STUDIES OF THE OPERATING BEHAVIOUR OF PRECALCINING PLANTS

N. Bodendiek, V. Hoenig,
Cement Industry Research Institute, Düsseldorf

Nowadays all newly built rotary kiln plants are equipped with precalcining systems [1][2][3][4][5]. At present, twelve of these plants are in operation in Germany, 9 of them with tertiary air duct. Through the use of staged combustion in precalcining kilns, it is possible to achieve an effective reduction in NO_x [6][7][8]. In addition to the staged combustion, an SNCR plant can be installed if a further NO_x reduction is necessary [9][10]. Although the staged combustion process and the SNCR process have already been used individually for many years, there nonetheless still remain gaps in our knowledge concerning the relationships between the formation of NO and the degradation of NO [11].

Factors Influencing NO Formation and Degradation

The chemical reaction mechanisms in the formation and the degradation of NO in the calciner are very complex. Both homogeneous reactions and reactions catalysed on solids take place [8][12]. The local conditions prevailing in the gas flow in the calciner, in particular the local concentration of oxygen, are of decisive importance. The most important local factors are shown in Table 1:

Temperature	
Concentration	O_2
	NH_3 , HCN (and similar compounds)
	NO
	hydrocarbon radicals
	OH radicals
	CO
	catalytically active solids (raw meal, char)
	nitrogen-containing residual char
(Residence time)	

Table 1: Local factors influencing NO formation and degradation

This also means that the flow conditions in the calciner also play an important part in the formation and in the degradation of NO. Owing to the fact that the gas viscosity at temperatures of ca. 850°C is comparatively high, intensive mixing of fuel, combustion air and raw meal can only be achieved with difficulty. Hence as a rule fuel-rich and oxygen-rich gas streamers are formed in the calciner.

Studies Performed

If the calciner is in simplified terms regarded as a stirred vessel, as a kind of black box, into which the fuels and combustion air are fed, and as a result a certain output of NO is created, many effects can only inadequately be described.

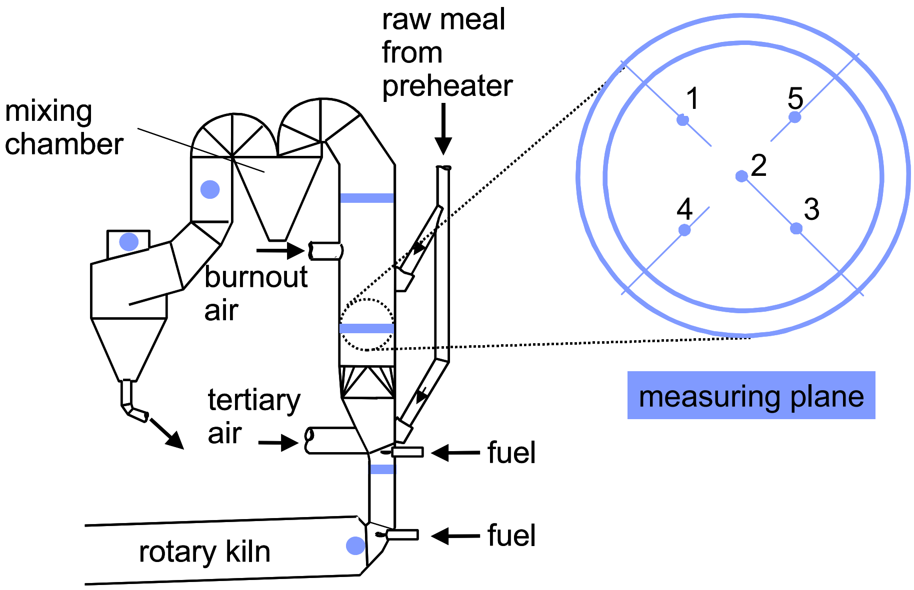

Figure 1: Measurement of the gas concentration (profile measurements)

Instead it is necessary to look inside this black box. Under normal operating conditions this is scarcely possible, since relevant measurements are very costly. Hence for some years the Research Institute of the Cement Industry has been carrying out systematic experiments on several kiln plants from various plant manufacturers. In the region of the calciner, several measurement points were installed in order to determine the local gas composition. Figure 1 shows the position of the measurement points in the case of a calciner from Krupp Polysius. Similar measurements have already been carried out on calciners from other plant manufacturers.

