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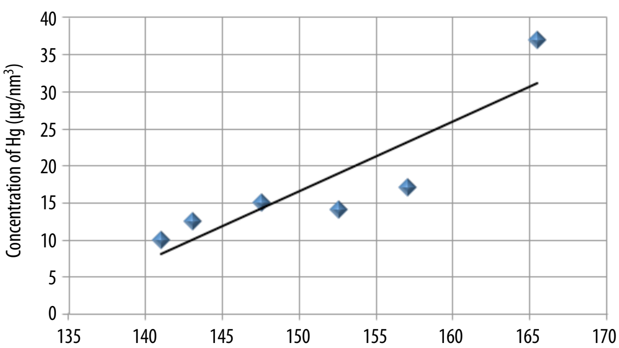
Alternative fuels - What about the environment? - Part 3

Alternative fuels are now a firmly-established reality in well-developed cement industries around the world and increasing amounts of alternative fuels are also being used in developing economies. In the third part of his research into the use of alternative fuels in the German cement industry, MVW Lechtenberg & Partner's Dirk Lechtenberg digs deeper into the German cement industry. Parts 1 and 2 of the report were published in the October and November 2013 issues of *Global Cement Magazine*.

On 15 October 2012 the Environment Council of the German Federal Parliament carried out an expert hearing on the government's plan for the implementation of the European Industry Emissions Guideline (IED).

The theme of coincineration of alternative fuels was also intensively discussed. It was emphasised at the hearing that mercury emissions from cement plants can be significantly reduced through a series of measures.

According to expert statements, "It primarily involves production-integrated measures and secondly cleaning technologies, which for old plants a minimum limit value of 10mg/m^3 (daily average value, 10% residual oxygen content) can and should be adhered to. In the case of production-integrated measures it involves a combination of additional preheating stages (reduction of waste gas temperature of around 320°C to 270–280°C, which means simultaneously improved energy efficiency), controlled waste gas conditioning (i.e. improved cooling) and targeted dust removal."[1]



Right - Figure 1: Correlation between exhaust temperature (°C) and Hg concentration at a German cement plant. The points show daily averages over a three year period.

This combination is specific in all individual cases of a cement plant and needs to be individually addressed from a technical control point of view according to expert statements. Apart from the lower mercury limit value a temperature limit value is expedient.

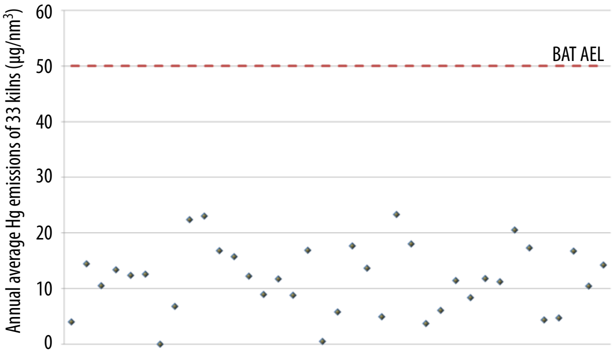
A limit value of 110°C would, according to the experts, in conjunction with the mentioned filter dust removal, lead to a considerable reduction in mercury emissions. Figure 1 shows a typical example of the correlation of waste gas temperature and mercury emissions. Were the waste gas temperatures reduced from e.g. 165°C to around 140°C then the mercury emissions would be reduced by more than 50%. "With a targeted cooling to below 110°C and removal of the contaminated filter dust, an emissions limit value of 10µg/Nm^3 can surely be adhered to."[1]

Should, say the experts, the stated production-integrated measures for compliance with the 10µg/nm^3 limit value not be possible in individual cases, adsorption technologies for lowering are available.

BAT on mercury

As already explained, mercury emissions are the focus of discussions.

