

# EFFECTS OF PROCESS TECHNOLOGY ON THE BEHAVIOUR OF MERCURY IN THE CLINKER BURNING PROCESS

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## Legal Background

In the European Incineration of Waste Directive, which had to be adopted by national law by the end of 2002, a limit value of 0.05 mg/m<sup>3</sup> for mercury (Hg) is specified [1]. In Germany the implementation of the limit value into national law is taking place by amendment of the 17th Ordinance of the Federal Environmental Impact Law. (17. BImSchV) [2]. In this Ordinance, a limit value of 0.03 mg/m<sup>3</sup> for mercury had already been introduced early in 2001 for waste incineration plants. For co-incineration plants, such as for example cement works, this value applies only for the exhaust gas flow from the wastes.

With the current amendment of the 17. BImSchV, the requirements for co-incineration plants are to be raised still further. They are largely to be made equivalent to the dedicated waste incineration plants. As in the European Incineration of Waste Directive, demanding emission limit values particularly for the co-incineration of wastes in production plants. They replace the so-called “mixing rule” which had to be previously applied. Different from the European Incineration of Waste Directive the 17. BImSchV sets a mercury limit value for cement works of 0.03 mg/m<sup>3</sup> as the daily average value. This limit value is independent of the waste substitution. Under an exemption rule, a limit value of 0.05 mg/m<sup>3</sup> as the daily average can be specified, if proof can be provided that the mercury emissions are predominantly raw material-based and do not originate from the wastes.

## Mercury Inputs

Against this background, the Research Institute of the Cement Industry has in the past two years carried out studies with the aim of extending existing knowledge concerning the behaviour of mercury in the clinkering process under varying operating conditions.

Like all trace elements, mercury is introduced into the clinkering process only in small amounts via the fuels and the raw materials. The mercury introduced into the combustion process accumulates in the external cycle of the kiln system between preheater, raw mill and exhaust gas filter, which acts as a temporary buffer for the mercury in the cycle. Of especial importance for the accumulation of mercury in the external cycle are the temperature profile in the exhaust gas path, the mode of operation (mill-on/mill-off operation) and the degree of raw meal removal from the dust filter [3].

In kiln test carried out by of the Research Institute of the Cement Industry at four cement works, mercury concentrations in limestone and marl of between 0.02 and 0.13 mg/kg were found, depending on the different deposits. Within an test period of 4 weeks, the mercury content in the raw material at one plant varied by a factor of 2. On the other hand, the mercury concentrations in the different fuels – at all works, secondary fuels were also used as well as coal – were almost constant over the test periods and were of a similar order of magnitude.

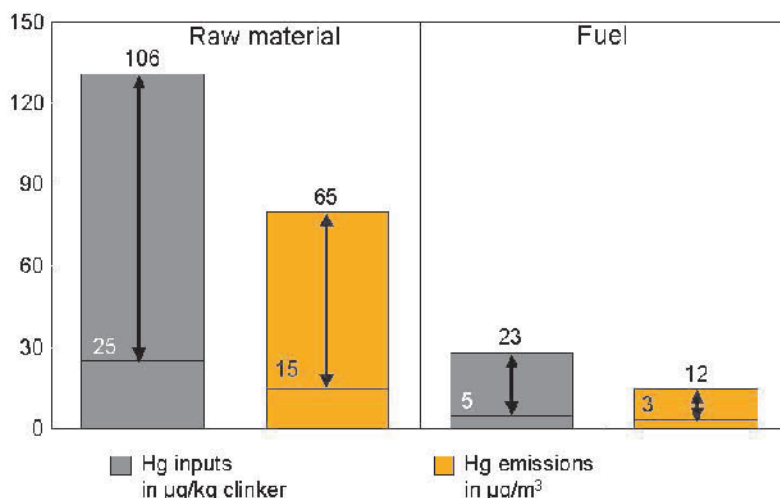


Figure 1: Mercury inputs and mercury emissions resulting from these

On the basis of the aforesaid mercury concentrations, specific mercury intakes of 25 to 106 µg/kg clinker via the raw materials and 5 to 23 µg/kg clinker via the fuels were found at the plants studied, figure 1. In percentage terms, the

mercury input via the raw materials was more than 80% of the total intakes. On the pessimistic assumption that almost all the mercury is emitted, with the plant in the equilibrium state this would give mercury emissions of up to 77  $\mu\text{g}/\text{m}^3$ . 65  $\mu\text{g}/\text{m}^3$  of these emissions were raw material-related and up to 12  $\mu\text{g}/\text{m}^3$  fuel-related. On account of the markedly higher mass flow of the solid raw material compared to the fuel mass flow, the level of the mercury cycle at all four different works was thus decisively determined by the inputs via the raw materials.

