THE CEMENTERIA DI MONSELICE

The Cementeria di Monselice (CM), which is the subject of this paper, is a cement plant owned and operated by the Radici family. CM is located in the Veneto region of Italy, near Padova, and in the town of Monselice. Two other cement plants are located in the same area. Geographically the region is within the great Po Valley that lies between the Alps to the North and the Appenines to the South. The location of CM is shown in the Figure 2.

The town is a of historical significance and the region is well known for its agriculture, industry, commerce, culture and tourism. The University in nearby Padova is one of the greatest and oldest institutions of higher learning in the world. Venice was the seat of a great republic that dominated the commerce of the Adriatic Sea and beyond for hundreds of years. There are numerous resorts near Monselice frequented by visitors who enjoy the natural and healthy thermal baths.

Figure 2. Location of Monselice in Italy. Location of Cementeria di Monselice within Town.

Following are photographs taken by one of the co-authors during a recent visit. A new stack associated with some of the recent projects is visible in the second photograph below. The plant was originally built in 1954 and subsequently modernized to its present PH design in 1990. The capacity is 1800 metric tons per day (denoted as tpd) of clinker.

Figure 3. Photograph of Cementeria di Monselice from East. Preheater Tower, Feed Silo, Stack

The plant produces pure Type I cement (pure ground clinker) as well as various Type II cements and pozzolanic cement. Raw materials are primarily limestone from Monti Berici region and clay.

The key fuels are coal and petroleum coke. The plant does not fire wastes. The applicable NO_X limit is 800 mg/Nm^3, however lower limits are currently applied in Italy depending upon the region and local environmental authorities.

Despite the beauty of the area, evidence of ambient air quality deterioration is evident. The likely constituents are photochemical smog (ozone) and fine particulate precursors generated by wide scale transportation and industrial sources.

According to the conclusions of the Venetian Regional Environmental Protection Agency (ARPAV) 2005 Report, regional policy is directed towards the reduction of emissions of O_3 precursors, namely NO_X and volatile organic compounds (VOC). Furthermore fine "secondary" particulate matter is derived from SO_X and NO_X as ammonium nitrates and sulfates and nitric and sulfuric acid. The report draws attention to the policy of reduction of benzo(a)pyrene (a hazardous air pollutant - HAP) and the need to improve monitoring of heavy metals.

In addition, CM itself was believed by local residents to be one of the sources of objectionable odors that are detected during certain meteorological conditions. Within the regulatory environment and desire to be "a good neighbor", CM selected a strategy consistent with the multi-pollutant control objectives to reduce precursors of O_3 and fine particulate precursors as well as HAP.

BEST AVAILABLE TECHNIQUES (BAT) FOR NO_X CONTROL

The immediate need was to help address the regional O_3 concern. The primary focus is on NO_X emission control, although VOC is also a key O_3 precursor. After accomplishing basic reductions by good combustion techniques, there are two alternatives worth serious consideration. They are selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR).

The published BAT conclusions for NO_X-control of cement kilns are inconsistent with target values between 200-800 mg NO_X/Nm[3]. Additionally, those values are averaged between a half hour as minimum and as long as 30 days. These emission values equate to approximately 0.6-2.5 lb/ton clinker assuming an energy-efficient preheater (PH) or preheater/calciner (PH/C) kiln.

Sweden, for example, set BAT at 200 mg/Nm^3, Germany at 500 mg NO_X/Nm^3 with more stringent standards (as low as 200 mg NO_X/Nm^3) applicable to kilns that burn waste and Italy set BAT at 800 mg/Nm^3.

The most recent BAT (termed as BACT) determinations in the United States have been for new projects in Florida and Arizona. The Florida projects included limits of 1.95 lb/ton (roughly 675 mg/Nm^3) and averaged over 30 days.[3] The expectation is that these limits will be achieved by SNCR. The BAT limit for the Arizona project was set at 2.4 lb/ton (roughly 800 mg/Nm^3) on a 24-hour basis achievable by SCC or SNCR.

