NO_x lower than 200mg/Nm^3?

by Petro Miljö AB, Sweden

Petro Miljö was established in 1992, part of the Petrokraft AB group, which belongs to one of the key companies in the global shipping industry. Today, it is one of the most important suppliers of SNCR systems in the combustion industry, with more than 150 installations worldwide.

Thanks to SNCR systems it is usually considered possible to obtain a maximum NO_x reduction of about 50-65 per cent. To comply with the strict Swedish environmental regulations, Petro Miljö has, however, developed a SNCR system with much higher abatement degrees while maintaining a low level of ammonia slip, which is able to compete with SCR systems. In recent years it has even developed the SNCR 'low-NO_x' system.

This article publishes the results of 14 tests which were carried out in cement plants with a precalcination cyclone tower with a secondary burner. The aim of the tests was to show if a NO_x reduction down to 200mg/Nm^3 can be obtained with Petro SNCR technology.

Test description

The tests were carried out by injecting the reduction agent in the precalcination cyclone tower. A mobile SNCR system in different positions with different flows of reduction agent was used for this purpose.

Because of the immediate effect of the reaction it was decided to carry out several 30-minute proofs, verifying the baseline value before and after each proof concerning NO_x, NH_3 in the stack and CO.

Injection technology is the result of long experience by Petrokraft in the field of industrial burners. It has proved to be very efficient and can be easily adapted to different usage conditions

Mobile system

The mobile system consists of:

- 1000l tanks for the storage of the reduction agent
- pressurisation pump for the reduction agent
- measuring module for the reduction agent. This module makes it possible to measure the reduction agent manually.
- distribution module for the reduction agent and softened water. By means of this distribution module it is possible to distribute the reduction agent to the different injectors. The flow is shown by the relevant rotameter.
- injectors – injection technology is the result of a long experience by Petrokraft, in the field of industrial burners. Injectors have proved to be very efficient and they can be easily adapted to different usage conditions. The maximum number of injectors which can be connected at the same time is four.

Result reliability

- Process measures – the plants in object are provided with an online analyser which continuously measures NO_x, NH_3, CO and other concentrations as well as the flue gas flow in the kiln. The parameters which seem to have the largest margin of error are the measurement of NH_3 in the stack and the gas flow.
- Reduction agent flow – the reduction

Key test data

Number of tests:	14
Time:	2006-10
Plant location:	8 plants in Italy, 2 in Spain, 1 in France, 3 in Germany
Reduction agent used:	ammonium hydroxide NH_4OH (<25% NH_3), from now on referred to as NH_4OH
Test length:	3 days on average
Length of each proof:	minimum 30-120 minutes for each test
Number of proofs for each test:	from a minimum of 15 to a maximum of 36 injection proofs

Table 1: main results obtained during the 14 tests

Test no.	NO_x baseline (mg/Nm^3 @10% O_2)	NO_x with injection (mg/Nm^3 @10% O_2)	NO_x reduction (%)	NH_3 slip (mg/Nm^3 @10% O_2)	Delta CO (mg/Nmc)	Directmode (%)
2	1645	185	89	13	insignificant	100
3	860	164	81	n.a.	260	no
4	866	123	86	insignificant	350	no
8	679	168	75	9	150	100
9	1241	141	89	5	insignificant	50
12	860	127	85	insignificant	no correlation	60
14	1310	240	82	110	380	no
15	1255	159	87	18	320	30
16	908	71	92	8	insignificant	100
17	1451	123	92	5	insignificant	100
18	1391	182	87	22	insignificant	no
19	935	180	81	40	140	100
20	1270	94	93	5	17	100
21	1067	175	84	33	340	100

agent flow is measured by means of a rotameter, with a two per cent margin of error as a maximum. When comparing the level in the tank there is a 0.5 per cent margin of error.

Proof repeatability – in general, the plants showed a rather steady trend of nitrogen oxides, even if not continuously. The results showed a good repeatability. From a minimum of 15 to a maximum of 36 proofs per plant were carried out.

It is possible that there may be an error in the calculation of reaction efficiency, which is basically due to an error in measuring the flue gas flow.

Specifications concerning result evaluation

The results are based on the average values of the process variables calculated in the injection period, in particular as far as NO_x, CO, NH_3, O_2 and the flue gas flow are concerned.

The baseline value of reference for NO_x, CO and for ammonia in the stack was calculated by taking into consideration a period of 15-30 minutes with injections before and after the proof. The baseline value used for calculation is the average value before and after the proof.

The stoichiometric ratio, the ratio between the moles of NO_x abated and the moles of NH_3 injected, is taken into consideration to evaluate reaction efficiency.

