

Low-Temperature SCR

– Intelligent and Cost-Effective Regeneration without Excess Emissions –

Mario Marcazzan

1.	Pollutant capture principle.....	408
2.	<i>Closed-loop</i> regeneration principle	409
3.	Advantages of <i>closed-loop</i> regeneration (VE patent).....	414

Selective catalytic reduction (SCR) technology is a well-established and proven way to reduce NO_x in the waste to energy industry to a level $< 80 \text{ mg/Nm}^3$.

Low-temperature SCR (lt-SCR) typically operates at a temperature of about 180°C and needs regular on-line regeneration of the catalyst (in other words reheating by means of a gas burner at a temperature higher than 320°C during several hours) in order to prevent poisoning from salts (compounds of ammonium and sulphur) deposit.

In order to minimize poisoning and allow greater span between regenerations (thus reducing gas consumption) lt-SCR is normally installed *tail-end*, that means downstream of the neutralizing/de-dusting step (often dry or semy-dry process based on lime or bicarbonate).

This means that during catalyst regeneration no further treatment is applied to flue gases before emission to the atmosphere, and that emission level is strictly related to pollutants *unwinding* from the catalyst.

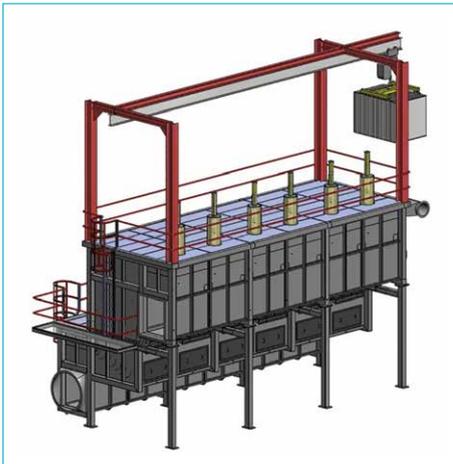


Figure 1: SCR reactor, bulk

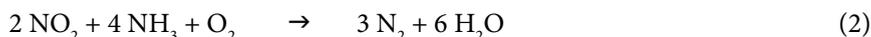
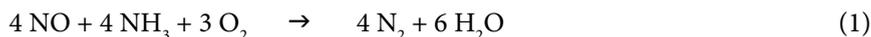
Laboratory tests show that regeneration can lead to SO_2 and even greater SO_3 unwinding, which can result in exceeding emission limits values (ELV).

Vinci Environnement (VE) patented system allows the recycling of flue gases upstream of neutralizing step during regeneration (*closed-loop* regeneration) and thus insures that ELV are met under all operating conditions.

1. Pollutant capture principle

SCR converts nitrogen oxides to nitrogen and water, by injecting ammonia and using a catalyst at temperatures of 180 °C or higher.

The SCR process results in the following chemical reactions:



Since more than 95 % of the nitrogen oxides in the flue gases from waste incineration are present under NO form, the reduction occurs essentially according to equation (1) above.

For temperatures above 700 °C, reactions also happen without catalyst (non-catalytic selective reaction, SNCR process). This process has one major weakness: the injection of ammonia in quantity larger than the stoichiometric is mandatory in order to obtain a high degree of reaction; part of ammonia left-over from the reaction is burnt and part is present in the flue gases (ammonia *leakage* or slip). It is difficult to reach a NO_x emission level of about 80 mg/Nm³ without the addition of expensive additional devices for the capture of ammonia slip (example: wet scrubbers).

In the lt-SCR process, using a ceramic catalyst, the reaction temperature can be reduced to 180 °C, which is a suitable level for the flue gas treatment process.

The catalyst consists essentially of TiO₂ (titanium oxide) as support layer, V₂O₅ (vanadium pentoxide) and WO₃ (tungsten oxide) as active substances and is available under honeycomb panels or bulk pellets form.



Figure 2: Honeycomb (left), bulk pellets (right)

The reduction is accompanied by degrees of separation up to ninety percent with an injected quantity of ammonia close to stoichiometric ratio and a limited residual ammonia slip. Slight conversion of SO₂-SO₃ occurs as an undesirable side reaction which can adversely affect the activity of the catalyst.