As previously mentioned, the Italian BAT NO_X limit is 800 mg/Nm^3 (roughly 2.5 lb/ton). However the trend is towards lower emissions, at least for new projects. For example the applicable limit at the Italcementi modernization project in Bergamo is 500 mg/Nm^3 (~1.4 lb/ton) when using liquid and solid wastes.[4] The limit was foreseen as achievable by a combination of a Low NO_X kiln burner, SCC and SNCR.

There are limitations to the SCC technologies (some more than others) when attempting to achieve low emissions that are manifested as production interruptions. Similarly, SNCR can have certain site-specific limitations that are ultimately expressed as in some applications as excessive ammonia (NH_3) consumption, emissions, and potential for (detached) plume formation when attempting to achieve very low NO_X emissions. Discussions of some of the possibilities and limitations of SCC and SNCR are given in publications by one of the co-authors.[5, 6, 7]

The ultimate limitations of SCC and SNCR and trend towards multi-pollutant control, necessitate the examination of SCR as a control strategy in a growing number of applications.

PRINCIPLE AND DESCRIPTION OF SCR TECHNOLOGY

The following discussion is a description of SCR principle including the key pollutant destruction reactions that can occur when SCR is applied within cement pyroprocessing. The principle of the SCR of procedure is shown in the following Figure 4. The key to SCR is the catalyst, over which the exhaust gas and reducing reagent are contacted at temperatures between 170 and 400°C. High conversion can be realized by the catalyst with short retention times.

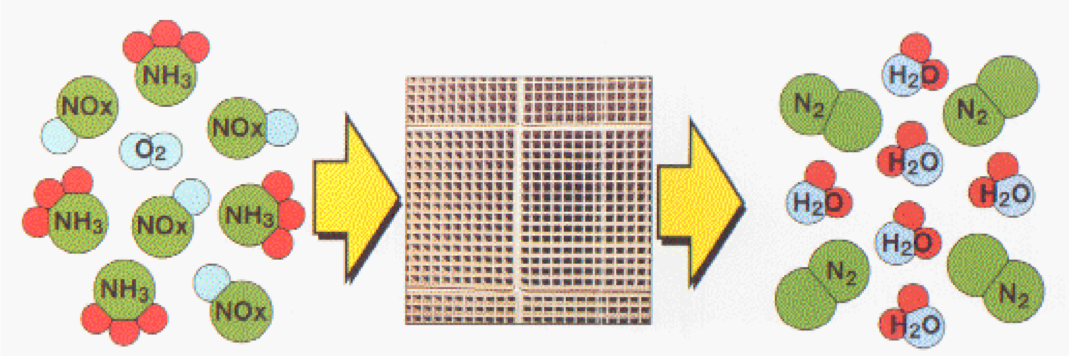

Figure 4. Raw Gas with NO_X and NH_3. Reaction over Catalyst. Yields Nitrogen and Water

On the order of 98 percent of the NO_X present in the flue gas from cement kiln is in the form of nitrogen oxide (NO).

Equation 1. NO and reagent ammonia (NH_3) react in the presence of a catalyst and are converted to molecular nitrogen (N_2) and water vapor:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

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. This partly explains, why NO_X-removal efficiencies by SCR can be greater than 90 % with practically no ammonia slip. As usual for catalytic processes, the catalyst itself is not a reactant and is not consumed in the process.