Apart from the standard measurement points “kiln inlet” and “raw gas after heat exchanger”, these included the level before and after addition of the fuel, after input of the burn-out air, after the mixing chamber and above the lowest cyclone stage. In order also to detect gas streamers here, measurements were made not only at one, but rather at as many points as possible in the flow cross-section and then concentration profiles were constructed. Water-cooled probes were used for each gas sampling. The measurement data firstly provide an exact picture concerning the mixing of fuel and combustion air, so that appropriate optimisation measures can be taken. Secondly, it is possible in this way to determine where in the calciner the formation of NO takes place, and where it is degraded.

Results of the Experiments with Staged Air Supply

In Figure 2, the NO mass flow is plotted against the gas residence time in the calciner.

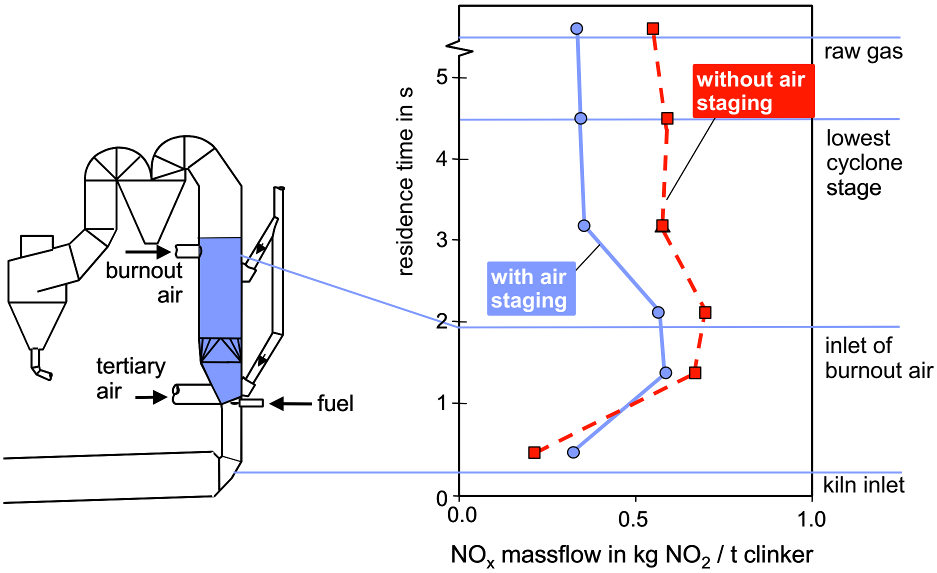

Figure 2: Course of NO formation or NO degradation in the calciner (operating experiment 1).

In the operation set-up with and also without staged air supply, it can be seen that in the course of the combustion firstly an increase in NO occurs in the lower part of the calciner and thereupon a decrease in NO again in the upper part of the calciner. The NO formation in the lower part is presumably mainly attributable to the fact that at the level of the fuel input a considerable part of the tertiary air is also added and fuel and combustion air are not completely mixed. Measurements have shown that because of streamers formation in the vicinity of the burners, local oxygen contents of up to 5 % can be present. Hence the HCN and ammonia compounds liberated in the pyrolysis of the fuel can hardly contribute to an NO decrease, but rather still lead to additional NO formation. For the same reason, the NO-degrading action of hydrocarbon radicals at this point is also very slight. The decrease in NO in the upper part of the calciner is attributable partly to the fact that as combustion progresses there is increasing formation of CO, which in the presence of calcium oxide can reduce NO to N_2. Moreover, wet chemical measurements have shown that ammonia concentrations of up to 200 ppm can be present at this point in the calciner. It is to be presumed that, as in the SNCR process, a considerable part of the NO degradation takes place via the reaction with ammonia.

