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With 50 years of success under its wing, Mordowcement embarks on a new programme of extensive upgrades for its plants with new semi-dry processing units and higher milling capacity.

**Superior refractory linings**  
*by E Olsen, Hoganas Bjuf Asia Pacific, Malaysia*

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A great deal of information exists regarding air pollution control in the cement industry in general and NO\textsubscript{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.\textsuperscript{1} The Italian language counterpart is Linee Guida Per l’individuazione e l’Utilizzazione delle Migliori Tecniche Disponibile – Produzione di Cemento (2004).\textsuperscript{2} The reader is referred to these documents and the updates for discussions on:

- formation of thermal and fuel NO\textsubscript{X}.
- primary measures to reduce NO\textsubscript{X} formation such as flame cooling and Low NO\textsubscript{X} kiln burners;
- secondary measures including staged combustion in the calciner in a reducing atmosphere
- 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 Cementeria di Monselice**

Cementeria di Monselice (CM) 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 which lies between the Alps to the north and the Appennines to the south.

The town is 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 frequented by visitors who enjoy the natural and healthy thermal baths.

![Figure 1: SCR reactor at Cementeria di Monselice](image1)

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. With the system demonstrating the ability to achieve significantly less than 200mg per normal cubic meter (mg NO\textsubscript{X}/Nm\textsuperscript{3}) and, emissions of volatile organic compounds and ammonia being reduced or minimised, this article demonstrates why high dust SCR is a proven and cost-effective multi-pollutant control strategy.
The applicability of NO\textsubscript{X} control is 800mg/Nm\textsuperscript{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\textsubscript{3} precursors, namely NO\textsubscript{X} and volatile organic compounds (VOC). Furthermore fine ‘secondary’ particulate matter is derived from SO\textsubscript{X} and NO\textsubscript{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 odours that are detected during certain meteorological conditions. Within the regulatory environment and desire to be ‘a good neighbour’, CM selected a strategy consistent with the multi-pollutant control objectives to reduce precursors of O\textsubscript{3} and fine particulate precursors as well as HAP.

**Best Available Techniques (BAT) for NO\textsubscript{X} control**

The immediate need was to help address the regional O\textsubscript{3} concern. The primary focus is on NO\textsubscript{X} emission control, although VOC is also a key O\textsubscript{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\textsubscript{X}-control of cement kilns are inconsistent with target values between 200-800mg NO\textsubscript{X}/Nm\textsuperscript{3}. Additionally, those values are averaged between a half hour as minimum and as long as 30 days. These emission values equate to approximately 0.6-2.5lb/t clinker assuming an energy-efficient preheater (PH) or preheater/calciner (PH/C) kiln.

Sweden, for example, set BAT at 200mg/Nm\textsuperscript{3}, Germany at 500mg NO\textsubscript{X}/Nm\textsuperscript{3} with more stringent standards (as low as 200mg NO\textsubscript{X}/Nm\textsuperscript{3}) applicable to kilns that burn waste and Italy set BAT at 800mg/Nm\textsuperscript{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 1.95lb/t (roughly 675mg/ Nm\textsuperscript{3}) and averaged over 30 days. The expectation is that these limits will be achieved by SNCR. The BAT limit for the Arizona project was set at 2.4lb/t (roughly 800mg/Nm\textsuperscript{3}) on a 24 hour basis achievable by SCC or SNCR.

As previously mentioned, the Italian BAT NO\textsubscript{X} limit is 800mg/Nm\textsuperscript{3} (roughly 2.5lb/t). However, the trend is towards lower emissions, at least for new projects. For example the applicable limit at the Italcementi modernisation project in Bergamo is 500mg/Nm\textsuperscript{3} (~1.4 lb/t) when using liquid and solid wastes. The limit was foreseen as achievable by a combination of a Low NO\textsubscript{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\textsubscript{3}) consumption, emissions, and potential for (detached) plume formation when attempting to achieve very low NO\textsubscript{X} emissions. Discussions of some of the possibilities and limitations of SCC and SNCR are given in publications by one of the co-authors.

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.

**SCR principle and description**

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 Figure 3. 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 realised by the catalyst with short retention times.