Type of cement plants

The cement plants tested are preheater/precalciner cement kilns burning mainly petcoke and alternative fuels, but not all of them have a modern design.

Thermal profile

The temperature window in the injection zone in the plants is about 850-900°C.

Analysing the results

Is it possible to reduce down to NO_x values lower than 200mg/Nm³?

Depending on the amount of alternative fuel used, the NO_x limit can be much lower than 500mg/Nm³ at 10 per cent O_2. At the same time, lower limits for the future are expected in the European Union. Therefore, the target for the $DeNO_x$ systems is increasingly to get down to 200mg/Nm³. Petro Miljö AB is certain that it is possible to reach these strict limits.

One good example is a $DeNO_x$ system installed 1997 in Sweden, which is currently operating reducing from 800-1000mg/Nm³ down to values around 200mg/Nm³ at 10 per cent O_2 with very limited NH_3 slip.

With the 14 tests, Petro Miljö AB can show that these results are not an exception, and can be reached even on other plants. Table 1 summarises the main results obtained during the 14 tests.

The average values from the tests are as follows:

NO_x baseline:	1124mg/Nm³ at 10 per cent O_2
NO_x with injection:	152mg/Nm³ at 10 per cent O_2
NO_x reduction:	86 per cent
Ammonia slip:	24mg/Nm³ at 10 per cent O_2
CO formation:	245mg/Nm³

As the figures show, the results are much better than expected from a SNCR system, thanks to the right injector location, the performance of the Petro Miljö injectors, the injection strategy and the type of reagent. Please note that the control software is crucial to keep the same performance even over a long period of time. In the first 10 years, Petro Miljö has developed a reliable but sophisticated control software in operation in over 150 applications (about 30 cement plants).

Reduction:

- The average value of the reduction which took place in the 14 tests corresponds to 86 per cent, the maximum value is 94 per cent. Note that even higher reductions might be possible, but could cause high ammonia slip.
- The average value of the NO_x with injection is 152mg/Nm³ at 10 per cent O_2, significantly lower than the target, with some values even below 100mg/Nmc.
- The 200mg/Nm³ target can be reached starting from a NO_x baseline even higher than 1600mg/Nm³ at 10 per cent O_2 (see Test no. 2)

NH_3 slip formation

The unreacted ammonia, the ammonia slip, can be absorbed by the raw meal or it passes through the hot process and reaches the stack.

The amount of unreacted ammonia is increasing significantly with low temperature (about 840°C) and bad injection of the ammonium hydroxide.

During the tests the following results were noticed:

- the ammonia slip changed significantly when the operation of the plant switched to direct mode (the flue gases do not pass through the raw mill). For example, in two plants the ammonia slip increased from values lower than 1mg/Nmc to 80 and 90mg/Nm³, respectively when switching to direct mode (without any injection). But this effect has not been observed for all the tests.
- the difference in ammonia slip between direct mode and combined mode was very limited for a few applications (see Figures 1 and 2)
- for some applications, the ammonia slip at very high reductions was lower than 10mg/Nm³ even in direct mode (see Figures 2, 5 and 7).

From these observations it can be deducted that:

- in some cases the operation of the raw mill can act as an excellent slip cutter (close to 100 per cent absorption), in other cases it can be ineffective
- the ammonia slip is absorbed not only in the mill. It is more likely that the slip is absorbed in bag filter, and that the direct mode is affecting the operation of the bag filters, for example in terms of cleaning
- the ammonia slip at the stack depends not only on the temperature,