Equations 2 and 3. NO_2 is also reduced in a manner similar to the reduction of NO:

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{2}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{3}$$

Equation 4. Also the oxidation of SO_2 can occur and may cause additional effects as described in a section below:

$$2SO_2 + O_2 \rightarrow 3SO_3 \tag{4}$$

Equations 5 and 6. Hydrocarbons can be oxidized on the catalyst. As a specific example, the equations for the proven oxidation of dioxin and furan on the catalyst are shown:

$$C_{12}H_nCl_{8-n}O_2 + (9 + 0.5n)O_2 \rightarrow (n-4)H_2O + 12CO_2 + (8-n)HCl \tag{5}$$

$$C_{12}H_xCl_{8-n}O + (9.5 + 0.5n)O_2 \rightarrow (n-4)H_2O + 12CO_2 + (8-n)HCL \tag{6}$$

Equation 7 and 8. Insufficient operating temperatures of the SCR will form ammoniated sulphate compounds:

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \quad \textit{(ammonium sulphate)} \tag{7}$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \quad \textit{(ammonium bisulphate)} \tag{8}$$

Ammonium sulphate can evaporate and then recondense in the exhaust gas as particulate matter. Ammonium bisulfate is a sticky reaction product that can form and settle at the catalyst surface when there is a sub-stoichiometric NH_3/SO_3 ratio.

The determination of minimum acceptable operating temperature for the SCR must take into consideration the amount of NH_3 and SO_3 content before and after the SCR reactor. A safety margin between the theoretical sublimation temperature of the various compounds and the operating temperature is essential for a trouble free operation and long catalyst lifetime.

SCR installations for some applications operate successfully at temperatures as low as 170 °C when very minimal amounts of SO_3 are present in the flue gas. At such low temperatures, however, the catalyst activity is considerably reduced, thus requiring a higher specific catalyst volume than is necessary at higher temperatures.

The catalyst itself consists of active metals and substrates. The combination of mainly V_2O_5 as active component and TiO_2 as ceramic base formed as a honeycomb structure has shown the best results so far for cement kiln applications. Other known active components consist of tungsten, iron, chromium, nickel or copper; precious metals (e.g.: platinum, palladium, rhodium, ruthenium); zeolites; and activated carbon (Haug et al., 2002).[8] Other known catalyst structures are plate, molded wire, pellets or dust.

The basic requirements of an SCR catalyst for cement kiln application are:

- Suitable to handle gas with dust on the order of 100 g/m^3;
- High activity and selectivity;
- Low oxidation rate of SO_2 to SO_3;
- Chemical and mechanical stability; and
- Small pressure loss.

A key parameter for the operational behavior of a SCR plant is the NH_3 slip. This parameter will rise when foreseen deactivation of the catalyst has been reached and also depends on the uniformity of the NH_3 distribution.

In determining the position of the SCR reactor, one differentiates between untreated raw exhaust gas (high dust) configuration and the clean exhaust gas (low dust) configuration. Only the high dust application is discussed here.

In the raw gas (high dust) configuration, the catalyst is located within the process in the dusty exhaust gas stream and within a prescribed temperature range. The SCR system consists of:

- A storage tank and metering station for aqueous ammonia solution;
- Ammonia injection; and
- The catalytic reactor.

The placement of the catalyst in the raw gas circuit rather than after the main particulate control device has certain advantages. The reaction occurs within an optimal temperature window thus avoiding expensive reheating. Also less false air is present because the SCR is placed before the induced draft fan(s).

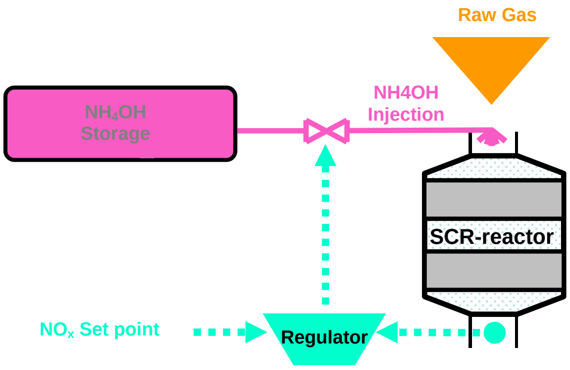

Figure 5. Basic SCR System Components

The disadvantages are high dust load and the more probable presence of catalyst poisons. Thus catalyst lifetime is determined and can be shortened by the extent of erosion and deactivation. Additionally catalyst channels must be substantially larger and, consequently, with increased catalyst volume.