The BAT (Best Available Techniques) Reference Document (BREF) for the cement (as well as lime and magnesium oxide) industry represents the results of information exchange between EU Member States, the industries concerned, non-governmental organisations that promote environmental protection and the Commission. The purpose is to draw up, review and where necessary, update BAT reference documents as required by the Directive on industrial emissions (integrated pollution prevention and control (2010/75/EU).[2] The BAT also caters to the sources of mercury, i.e. raw materials and fuels. Focusing on the main natural raw materials for raw meal production, the BAT provides a range of 0.02–0.15mg/kg Hg in clay and argillite, while limestone, marl and chalk contain <0.01–0.13mg/kg Hg. Technical raw meal contains <0.01–0.5mg/kg Hg, which is mainly contributed by natural calcareous and argillaceous materials, but also by natural iron ores or secondary raw materials. Mercury can be found also in natural fuels. For instance, hard coal and lignite contain 0.1–3.3mg/kg Hg. Therefore, even natural materials, either raw materials or fuels, contribute to a cement plant's Hg emissions.



Left - Figure 2: Average mercury emission values in 2008, 2009 and 2010 from 33 German cement kilns. BAT AEL = emission limit associated with BAT as daily value.

According to measurements performed on cyclone preheater kilns, more than 90% of the Hg exists as particles that are formed at exhaust gas temperatures of below 130°C.[2] In this case Hg is almost completely removed from the exhaust gas by the dust collector. Owing to the high collection efficiency of modern dust collectors, concentrations of Hg in the clean gas are often below the detection limit. In order to prevent recirculation of Hg, dust should be extracted from the filter system and can be used for cement grinding. Another possible way to reduce mercury emissions is to reduce the offgas temperature after the conditioning tower to improve the precipitation of mercury and its compounds during dust filtration.[2] Moreover, the injection of activated carbon into the flue gas affords further emission reduction of Hg. For Hg, the BAT-associated emission level of less than 50µg/nm³ can be achieved.[2]

In German cement plants during 2008-2010, the mercury average values in Figure 2 were determined. The emission values lie far below the current BAT limit values, with a mean value across all 33 kilns of 10.4µg/Nm³. Notably, many of the measurements show very low values near the verification limits.

Nevertheless, far reaching emission limit values are also being prepared for this. New types of technologies are now available, including bromine-supported mercury separation technologies, which enable further reductions in mercury emissions.[3]

How strictly Hg emissions are regulated in Europe only becomes evident after an international comparison. The BAT limit value is reflected in the EU Directive on Industrial Emissions (IED). The IED has set the Hg emissions limit value at 0.05mg/Nm³ (50µg/Nm³),[4] which is much stricter than in Pakistan (10mg/Nm³),[5] or the Philippines (50mg/Nm³).[6] The regulations for Indian cement plants merely dictate that during the co-processing of hazardous waste, Hg is monitored and reported to State and Central Pollution Control Boards.[7] In contrast, the Australian Protection of the Environment Operations (Clean Air) Regulation 2010 demands a limit value of 0.2mg/Nm³,[8] much closer to the EU Directive.

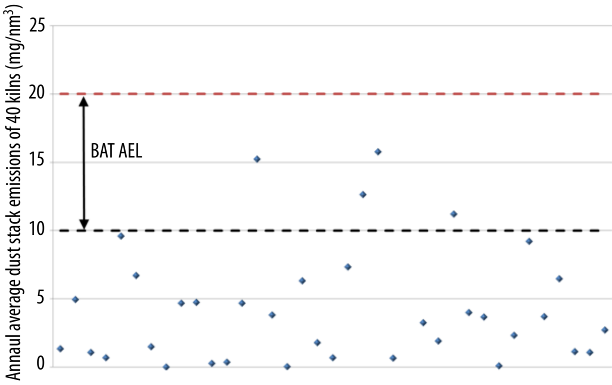
As a yardstick, "A comparison of actual limit values for mercury emissions in various countries of the world can certainly be of benefit and compare this with" (BVT = Best Available Technologies).

The above detailed information on the topic of mercury emissions shows how differently the discussion is handled by plant operators, scientists and politicians.