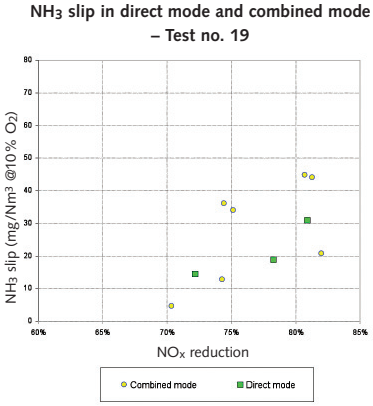

Figure 1: NH_3 slip in direct and combined mode

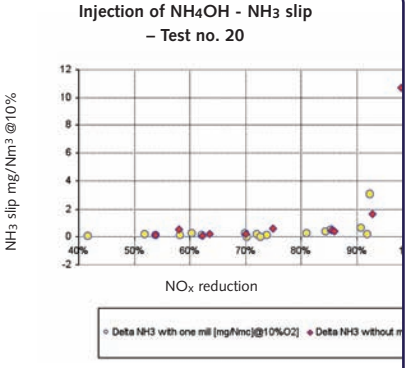

Figure 2: NH_3 slip in direct and combined mode

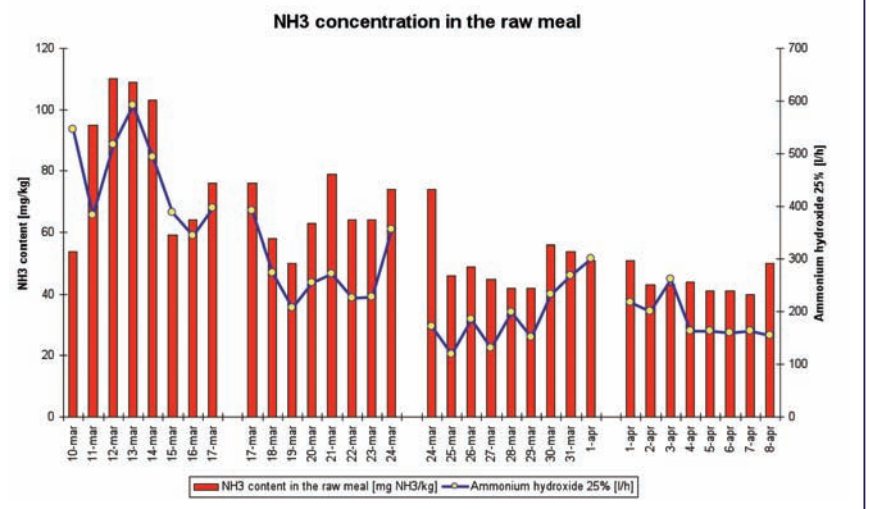

Figure 3: NH_3 absorption in the raw meal – Test no. 14

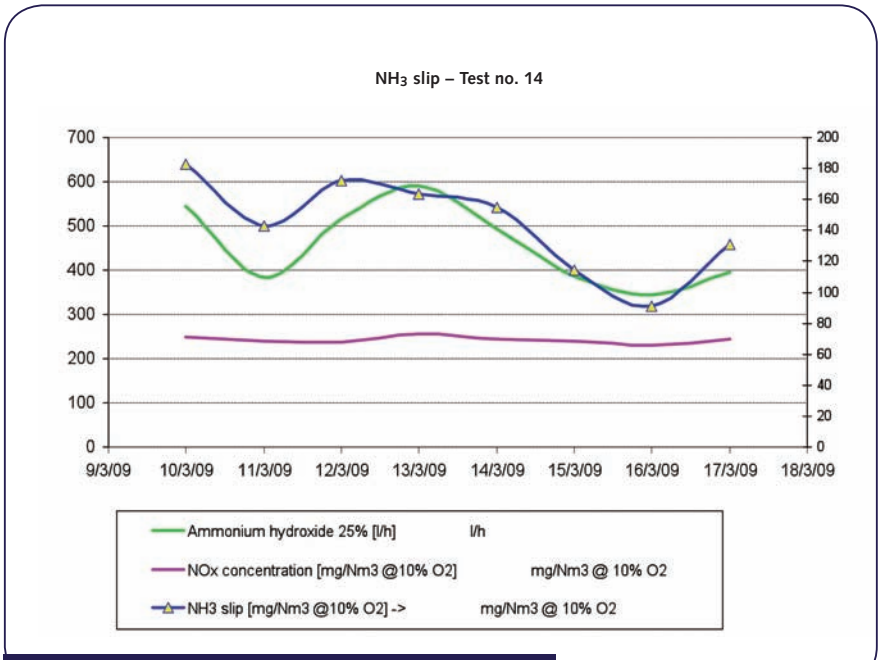

Figure 4: NH_3 slip during one week of continuous injection

the performance of the injectors and the reduction rate, but it is affected significantly by the raw mill and bag filter, and therefore the slip is difficult to foresee.

What happens with the absorbed ammonia slip?

The ammonia slip has been analysed more deeply during a four-week test (continuous injection of ammonium hydroxide, see Test no. 14). In this case, due to a very low residence time and a low temperature, the ammonia slip was particularly high. Figure 3 shows clearly a correlation between NH_3 content in the raw meal and the amount of injected reagent.

The NH_3 in the meal will be introduced in the process again, where it might accumulate or oxidise.

Figure 4 shows that the trend of the ammonia slip is following the flow of injected reagent, but it is not increasing during the week due to accumulation in the process. This is indicating that the ammonia slip will likely oxidise, forming N_2 and water, or NO_x. The ignition temperature of ammonia is about 630°C.

If for example 20mg/Nm ^{3} of ammonia slip is absorbed and re-introduced in the process, this might cause in the worst case 54mg/Nm ^{3} of NO_2, approximately up to only five per cent of the typical NO_x baseline.