The lt-SCR module shall then be installed downstream of a flue gas treatment particularly effective in eliminating SO_x.

The presence of residual sulfur in the incineration flue gases leads to slow deactivation of the catalyst (poisoning), due to salt deposit on the catalyzer surface. This phenomenon is reversible (which is not the case with heavy metals poisoning), and leads to the implementation of regeneration phases: reheating of flue gases flowing through the catalyst in order to vaporize and eliminate salt deposit.

As part of the process implemented by VE, these operations are carried out at temperatures close to 350 °C; these temperature are reached by means of a gas stream burner ignited by natural gas. In order to optimize the energy consumption associated with this operation, VE has developed and patented a regeneration loop to recycle the gas flow charged with sulfur in order to recover the sensible heat from the warmed flue gases (*closed-loop* regeneration).

2. Closed-loop regeneration principle

The low Temperature catalytic DeNO_x process is characterized by the necessity of cyclically regenerating the various catalytic modules in order to eliminate the salts which have deposited in the form of sulphates and which obstruct the active sites. The catalytic activity and NO_x treatment performance are directly related to the number of active sites available.

The regeneration consists in isolating a compartment from the flue gas circuit and introducing clean flue gases heated at 350 °C in order to desorb the salts from the surface of the catalyst.



Figure 3: SCR reactor, pellets

The reactor is split into several (standard: 3) compartments (cells) which can be isolated by a register located at each of their inlet. In order to ensure continuous operation of the incineration line, each cell is regenerated at a time. Number of cells may vary according to the size and design of the plant.

The desorption results in sublimation of SO_2/SO_3 , HCl , and NH_3 . The flue gases leaving the catalytic module are thus charged in pollutants; they are recycled upstream of the flue gas treatment (VE patent) in order to avoid atmospheric pollution during regeneration phases. The pollutants desorbed during the regeneration of the catalyst are then neutralized in the flue gas treatment circuit.

The regeneration cycle is as follows:

- temperature increase from 178 to 350 °C in about six hours,
- constant temperature at 350 °C during ten hours,
- temperature decrease from 350 °C to 178 °C in about six hours.

A regeneration cycle takes about 22 hours per cell or a complete regeneration of the catalyst in 66 cumulative hours. The number of regenerations per year varies between 2 and 8 according to the operating conditions (namely the pollutants content and flue gas temperature upstream the reactor) and catalyzer characteristics.

The regeneration flue gas stream is heated by a gas burner. A part of the flue gas is removed at the outlet of the bag filter thanks to a damper positioned upstream of the catalytic converter (intake register). These flue gas are directed passed through the gas burner and reheated to the temperature required for regeneration. The burner is directly integrated into the wall of the regeneration line metal duct. A fan, positioned downstream of the burner, circulates the fumes in the regeneration circuit.

At the end of the regeneration cycle, a fresh air purge is carried out after the closing of the flue gas inlet register in order to blow out the regeneration duct.