In the kiln plant studied, the tertiary air input into the calciner could be adjusted with a slider valve in such a way that the tertiary air can either be input 100 % together with the fuel or optionally with 40 % bypassing the fuel input, in the upper part of the calciner. By this technique, referred to as staged air input, an oxygen-poor zone is created in the lower part of the calciner. The NO profiles presented in Figure 2 show that by means of the staged air input, the formation of NO in the lower region of the calciner is boldly reduced. This confirms the supposition that it is in particular the oxygen concentration at the location of the fuel input that has a considerable influence on NO formation and/or degradation in the calciner. At low oxygen concentrations, the HCN, ammonia and hydrocarbon compounds liberated in the pyrolysis of the fuel contribute more strongly to the degradation of NO, so that part of the newly formed NO is reduced again to N_2.

In order to obtain a simple assessment parameter for the combustion conditions in a furnace, the so-called stoichiometric air ratio is often used. It is defined as the ratio of the available oxygen supply to the minimum oxygen supply required for combustion and is as a rule calculated by an assessment of the quantities of fuel and air. For the precalciner plant studied, this estimated stoichiometric air ratio was 1.06, if regular fuel was used and the plant was operated without staged air supply. By means of an altered operating setting, in which an oxygen-poor zone for NO reduction is created by partition of the tertiary air in the lower part of the calciner, the estimated stoichiometric air ratio could be lowered to a value of 0.95. On the use of coarse fuels, by which 30 % of the regular fuel in the calciner was replaced, an estimated stoichio-metric air ratio of 1.02 was found.

However, in the calculation of the estimated stoichiometric air ratio the simplifying assumption is made that the fuel is immediately and completely converted and is not, as in the real situation, subject to mixing and combustion kinetics. In order to study the effect of the kinetics in more detail, the gas composition in the reduction zone was determined in all experiments, and dust samples were taken from the gas flow in the calciner. The local degree of CO burn-out could then be determined from the measured CO concentration, and the local degree of char burn-out from the carbon content of the dust samples. The effective stoichiometric air ratios calculated from this are compared with the estimated stoichiometric air ratios in Table 2.

	Experimental setting 1	Experimental setting 2	Experimental setting 3
Fuel used	regular fuel	regular fuel and coarse fuel	regular fuel
Experimental setting	with staged air input	with staged air input	without staged air input
Estimated stoichiometric air ratio	1.06	1.02	0.95
Effective stoichiometric air ratio	1.23	1.16	1.01

Table 2: Estimated and effective stoichiometric air ratios (Operating experiment 1)

The result of the assessments shows that the stoichiometric air ratios actually arising in the reduction zone at all operating settings were about 0.1 higher than those calculated from the estimate. It is thus necessary to take account of the combustion kinetics in the design of a calciner with staged combustion. This applies especially for the use of coarse fuels and fuels of low reactivity. For practical operation, this means that for the establishment of an effective stoichiometric air ratio of for example 0.9, the fuel and air ratios must be regulated so as to give an estimated stoichiometric air ratio of ca. 0.8.

Effect of the Stoichiometric Air Ratio on NO Formation and Degradation

In power station technology, it has been found that the optimal stoichiometric air ratio for NO_x reduction during coal combustion is usually ca. 0.85 – 0.9 [13][14][15]. However, the question arises as to how far the findings from power station technology are transferable to the cement production process.