BAT on dust

For dust emissions from flue gases of clinker kilns the BAT aims to reduce dust (particulate matter) emissions by dry exhaust gas cleaning with either electrostatic precipitators, fabric filters or hybrid filters. The BAT-associated emission limit is below the range of <10–20mg/Nm³ as daily average values. If fabric filters are used, dust emissions are below of the lower level of that range.[2]

Owing to the increasingly strict legal directives, those applications that employ electrostatic precipitators are decreasing. Filter installations are increasingly being carried out using bag filters or combined bag/electrostatic precipitators to meet increasing environmental demands. An excellent overview of current trends in process filters in the cement industry and their positive effects on environmental impact is provided by the overview article.[10]



Left - Figure 3: Average dust emission values in 2008, 2009 and 2010 from 40 German cement kilns. BAT AEL = emission limit associated with BAT as daily value.

Figure 3 shows the dust emissions from 40 kilns in German cement plants as mean values in each case during 2008, 2009 and 2010. With the BAT-AEL illustrated in the diagram (as daily mean values) one has reference points for the evaluation of real dust emissions in German cement plants. With the help of the most modern filter technology, dust emissions of <20mg/Nm³, and in most cases even <10mg/Nm³ will surely be complied with.

The strict limitation of dust emissions is prescribed by the EU Directive on Industrial Emissions (IED), which prescribes a limit value of 20mg/Nm³. An increase to a maximum of 10mg/Nm³ is demanded by the newest German BImSchV dated May 2013.[9] In many countries outside of Europe far weaker limit values apply, e.g. Australia (<50mg/Nm^3),[8] Philippines (<150mg/Nm^3),[6] India (50–400, according to local geographical situation, capacity and age of the cement plant).[7]

BAT on NO_x

Flue gas emissons with respect to NO_x are reduced by a variety of BAT measures:[2]

a) primary measures such as:

i. Flame cooling,
ii. Low-NO_x burners,
iii. Mid-kiln firing,
iv. Addition of mineralisers to improve the burnability of the raw meal (mineralised clinker),
v. Process optimisation.

b) Staged combustion (conventional or waste fuels), also in combination with a precalciner and the use of optimised fuel mix,

c) SNCR,

d) SCR, subject to appropriate catalyst and process development in the cement industry.

Figure 4 shows the NO_x emissions from 40 kilns in German cement plants as mean values in each case during 2008, 2009 and 2010:

For orientation the BAT-AEL are recorded in the diagram as daily mean values. For preheater kilns the BAT-AEL lies between 200-450mg/Nm^3, increasing to 500mg/Nm^3 if the NO_x base level (without lowering measures) stands at over 1000mg/Nm^3. Each cement plant is making efforts to reduce process-induced NO_x emissions by a series of measures. During 2008-2010, 38 kilns reduced the nitrous gases assisted by SNCR technology and to some degree – in the case of nine kilns - in conjunction with staged calcination. In 2010 an SCR installation was commissioned to demonstrate catalytic NO_x reduction. However, without the multi-faceted measures the NO_x emissions stand way above the illustrated level - and as a result also above the limit values, which the (to date) applicable 17.BImSchV (at 500mg/Nm^3) prescribed.[11]

By applying SNCR BAT is:[2]

a) To apply an appropriate and sufficient NO_x reduction efficiency along with a stable operating process,

b) To apply a good stoichiometric distribution of ammonia in order to achieve the highest efficiency of NO_x reduction and to reduce the ammonia slip,

c) To keep the emissions of NH_3 slip from the flue-gases as low as possible.