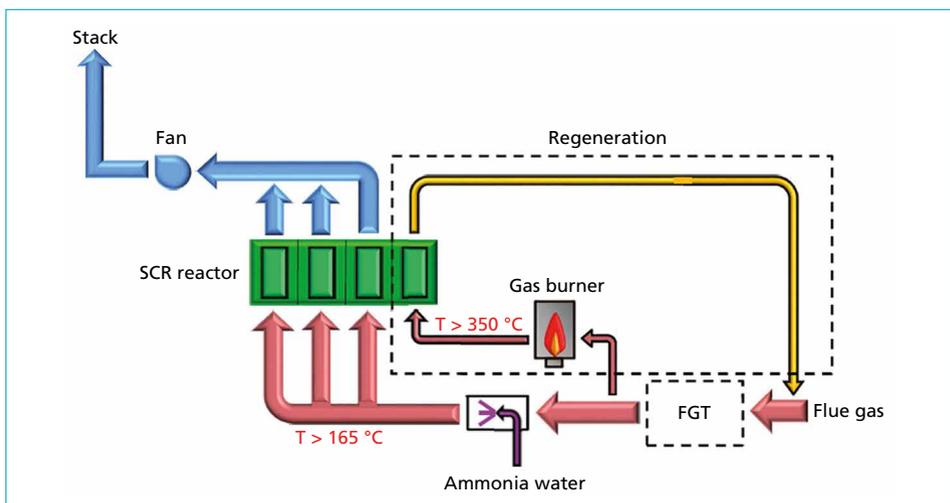


Figure 4: Closed loop regeneration

Pilot tests pollutants unwinding (break-up) during regeneration

In order to develop and validate the regeneration principle, pilot tests were carried out with different recycling rates. The level of regeneration of the catalyst and the quality of the regeneration were evaluated in different configurations, with regard to the residual sulfur level on the catalyst and by performance tests compared to a new catalyst.

Tests were performed on a pilot unit with a sulfur-loaded catalyst taken from a working reactor. The regeneration was carried out under operating conditions similar to those practiced on an industrial site, namely temperature and hourly volumetric velocity (VVH h^{-1}).

The pilot unit (Figure 5) was equipped with a catalytic reactor of 200 mm or 100 mm diameter provided with heat insulated and thermocouples, a fan with a capacity of 2 to 10 Nm^3/h , two in-line heaters, a gas/liquid heat exchanger for controlling the temperature of the gas downstream of the reactor prior to recycling, and an infrared sulfur dioxide analyzer.

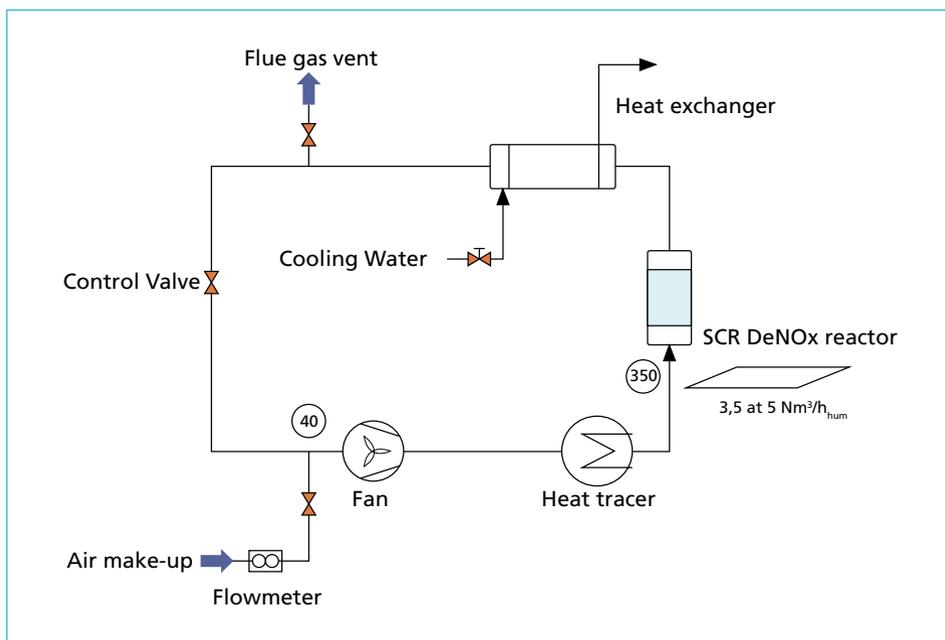


Figure 5: Test pilot unit

The catalytic activity tests were carried out on the same equipment but with a catalytic reactor of 86 mm diameter heat insulated, with a reaction mixture reconstituted from pure gases (flow rates of NO and NH_3 regulated using mass flowmeters).

The reconstituted gas mixture was brought to temperature by means of electrical heaters. The humidity of the synthesis gas is regulated by means of a water injection pump connected to a vaporizer. The water content was set at twenty percent by volume.

The nitrogen oxide contents upstream and downstream of the reactor are measured by chemiluminescence, allowing evaluation of the conversion rates and to the specific activities of the catalysts tested.