STATUS OF SELECTIVE CATALYTIC REDUCTION TECHNOLOGY

The SCR technique has wide application in the reduction of NO_X at coal-fired power plants and waste-to-energy (WTE) plants. There is more than sufficient practical experience available for these applications. SCR, with its multi-pollutant control potential, is today applied in most new coal-fired plants in the United States and Europe, many WTE installations in Europe, and on combined cycle gas-fired power plants in the United States.

By contrast in the Cement Industry until mid of 2006, SCR has been only tested at various pilot plants and one full scale plant was built in Germany. ELEX operated pilot plants at three cement plants located in Italy, Austria and Sweden. Early results of these pilot tests were published by one of the co-authors. [9] A considerable number of publications followed, primarily based on experience from these pilot plant tests. These include, for example, the Cembureau Report (1997), the Austrian Federal Environmental Office (UBA, 1998) and the Dutch Report (1997) that were submitted in support of the previously-mentioned European Commission (2000) BAT document.

Several reports have been prepared with respect to the first commercial scale demonstration of a high dust SCR system at the German facility described above and after preparation of the assessment above. These were prepared by representatives of the plant, the German Federal Environmental Office, and the manufacturer's representative. [10, 11] The actual status is detailed in a trip report by one of the co-authors who recently visited the facility.[12] During that visit, the plant was using a backup SNCR system to meet 500 mg/Nm^3 and conducting studies to compare costs with the SCR system.

DESCRIPTION OF SCR SYSTEM AT CEMENTERIA DI MONSELICE

The high dust SCR configuration installed at CM is shown in the following diagram:

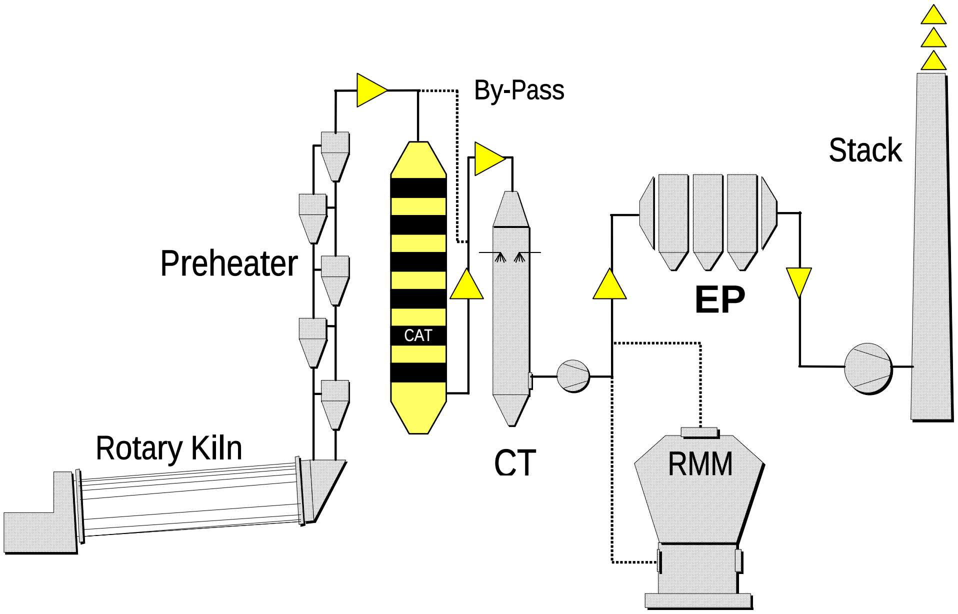

Figure 6. Flow Diagram of the High Dust SCR Unit at Cementeria di Monselice

The plant has a PH kiln, but setup is applicable as well to a PH/C kiln. The appropriate temperature regime exists within the exhaust gas stream exiting the uppermost cyclone. At Monselice the temperature range at this point is typically in the order of 320 -350°C. The aqueous ammonia solution is injected in the gas stream below the uppermost cyclone. Any position is acceptable if complete evaporation and good distribution are achievable. The lowest point for NH_3 injection would actually be the SNCR configuration.