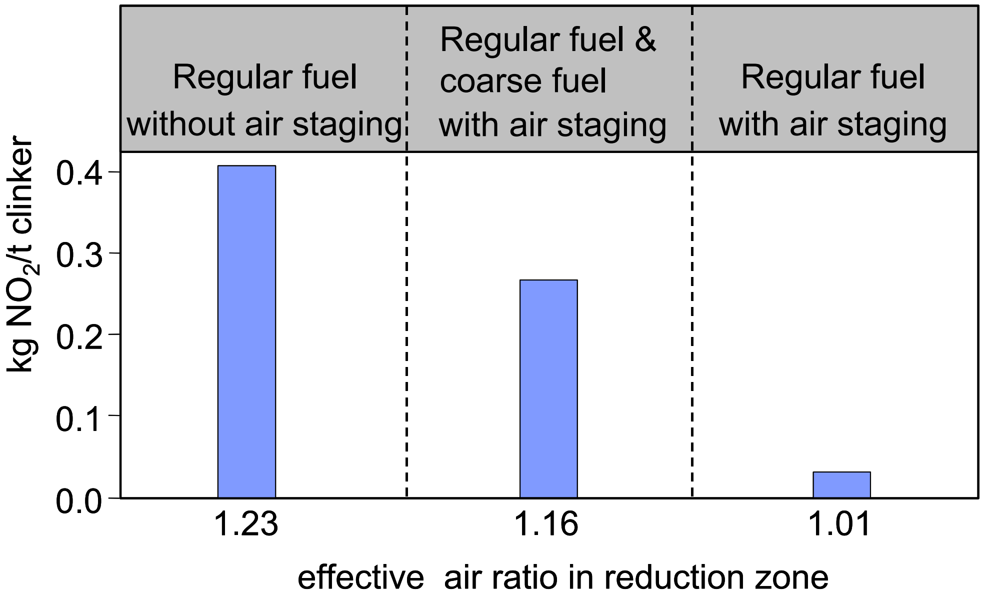

Figure 3: NO formation in calciner (Operating experiment 1)

Figure 3 shows the increase in the NO mass flow in the calciner determined in the experiments. Although at all experimental settings there was NO formation in the calciner, the NO_x emissions for the plant were markedly below those of a conventional plant with no precalciner technology. The reason for this is that no thermal NO is formed in the calciner and the conversion ratio of fuel N to NO is comparatively small. In the experiments on the plant studied, it can be seen that the formation of NO in the calciner decreases with decreasing stoichiometric air ratio in the reduction zone. This corresponds to the operating experience that has been obtained in many cement works and is also in agreement with the experience from power station technology. However, a further decrease in the stoichiometric air ratio could not be achieved in the studied plant by means of process technology measures. Only in experiments on another plant also operating settings at which very low stoichiometric air ratios were set in the calciner could also be investigated. In that case, lignite was used as the regular fuel, as in the previously described experiments.

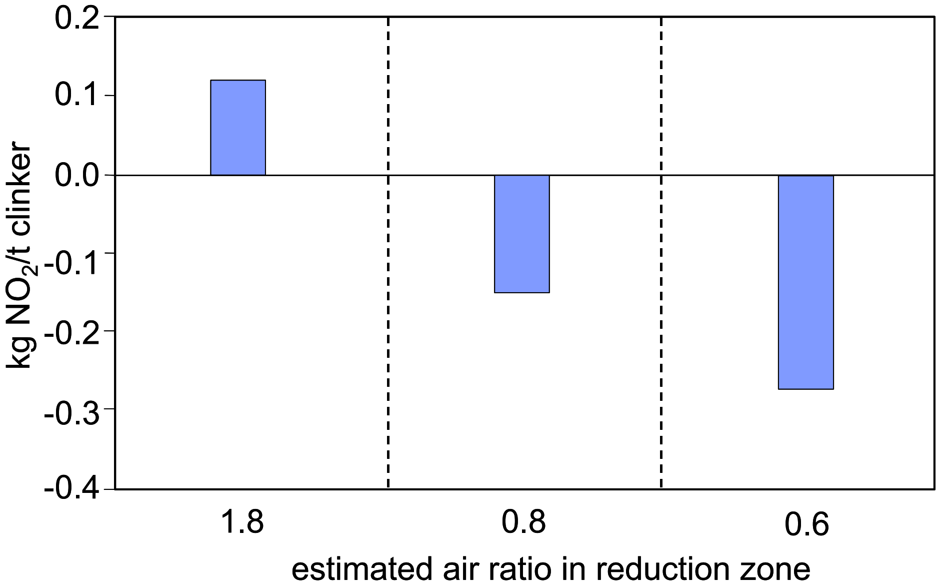

Figure 4 : NO formation and NO degradation in calciner (Operating experiment 2)

Figure 4 shows the increase or decrease in the NO mass flow as a function of the stoichiometric air ratio in the reduction zone. As in the first kiln plant, with decreasing stoichiometric air ratio there is a decrease in the formation of NO in the calciner. By decreasing the stoichiometric air ratio to values of 0.8 and 0.6, it is even possible to achieve a decrease in the NO mass flow. This means that in the calciner not only is the fresh formation of NO from fuel N stopped, but also NO from the main furnace is degraded [16]. The optimum value for the stoichiometric air ratio in the reduction zone of the calciner is apparently neither 0.9 nor 0.8, but markedly lower still.