Therefore, the mill plus the bag filter can act as an excellent slip cutter and the SNCR system can reach very high reductions rates with very low ammonia slip at the stack.

Depending on the type of plant, the slip can be absorbed even in direct mode (see Figure 2).

CO formation

The SNCR reaction may cause a CO increase as it is a reducing reaction.

CO formation noticeably depends on the process conditions as well as on the oxygen and CO concentration which is already present in the flue gas.

As you can see from Table 1, for some applications the CO increase can be around 300mg/Nm ^{3}, while for others the effect is very limited.

Trend

Figures 5 to 7 show examples of which point out the NO_x reduction trend to values below 200mg/Nm ^{3} at 10 per cent O_2.

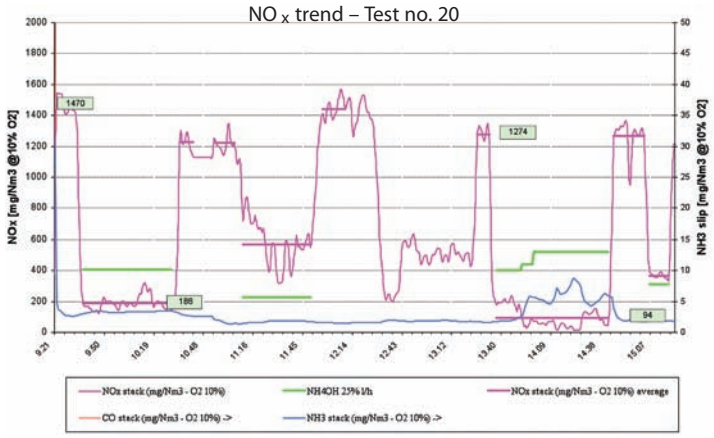

Figure 5: NO_x trend

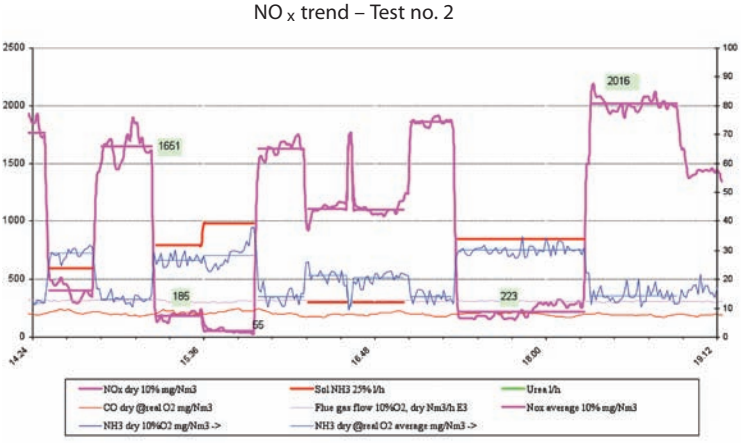

Figure 6: NO_x trend

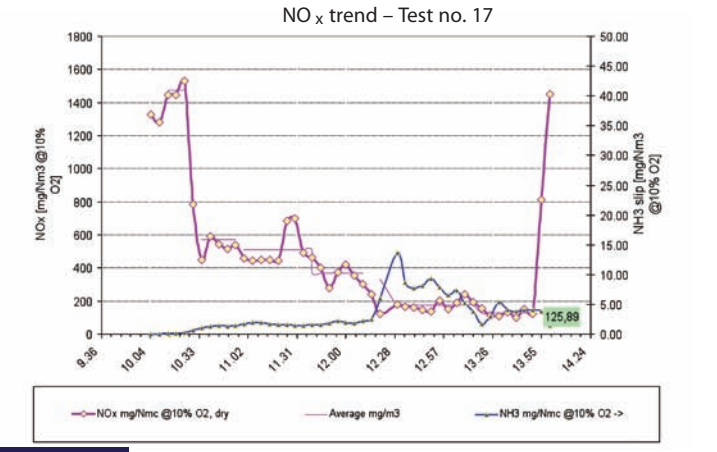

Figure 7: NO_x trend

Conclusions

- Petro Miljö AB showed with the 14 tests on cement plants with preheater/precalciner that the Petro SNCR technology can reduce the NO_x value from over 1000 to 200mg/Nm ^{3} at 10 per cent O_2, thanks to the correct injector location, the performance of the Petro injectors and the Petro software by using ammonium hydroxide.
- The average NO_x value of the tests is 152mg/Nm ^{3} at 10 per cent O_2, with an overage reduction of 86 per cent.
- The tests showed that the ammonia slip can change depending on the type of mill and bag filter, but for most tests remains below 30mg/Nm ^{3} at 10 per cent O_2.