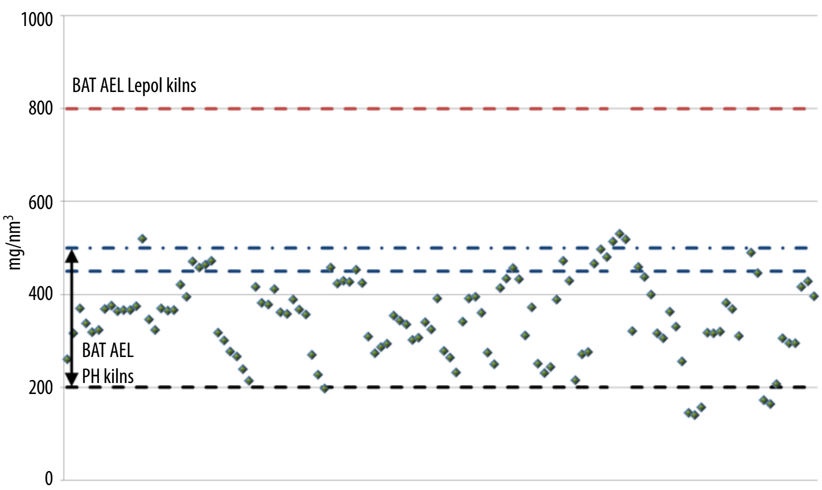
The reduction of NO_x by ammonia or urea greatly depends on the temperature in the case of SNCR. At approximately 800°C the reaction speed on implementation is low, so unconsumed NH_3 can escape with the off-gas:

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

While at temperatures above 800°C NH_3 with NO_x transforms into nitrogen:

$$2\,NO_2 + 4\,NH_3 + O_2 \rightarrow 3\,N_2 + 6\,H_2O$$

An NH_3 slip occurs very easily at this juncture if excessive stoichiometric NH_3 (or another reduction medium which releases NH_3) is injected into the flue-gas in order to postpone the second reaction illustrated above. "The correlation between the NO_x abatement efficiency and the NH_3 slip has to be considered. Depending on the initial NO_x level and on the NO_x abatement efficiency, the NH_3 slip may be higher, up to



Right - Figure 4: Average dust emission values in 2008, 2009 and 2010 from 41 German cement kilns. BAT AEL = emission limit associated with BAT as daily value.

50mg/Nm^3. For Lepol and long rotary kilns the level may be even higher."[2]

By employing SCR considerably lower NO_x values and NH_3 emissions levels are achievable in contrast with the blanket employment of SNCR as utilised in the German cement industry.

"Considering the high reduction potential, the successful pilot tests, the two full scale SCR installations and the fact that SCR is state-of-the-art technique for comparable installations in other sectors, SCR is an interesting technique for the cement industry. There are at least two suppliers in Europe that offer full scale SCR to the cement industry with guaranteed performance levels of 100–200mg/Nm^3" according to the BREF Dokument.[2] "SCR capital expenditure is still higher than for SNCR"

As a result, technologies are available for NO_x reduction, but owing to high costs and a lack of long-term experience, they have not (yet) won through.

Summary

For almost 25 years alternative fuels have been utilised in German cement industry and at around 61% are a firm constituent in thermal energy supply in the cement industry as well as in the sustainable German waste economy.

Constantly increasing demands on environmental protection were constantly implemented in the plants so the currently applicable emissions values for e.g. dust emissions fall well below.

Further restrictions mentioned in the discussions, especially with regards to NO_x, accompanied by NH_3 emissions restrictions, but also raw material - and fuel-dependent emissions (Hg), will decide whether the German cement industry can further prevail, or whether in the future plants will need to be shut in favour of clinker importers from other countries with considerably higher emission limit values. A political assessment is needed with regards to this issue.

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Kiln type	BAT-AEL (Daily average values)	Remarks
Suspension preheater rotary kilns	<200-450mg/Nm^3	The upper level of the BAT-AEL range is 500mg/Nm^3 if the initial NO_x level after primary techniques is >1000mg/Nm^3 Existing kiln system design, fuel mix properties including waste and raw material burnability (eg. special cement or white cement clinker) can influence the ability to be within the range. Levels below 350mg/Nm^3 are achieved at kilns with favourable conditions when using SNCR. In 2008, the lower value of 200mg/Nm^3 has been reported as a monthly average for three plants (easy burning mix used) using SNCR.
Lepol and long rotary kilns	400-800mg/Nm^3	Depending on initial levels and NH_3 slip