### Cycle studies

The observed ranges of variation in the mercury emissions suggested that the mercury has a dynamic cycle behaviour, which is determined above all by the different operating conditions of the kiln installation. As the studies have shown, the dynamic behaviour is influenced by the removal of meal from the exhaust gas filter, the waste gas temperature and waste gas management, the binding of the mercury in the feed material and the ratio between mill-on and mill-off operation time.

Figure 2 shows the result of a cycle study on a kiln installation shown by way of example over a period of one week. The kiln installation was operated mainly in mill-on operation, about 3 to 6 hours per day the mill was not in operation. During this week, mercury was discharged from the cycle by discontinuous removal of meal from the exhaust gas filter at times when the mill was not in operation. The development of an external cycle can clearly be discerned. Thus the greater part of the mercury is stored in the cycle. About half of the intake is emitted and is taken out of the cycle by the meal removal. Intakes into and outputs from the process maintain themselves in balance; the system is in equilibrium.

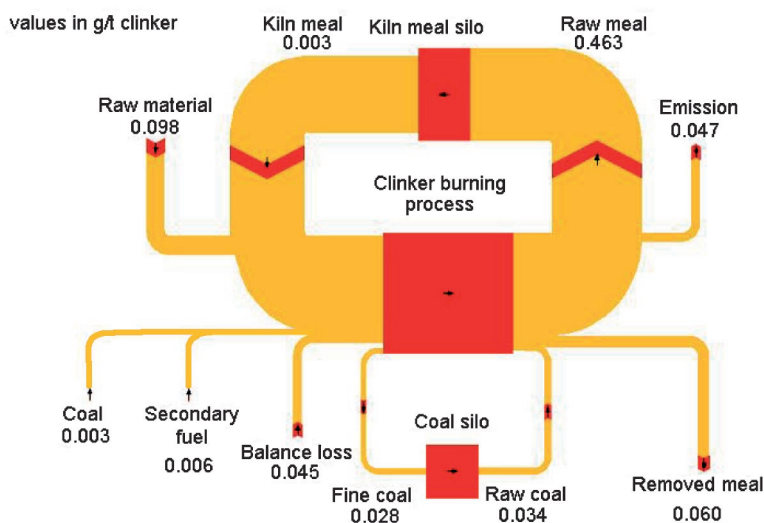


Figure 2: Mercury balance (with removal of meal)

In Figure 3, in which the mercury inputs and outputs with and without removal of meal are shown, it is also clear that with removal of meal the inputs and outputs equalise.

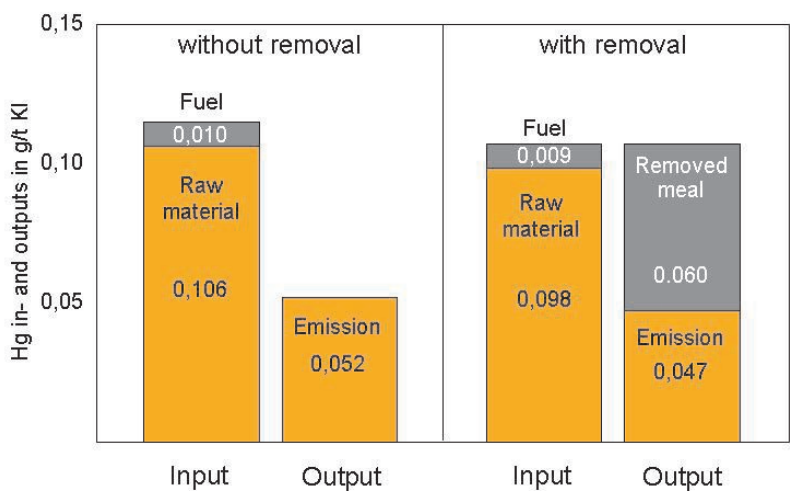


Figure 3: Inputs and outputs with and without removal of meal

On the other hand, if no meal is removed, markedly more mercury is introduced into the process than is removed. As a result, the quantity of mercury stored in the system continuously increased, and the cycle intensified with time.

### Dynamics of the Process

Material balances only reflect the behaviour of cycle substances in the stationary state or averaged over a certain test period. In order to obtain information about the dynamic behaviour, the plant data were also continuously recorded during the tests. In particular, the mercury mass flows in the plant were determined over time. If the whole kiln system is covered by such a balance, i.e. the entire kiln including the raw mill and the waste gas path being included, then their dynamics are above all determined by the mercury content levels in the materials used. If only the kiln itself is covered by the balance, Figure 4, the cycle dynamics are above all determined by the sequence and length of mill-on and mill-off operation periods. Because of the weekly rhythm of the operating states, markedly different inputs via the kiln meal into the preheater can occur. In the example shown, the inputs varied by a factor of 2 within one week. The rise until the middle of the week was attributable to the fact that at the weekend the kiln installation had been operated with the mill in operation. Emissions were the only output of mercury from the cycle. As a result, more mercury was introduced into the system than is removed. At the same time, in the present case, it must be borne in mind that because of the storage volume of the kiln meal silo, the inputs as kiln feed reaches the combustion process approx. 3 days after grinding.