An essential component of a high-dust SCR at a PH or PH/C cement kiln is additional equipment to prevent catalyst pluggage and to keep the gas passages clean.

The SCR installation at CM is designed for a kiln capacity of 2400 tpd. Six layers are available in the reactor for placement of the necessary catalyst elements. One layer is designed as spare. Only three layers were loaded with catalyst elements given the fact that the present kiln capacity is only 1800 tpd and that the catalyst activity is very high after 3’500 hours of operation.

RESULTS OF SCR TESTING AT CEMENTERIA DI MONSELICE

The following discussion outlines the test results of SCR testing carried out at CM. Installation of the SCR system at Monselice was completed on June 1, 2006. Thereafter the plant was under a continuous program of testing for a period of 6 weeks with the participation of the design firm, ELEX of Schwerzenbach, Switzerland.

A representative selection of achieved operating results with high and low NO_X removal efficiencies is summarized in Table 1 below.

Table 1. Results of Selective Catalytic Reduction Tests at Monselice di Monselice (2006)

Parameter	Units	Design	Actual	
Kiln Capacity	tpd	2400	1800	
Gas Flow	m^3/h norm, wet	160'000	110'000	
NO_x in	mg/m^3 norm,dry (mg/dscm)	2'260	1'530	1'071
Molar Ratio	NH_3/NO_X	0.905	0.89	0.20
NO_X out	mg/dscm @actual O_2	232	75	612
NO_X stack	mg/dscm @actual O_2	200	50	408
NO_X removal	Percent (%)	90%	95%	43%
NH_3 slip	mg/dscm	< 5	< 1	< 1
O_2 reactor	Percent (%)	2.5%	2.7%	
O_2 stack	% (Direct Operation)	5.0%	7.1%	
O_2 stack	% (Compound Operation)		8.8%	
Pressure Drop	millibars	15	< 5	
NH_4OH	25% Solution, kg/h	445	204	34
Fuel	Typically 80% petcoke blend with various types of coal as backup fuel			

Depending on the inlet NO_X and NH_3 injection rate, the NO_X reduction efficiency ranges from 43 to 95%. Values as low as in the order of 50 mg/m^3 were achieved at the stack. Correction to 10% O_2 would yield even lower concentrations and equate to less than 0.15 lb/ton clinker.

Ammonia in flue gas before the installation of the SCR system was measured at 50 - 150 mg/m^3. This ammonia of raw material origin is completely consumed in the SCR process thus reducing the emissions of a fine ambient particulate precursor to less than 1 mg/m^3. This conveniently results in a molar ratio (injected NH_3/NO_X) less than unity.

One can conclude from these results, that SCR efficiency (meaning the percent NO_X removal efficiency divided by the molar ratio) at Monselice is greater than or equal to 100%. This of course is only possible by the fact that ammonia from raw material is freely available in flue gas prior to the SCR reactor.

In addition, SCR and SNCR can differ dramatically in relation to ammonia consumption for identical NO_X removal efficiencies. The potential of the SCR process is best visualized by transferring above SCR operating data into tables established for the determination of SNCR efficiency. The results appear in Figure 7 below:

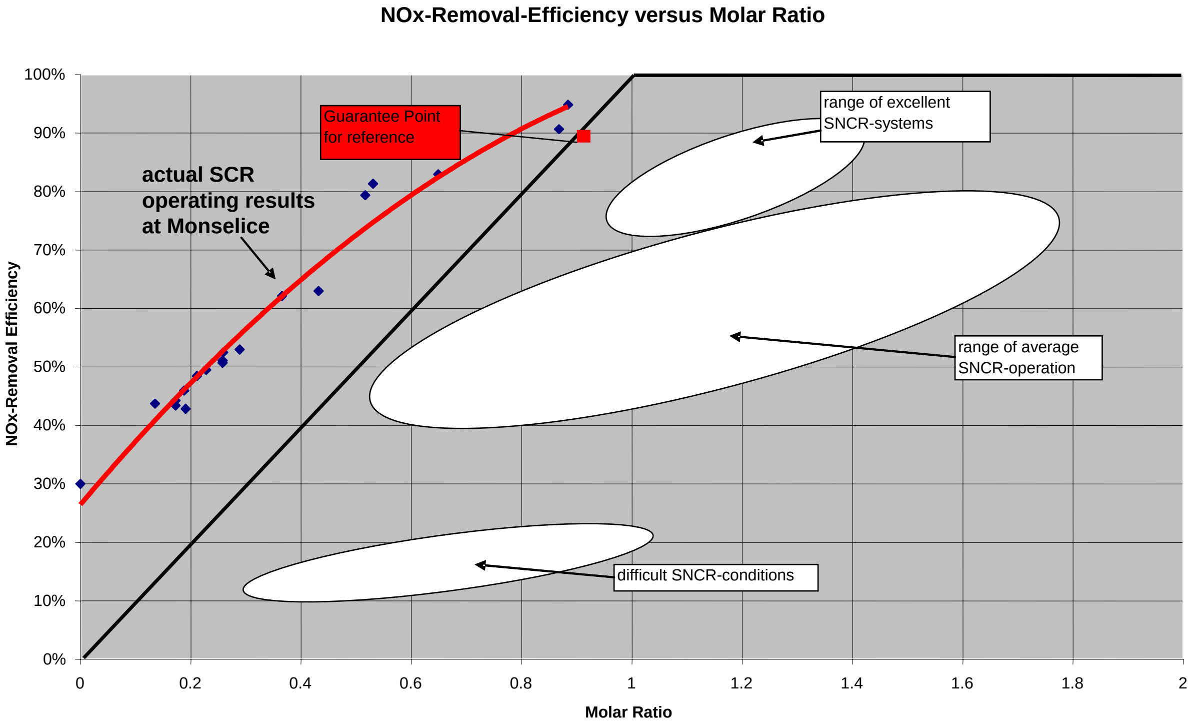

Figure 7. Percent NO_X Reduction versus Stoichiometric Ratio (injected NH_3/NO_X)

After the 6-week testing period CM took over the exclusive operation and monitoring of the SCR installation. The set point can be manually adjusted by the operator. For economical reasons, this set point is most of the time fixed at 400 mg NO_X/m^3 which is well within the permitted limit. For testing and demonstrations, it is lowered to values normally below 100 mg NO_X/m^3.

CONCLUSIONS

The SCR installation has proven its multi-pollutant control capabilities. Beside the extremely high and efficient NO_X-removal capabilites, NH_3 present in flue gas from raw material is completely used in the SCR process, thus considerably lowering the aqueous ammonia consumption, the related operating cost, a fine particulate precursor and potential odorant. In addition, 75 % oxidation of VOC is recorded. Almost all ozone precursors (NO_X and VOC) can be eliminated from the stack emissions of Cementeria di Monselice with the installed SCR process. These features will enable the Cement Industry to make use of a much wider range of raw materials and fuels whilst maintaining applicable emission standards and minimizing impacts on the environment.

SCR installation at Cementeria di Monselice at a glance:

Operating Time as end of October 06:	> 3‘600 h
Availability:	100%
NO_X removal efficiency:	up to 97%
NH_3 emissions before SCR was in operation	20 - 50 mg/m^3
NH_3 after commissioning of the SCR	< 1 mg/m^3
Savings in 25% NH_3(aq) consumption corresponding to	20 - 60 kg/h
VOC-oxidation:	75%
Other Benefits	Less air toxics, less Odor
Indicative operating costs for 90% NO_X-removal efficiency: (depending upon applied amortization period and interest rate)	1 – 1.3 €/t clinker

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KEY WORDS

Cement, BACT, BAT, SCR, Nitrogen Oxides, NO_X, Ammonia, NH_3

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