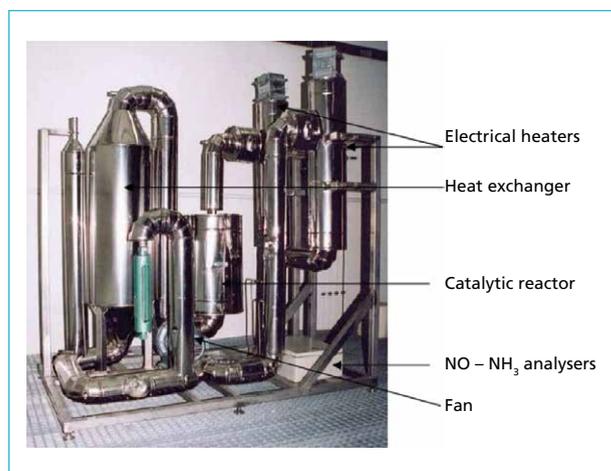


Figure 6: Test pilot unit

The tests simulating the regeneration process of the SCR catalyst on a pilot scale were carried out with a reconstituted sample of catalyst heavily loaded with sulfur (% S = 3.05 %).

The different regeneration configurations evaluated, correlated with the catalyst activity tests, highlighted the following:

- The dominant sulfur form detected downstream of the catalyst, during regeneration, is sulfur trioxide, which condenses to sulfuric acid or crystallizes in the form of salts at low temperatures; this is to be underlined because in actual application flue gas analyzers measure SO_x under SO_2 form, so the actual emission is under-estimated.
- The efficiency of the regeneration and hence the activity of the catalyst are closely related with the temperature level and homogeneous temperature distribution inside the catalyst.
- The partial recycling of the regeneration gas leads to a lower efficiency of the regeneration process but does not compromise this operation: the simulation of a loop recycling 60 % of the volumetric flow rate (actually representing 50 % of the sulfur mass flow due to losses in heat exchanges) results in a catalytic efficiency reduction of about 25 %, compared to the regenerated catalyst in the open loop condition. This means that it's important to carefully design the regeneration conditions (temperature and flow) in order to obtain the best pollutants unwinding.

Another test was carried out on the same micropilot unit described above, with the purpose of investigating and separating the ammonia which may have been adsorbed ($< 200\text{ }^\circ\text{C}$) from the ammonia released during the sublimation of the ammonium salt ($> 240\text{ }^\circ\text{C}$).

A continuous measurement of ammonia (UV fluorescence) and sulfur dioxide (IR spectrometry) contained in the flue gases was carried out during the regeneration of a catalyst sample under a neutral atmosphere (nitrogen), in order to avoid any oxidation of the ammonia released.

The heat treatment took place with a succession of temperature rises:

- 1) increase from 20 °C to 200 °C at 5 °C/min, followed by a plateau at 200 °C;
- 2) increase from 200 °C to 300 °C at 2 °C/min, followed by a plateau at 300 °C;
- 3) increase from 300 °C to 400 °C at 1 °C/min, followed by a plateau at 400 °C.

The duration of the plateaux was fixed following the phenomena observed.

Concentrations of ammonia and sulfur dioxide are shown in Figure 7: ammonia emission begins at 300 °C. with a concentration of about 40 ppmv. Also at this temperature the first releases of sulfur dioxide occur.

The concentration of sulfur dioxide increases considerably in the second temperature ramp with a peak at 2,200 ppmv. The ammonia concentration also increases with temperature but in much lower proportions (peaks at 200 ppmv).