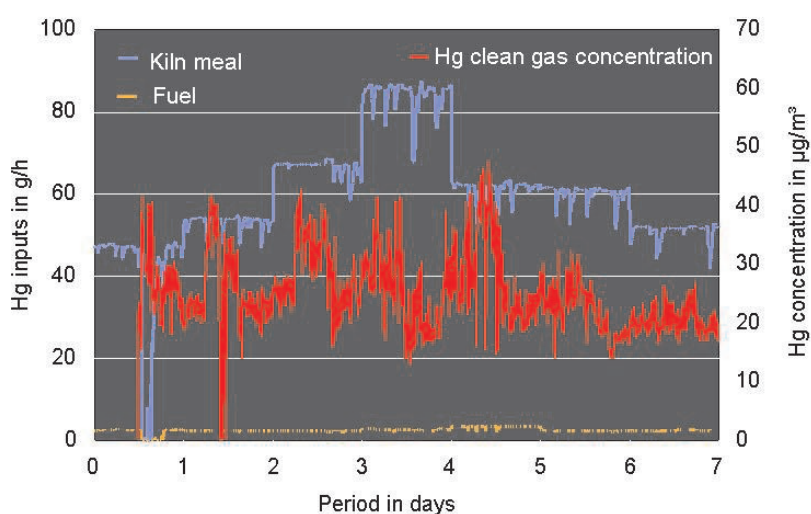


Figure 4: Internal cycle

If the cycle was relieved after the start of the week by the removal of meal in mill-off operation, the intakes via the kiln meal again decrease. However, no significant effect on mercury emission was observed here, since in the present case the exhaust gas temperatures were comparatively low, at 120 °C when the mill was in operation and 130 °C when the mill was not in operation, respectively.

### Effect of Exhaust Gas Temperature

In order to investigate the effect of the waste gas temperature on mercury emission in more detail and over a wider temperature range (130 to 170 °C), the studies were thereupon continued on two different rotary kilns (called A and B, Figure 5). Both in works A and also in works B, the external cycle was relieved by the removal of meal from the exhaust gas filter. Also, the proportion of meal removed at works A (6 kg/t clinker), was markedly lower than at works B (68 kg/t clinker).

Whereas at works A the mercury emissions tended to increase with increasing waste gas temperature, almost no effect was observed at works B. At works A, in particular with a temperature reduction from 150 to 137 °C under mill-off operation, a decrease in the mercury emissions could be achieved. However, above 150 °C, the temperature effect is negligible. This is due firstly to the condensation behaviour of the mercury, but secondly possibly also to the mode of binding of the mercury to the raw material or kiln feed. Over 90% of the mercury was present as elemental mercury, which at these temperatures is mostly present in gaseous form. Hence the formation of condensation nuclei on which the elemental mercury is partly adsorbed, so that it can then be separated in the filter, only takes place at lower temperatures.

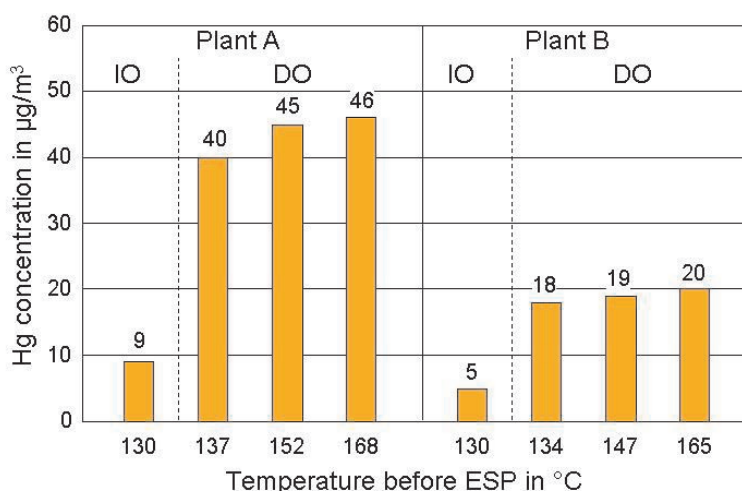


Figure 5: Effect of waste gas temperature on mercury emissions

At works B, the external cycle was relieved by the greater removal of meal and the high proportion of mill-off operation, to such an extent that no external cycle between preheater and exhaust gas cleaning plant had developed. This is the reason why on this plant a temperature reduction had no significant effects on the mercury emissions. Likewise, the mercury in the exhaust gas in this kiln plant was also present almost entirely in elemental form, so that the temperature effect was in any case weakened. In mill-on operation, the emissions at both plants were markedly lower than in mill-off operation. This is because of the lower exhaust gas temperatures in combination with the good binding capacity of the raw material in the raw mill. The higher material flow at mill-on operation results in a stronger adsorption of the mercury present in gaseous form onto the solid particles than in the case of mill-off operation. Further examinations on the adsorption behaviour are planned for the near future.