On the order of 98 per cent of the NO\textsubscript{X} present in the flue gas from cement kiln is in the form of nitrogen oxide (NO).
Equation 1. NO and reagent ammonia (NH₃) react in the presence of a catalyst and are converted to molecular nitrogen (N₂) and water vapor:

\[4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\]  

(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 NOₓ-removal efficiencies by SCR can be greater than 90 per cent 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. NO₂ is also reduced in a manner similar to the reduction of NO:

\[6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}\]  

(2)

\[2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}\]  

(3)

Equation 4. Also the oxidation of SO₂ can occur and may cause additional effects as described in a section below:

\[2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3\]  

(4)

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

\[C_{12}H_{x}Cl_{y}Cl_{z}O_2 + (9+0.5n)O_2 \rightarrow (n-4)H_2O + 12\text{CO}_2 + (8-n)\text{HCl}\]  

(5)

\[C_{12}H_{x}Cl_{y}Cl_{z}O_2 + (9+0.5n)O_2 \rightarrow (n-4)H_2O + 12\text{CO}_2 + (8-n)\text{HCl}\]  

(6)

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

\[2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)\text{HSO}_4\]  

(7)

\[\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4\]  

(8)

Ammonium sulphate can evaporate and then recondense in the exhaust gas as particulate matter. Ammonium bisulphate is a sticky reaction product that can form and settle at the catalyst surface when there is a sub-stoichiometric NH₃/SO₃ ratio.

The determination of minimum acceptable operating temperature for the SCR must take into consideration the amount of NH₃ and SO₂ 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 SO₃ 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 V₂O₅ as active component and TiO₂ 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). 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 100g/m³
- high activity and selectivity
- low oxidation rate of SO₂ to SO₃
- chemical and mechanical stability and
- small pressure loss.

A key parameter for the operational behaviour of a SCR plant is the NH₃ slip. This parameter will rise when foreseen deactivation of the catalyst has been reached and also depends on the uniformity of the NH₃ 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
- 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).

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 NOₓ 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-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 the facility.

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 NH3 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 2400tpd. 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 1800tpd and that the catalyst activity is very high after 3500 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 programme of testing for a period of six weeks with the participation of the design firm, ELEX of Schwerzenbach, Switzerland.

A representative selection of achieved operating results with high and low NOx removal efficiencies is shown in Table 1. Depending on the inlet NOx and NH3 injection rate, the NOx reduction efficiency ranges from 43 to 95 per cent. Values as low as in the order of 50mg/m³ were achieved at the stack. Correction to 10 per cent O2 would yield even lower concentrations and equate to less than 0.15lb/t clinker.

Ammonia in flue gas before the installation of the SCR system was measured at 50-150mg/m³. 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 1mg/m³. This conveniently results in a molar ratio (injected NH3/NOx) less than unity.

One can conclude from these results, that SCR efficiency (meaning the per cent NOx removal efficiency divided by the molar ratio) at Monselice is greater than or equal to 100 per cent. 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 NOx removal

| Table 1: results of Selective Catalytic Reduction tests at Cementeria di Monselice |
|----------------|----------------|----------------|
| **Parameter** | **Units**       | **Design**     | **Actual**    |
| Kiln capacity | tpd            | 2400           | 1800          |
| Gas flow     | m³/h norm, wet | 160,000        | 110,000       |
| NOx in       | mg/m³ norm, dry (mg/dscm) | 2260 | 1930 | 1071 |
| Molar ratio  | NH3/NOx         | 0.90%          | 0.89          | 0.20 |
| NOx out      | mg/dscm @actual O2 | 232   | 75  | 612 |
| NOx stack    | mg/dscm @actual O2 | 200  | 50  | 408 |
| NOx removal  | per cent (%)    | 90%            | 95%           | 43%  |
| NH3 slip     | mg/dscm         | < 5            | < 1           | < 1  |
| O2 reactor   | per cent (%)    | 2.5%           | 2.7%          |      |
| O2 stack     | % (direct operation) | 5.0%   | 7.1%          |      |
| O2 stack     | % (compound operation) | 8.8%   |   |  |
| Pressure Drop| millibars       | 15             | < 5           |      |
| NH3OH        | 25 % Solution, kg/h | 445 | 204 | 34  |
| Fuel         | Typically 80% petcoke blend with various types of coal as backup fuel | | | |

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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 6:

After the six-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 400mg NO\textsubscript{X}/m\textsuperscript{3} which is well within the permitted limit. For testing and demonstrations, it is lowered to values normally below 100mg NO\textsubscript{X}/m\textsuperscript{3}.

**Conclusions**

The SCR installation has proven its multi-pollutant control capabilities. Beside the extremely high and efficient NO\textsubscript{X}-removal capabilties, NH\textsubscript{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 odourant. In addition, 75 per cent oxidation of VOC is recorded. Almost all ozone precursors (NO\textsubscript{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 minimising impacts on the environment.

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**References**