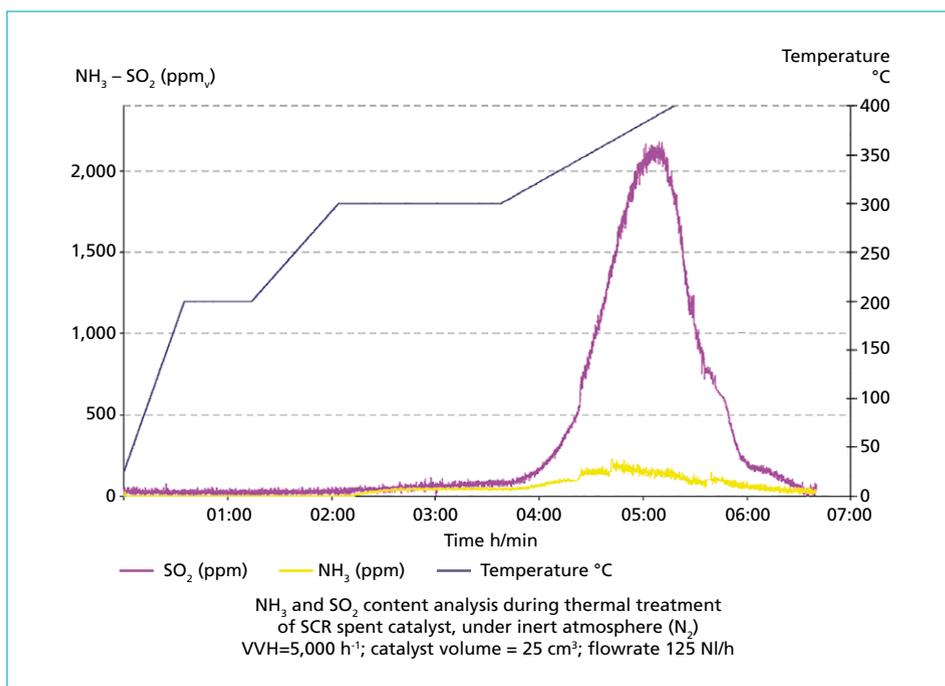


Figure 7: Pollutants unwinding during test regeneration

It is also important to underline that, the test being performed under neutral atmosphere (nitrogen), SO₂ break-up did not lead to sulphur emission under SO₃ form during regeneration.

The results from the tests show the risk of exceeding emission limits, especially for SO_x , during the regeneration phase, and justify the principle of recycling flue gas upstream of the flue gas treatment during regeneration, allowing emission control under any operation condition.

3. Advantages of *closed-loop* regeneration (VE patent)

Pollutants control even during regeneration

Recycling the flue gases from the reactor compartment undergoing regeneration upstream of the flue gas system allows pollutants neutralization disregarding of the operating condition of the SCR reactor (regeneration or not); stringent emission limits can be met and guaranteed.

This is paramount in our industry where the trend towards lower and lower emissions is well settled (waiting for the next Waste Incineration BREF).

Highly efficient regeneration also allows optimization of the de-diox capacity of the catalyst.

Efficient

Due to the recycling of flue gases during regeneration, part of the energy introduced in the stream by the gas burner may be recovered as sensible heat (according to flue gas treatment process), reheating flue gas upstream the SCR. For instance, with three cells and a flue gas treatment dry process operating at $180\text{ }^\circ\text{C}$, the temperature at SCR inlet is increased by about $25\text{ }^\circ\text{C}$, which allows a 18 % reduction of gas consumption (energy saved for $25\text{ }^\circ\text{C}$ flue gas reheating over a total of $140\text{ }^\circ\text{C}$).

Cost effective design

In comparison to a traditional mono-cell reactor, the multi compartment design of the catalyst naturally limits the variations of flue gas temperature and actual flow downstream the SCR during regenerations. This means that the design of the ID fan and stack can be optimized, and that the bottle neck in treatment capacity is strongly reduced due the regeneration condition.

Friendly to final (external) economizer

The trend towards an increasing energy efficiency of waste to energy plants makes necessary the installation of external economizers downstream of flue gas treatment in order to recover the sensible heat of the flue gases before evacuation to the stack. Flue gas condensing heat exchangers are also more and more current.

With traditional catalyst design, when regenerating the temperature of flue gases downstream of the SCR is greatly increased (320 to $350\text{ }^\circ\text{C}$); this means harder requirements for the design of the heat exchangers downstream (for instance, risk of

vaporization inside the economizer) and makes it impossible the recovery of the natural gas energy injected in the flue gases (designing final economizer for flue gas cooling from 320 °C to 140 °C during regenerations only does not make sense).

The multi compartment design of the catalyst naturally limits the increase of flue gas temperature downstream the SCR during regenerations (~200 °C in a 3-cell-design) and reduces carbon footprint of the plant (natural gas energy not spoiled).