Combination of Staged Combustion and SNCR Processes

In cases where the NO_x reducing action of the staged combustion does not suffice to maintain the stipulated emission values, isolated attempts have very recently been made to operate an SNCR plant in addition. The combination of these two processes is already described in the BAT Reference Document of the European Commission from the year 2000 as a so-called “Emerging Technique”, i.e. as a technology possibly usable in the future [17]. In order to investigate the interactions between the two processes, the Research Institute of the Cement Industry has carried out operating experiments on precalciner plants.

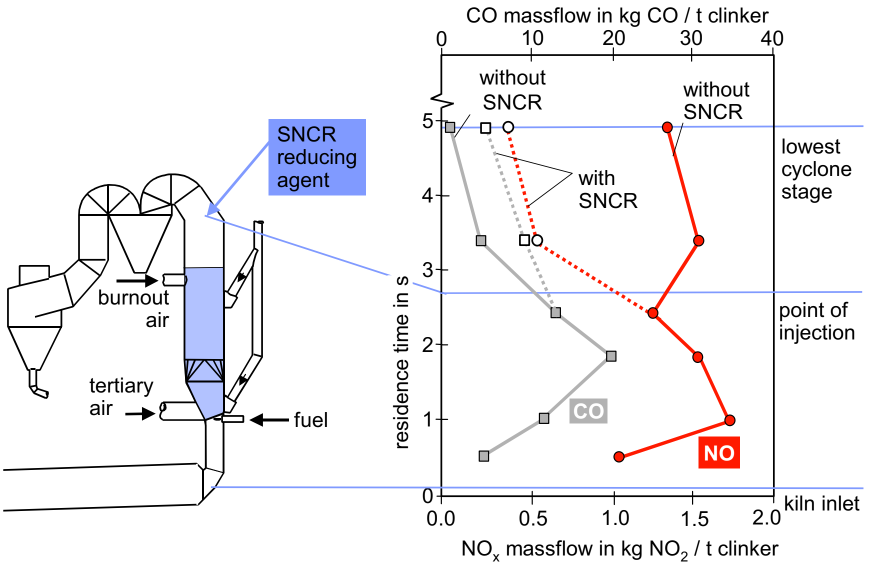

Figure 5: Combination of staged combustion & SNCR process (Operating experiment 3)

In Figure 5, the variation in the NO mass flow with the gas residence time is plotted for one of the kiln plants studied. By means of the staged air input, the staged combustion was adjusted in such a way that the NO reduction in the reduction zone proceeds optimally. By spraying in a reducing agent shortly before the mixing chamber, an additional 65 % reduction in the NO_x emission was achieved at an NH_3/NO molar ratio of 1.5. From the variation in the CO mass flow it can be seen that in the staged combustion a considerable quantity of CO is at first formed, which can however largely burn out in the region of the mixing chamber and in the bottom cyclone stage. By the operation of the SNCR plant, however, the CO burn-out is markedly impeded. The CO emission increased from 0.02 to 0.05 volume % in the SNCR experiments.

The reasons for the interactions observed have not yet been adequately explained. Possibly they are attributable to the fact that both for the SNCR reaction and for the CO degradation OH radicals are required, which are however not present in an adequate amount at the prevailing temperatures. As a result, a competitive situation between the two reactions could arise [9][18]. It seems advisable as a rule to separate the reaction space for the SNCR process spatially from that for the staged combustion. In the installation of an SNCR plant at an existing precalciner furnace, this can be achieved by selecting a point for the reducing agent injection at which the CO burnout has already proceeded sufficiently far. In the design of new calciners, an adequate residence time should be provided so that CO burn-out and SNCR reaction can proceed consecutively, without problems with ammonia slip arising. In future, it is intended to carry out further studies on kiln plants in which the interactions described between staged combustion and SNCR processes will be studied in yet more detail.