#### Effect of Meal Removal

Figure 6 shows the effect of the exhaust gas temperature at works B with and without removal of meal from the exhaust gas cleaning plant. With removal of meal, it was once again found that reduction of the exhaust gas temperature from 165 °C to 132 °C at mill-off operation had no perceptible effect on the mercury emissions, since the mercury cycle was largely relieved by the meal removal. With comparatively low mercury inputs via the raw material (0.02 mg/kg), the mercury emissions at mill-off operation were approx. 0.03 mg/m³, irrespective of the exhaust gas temperature. However, with increasing mercury input it must be assumed that the emission levels, under otherwise identical conditions, would be correspondingly higher.

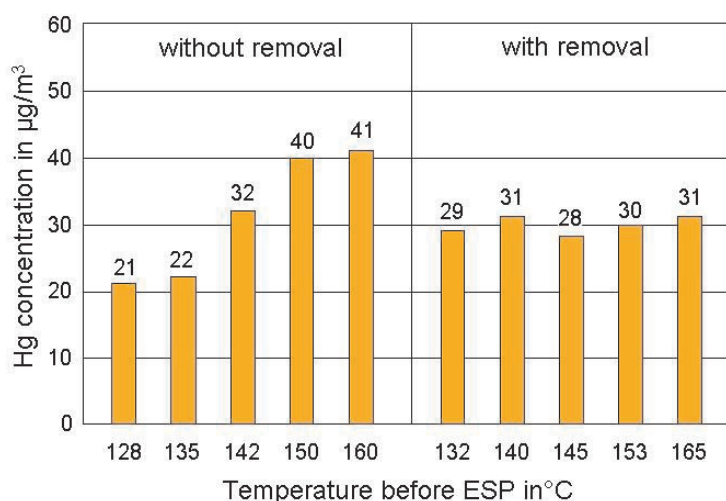


Figure 6: Effect of the removal of meal on mercury emissions

If on the other hand no meal is removed from the exhaust gas filter, then the mercury emissions also increase with increasing waste gas temperature. In this case, the external cycle is not completely relieved, so that with increasing temperature a higher proportion of the mercury is emitted. The mercury emissions increase from approx. 0.02 mg/m³ to

over 0.04 mg/m<sup>3</sup>. This once again clearly shows that by decreasing the exhaust gas temperature, above all at mill-off operation, a reduction in the mercury emissions is in principle possible, if the mercury cycle is relieved by dust removal. The higher the mercury content in the meal removed, the more effective the relief. Hence it is advisable, as far as this is technically possible, to carry out the removal of kiln meal at mill-off operation.

### Summary

The mercury inputs into rotary kiln installations in the cement industry are low. They are mainly determined by the natural concentration levels in the raw materials. Besides the mercury input, the meal removal, the exhaust gas temperature - above all at mill-off operation -, the degree of binding of the mercury to the raw material and kiln feed, the exhaust gas management and the ratio of mill-on to mill-off periods determine the mercury emissions. At the same time, these individual factors influence one another and can therefore only be varied or influenced to a limited extent. Thus, material and process technology limits are set to the reduction of the mercury emissions.

However, a reduction of the mercury emissions, in particular of the emission peaks at mill-off operation, is possible by deliberate meal removal. Here the magnitude of the mercury cycle level critically determines the achievable reduction effect. The lower the mercury cycle level the smaller the effect of temperature on the mercury emissions. The studies by the Research Institute of the Cement Industry have shown that at the plants studied a limit value of 0.05 mg/m<sup>3</sup> can be met, with the inclusion of all process technology-based reduction possibilities. However, a limit value of 0.03 mg/m<sup>3</sup>, which is specified in the German 17. BImSchV, cannot always be ensured owing to the limited effect on the mercury cycle level, and in particular on the mercury concentration in the raw material, irrespective of the fuel usage.

### References

- [1] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste
- [2] 17. Ordinance under the Federal Environmental Impact Law on incineration plants for wastes and similar combustible materials of 27 July 2001
- [3] S. Schäfer, V. Hoenig, Effects of process technology on mercury emissions from rotary kilns in the cement industry, Zement-Kalk-Gips, No. 11, 591 – 601, 2001