Modular/evolutive

With honeycomb catalyst, the solution is based on a 3-compartment standard design (number of cells may vary according to size or design conditions of the plant). Each compartment can be equipped with three layers of catalyst (in standard, two layers are installed, one is empty for further installation during catalyst lifetime). Equipment such as instrumentation, dampers is the same for every compartment.

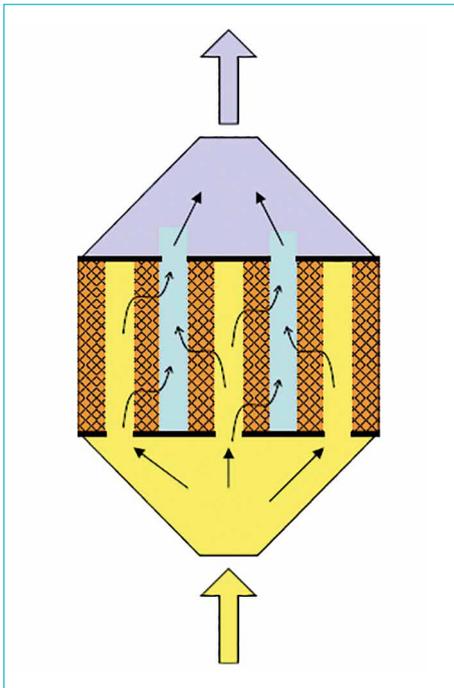


Figure 8: Reactor cell (bulk catalyst)

Arrangement can be adapted in order to allow easy adding of one additional compartment in order to cope with evolutions in the operating conditions of the plant (increase of waste lower heating value, decrease of emission limits, ...).

With bulk catalyst, the solution is based on a standard compartment design; number of cells is determined according to the size of the plant.

Reduction of gas burner power

Due to the modular multi-compartment design of the reactor, the gas burner power is reduced according to the number of cells installed, since only the reheating of a fraction of the total flue gas flow is needed.

The reduction of the gas burner nominal power proves interesting when local gas fares depend on the installed power (example: France).

Bibliografische Information der Deutschen Nationalbibliothek

Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.dnb.de> abrufbar

Thomé-Kozmiensky, K. J.; Thiel, S.; Thomé-Kozmiensky, E.;
Winter, F.; Juchelková, D. (Eds.):

Waste Management, Volume 7
– Waste-to-Energy –

ISBN 978-3-944310-37-4 TK Verlag Karl Thomé-Kozmiensky

Copyright: Elisabeth Thomé-Kozmiensky, M.Sc., Dr.-Ing. Stephanie Thiel
All rights reserved

Publisher: TK Verlag Karl Thomé-Kozmiensky • Neuruppin 2017

Editorial office: Dr.-Ing. Stephanie Thiel, Elisabeth Thomé-Kozmiensky, M. Sc.

Janin Burbott-Seidel and Claudia Naumann-Deppe

Layout: Sandra Peters, Anne Kuhlo, Ginette Teske, Claudia Naumann-Deppe,

Janin Burbott-Seidel, Gabi Spiegel and Cordula Müller

Printing: Universal Medien GmbH, Munich

This work is protected by copyright. The rights founded by this, particularly those of translation, reprinting, lecturing, extraction of illustrations and tables, broadcasting, micro-filming or reproduction by other means and storing in a retrieval system, remain reserved, even for exploitation only of excerpts. Reproduction of this work or of part of this work, also in individual cases, is only permissible within the limits of the legal provisions of the copyright law of the Federal Republic of Germany from 9 September 1965 in the currently valid revision. There is a fundamental duty to pay for this. Infringements are subject to the penal provisions of the copyright law.

The repeating of commonly used names, trade names, goods descriptions etc. in this work does not permit, even without specific mention, the assumption that such names are to be considered free under the terms of the law concerning goods descriptions and trade mark protection and can thus be used by anyone.

Should reference be made in this work, directly or indirectly, to laws, regulations or guidelines, e.g. DIN, VDI, VDE, VGB, or these are quoted from, then the publisher cannot accept any guarantee for correctness, completeness or currency. It is recommended to refer to the complete regulations or guidelines in their currently valid versions if required for ones own work.