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Refences

[1] Kehl, P.; Scharf, K.-F.; Scur, P.; Wirthwein, R; ZKG International 51 (1998) No. 8, pp. 410-426; The operating results from the first 30 months with the new kiln line 5 at the Rüdersdorf cement works.

[2] Philipp, J. ; Thormann, J. ; Bucholski, A. ; Müller, U.; ZKG International 50 (1997) No. 2, pp. 76-85; Design and operating results with the new kiln plant at the Bernburg works of E. Schwenk Zementwerke KG

[3] Grydgard, P. E. ; International Cement Review, May 2000, pp. 35-39; Millennium Plants

[4] Rhin, C; ; ZKG International 53 (2000) No. 4, pp. 196-203; The combustion of oil coke in the RSP-MINOX calciner

[5] Yoshida, S. ; Taguchi, S. ; World Cement, December 2002, pp. 41– 45; Advanced Technology

[6] Menzel, K; Bertschinger, P ; International Cement Review; June 1997,
pp. 65-72; Losing NO_x without losing money

[7] Torkheim, L.A.; Bjerketvedt, D.; Husum, I.; Hoidalen, O. ; ZKG International 51 (1998) , No. 1, pp. 12 – 23; NO_x reduction in a cement kiln with precalcining by reductive combustion of plastic

[8] Thomsen, K. ; Jensen, L.S. ; Schomburg, F. ; ZKG International 51 (1998) No. 10, pp. 542-550; Commissioning and operation of the ILC-LowNOx calciner at Lone Star in St. Cruz, California

[9] Rose, D. ; Adler, K. ; Erpelding, R. ; ZKG International 54 (2001) No. 7,
pp. 362-371; NO_x reduction with the SNCR process in kiln plants with staged combustion

[10] Hoenig, V. ; Hoppe, H. ; Bodendiek, N. ; ZKG International 54 (2001) No. 7, pp. 356-361; Possibilities and limits to NO_x reduction in the cement industry Part 2

[11] Young, G.L.; Seebach, M.; ZKG International 52 (1999) No. 6, pp. 304 – 321; NO_x reduction at kiln plants in the cement industry

[12] Scheuer, A.; Dissertation TH Clausthal 1987; Theoretische und betriebliche Untersuchungen zur Bildung und zum Abbau von Stickstoffmonoxid in Zementdrehofenanlagen

[13] Chen, S. L.; McCarthy, J. M.; Clark, W. D.; Heap, M. P.; Seeker, W. R.; Pershing, D. W.; 21st Symposium (International) on Combustion (1986), Combustion Institute, Pittsburgh; Bench and pilot scale process evaluation of reburning for in-furnace NO_x-reduction

[14] Mechenbier, R. ; Dissertation Ruhr-University Bochum 1989; Experimentelle Untersuchung der Stickoxid-Reduktion durch Brennstoffstufung mit Methan bei der Kohlenstaubverbrennung

[15] Burch, T. E. ; Tillmann, F. R. ; Chen, W.-Y.; Lester, T. W. ; Conway, R. B. ; Sterling, A. M. ; Energy Fuels (1991), 5, 231, Partitioning of Nitrogenous Species in the Fuel-Rich Stage of Reburning

[16] Hoenig, V. ; Hoppe, H. ; Bodendiek, N. ; ZKG International 54 (2001) No. 4, pp. 165-171; Possibilities and limits to NO_x reduction in the cement industry Part 1

[17] Integrated Pollution Prevention and Control (IPPC). Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries. EIPPCB, Seville, December 2001

[18] Ljungdahl,B. ; Larfeldt, J.; Powder Technol. 120 (2001) pp. 55-62; Optimised NH_3 injection in CFB boilers