Environmental protection in cement production
Legislation

New industry emissions directive
The new directive 2010/75 on industry emissions (IED) entered into force on 06.01.2011. The directive unites a total of seven previously separate environmental directives, including the directive on the integrated prevention and reduction of environmental pollution (IVU directive) and the waste incineration directive, which have been fundamentally revised in the almost three-year revision process. The objective of the directive is to introduce uniform environmental standards in Europe and, in particular, a better implementation of the so-called best available technologies (BAT). This should allow a higher environmental protection level to be targeted in Europe and the distortion of competition between the individual member states to be reduced.

The state of technology requirements for the industrial plants were previously regulated in the 1996 version of the IVU directive. However, in the past the European Commission constantly specified different environmental standards by way of numerous exemptions and a different interpretation of the IVU directive in the EU member states. Only a few of the states, including Germany, fully implemented the EU law.

The targeted unification still allows for deviations from the BVT, but only if additional proof can be provided that its application will lead to disproportionately high costs compared to the ecological benefits. Permits now also have to be reviewed and updated within four years and permit conditions have to be adapted accordingly after new BVT codes of practice are released.

The technical requirements for waste incineration and waste co-incineration plants are specified in Annex VI of the IED. This also includes specific requirements for rotary kilns used in the cement industry, in which waste is introduced as alternative fuel. The joint efforts ensured that the requirements of the European cement industry were not tightened significantly. A comparison of the European limit values to be complied with and the currently applicable provisions of the 17th German Federal Pollution Control Act (BImSchV) shows that there is essentially no need for action by the German legislator in order to implement the European provisions. The 17th BImSchV already provides stricter provisions for various parameters (dust, NOx, mercury) than those to be complied with based on the new European directives (Table II-1).

The member states have a total of two years to convert the provisions of the directive into national law by 2013. The member states also have the option of establishing more strenuous provisions. The Federal Ministry for the Environment (BMU) – independent of the European legislation – is planning to significantly tighten the requirements for cement works that use waste as an alternative fuel. The weighted average calculation will lapse for the dust fraction. A uniform annual average limit value of 10 mg/m³ (in normal operation) will be targeted in the future. The weighted average calculation will also be completely removed for nitrogen oxides (NOx) and a uniform emission limit value of 200 mg/m³ (in normal operation) will apply from mid-2018. However, this value does not currently correspond to the state of technology in every case and poses considerable challenges for the industry in the future. Furthermore, the ammonia emissions are also to be restricted to a daily average of 30 mg/m³ (in normal operation). The planned reduction of the mercury limit value to 0.02 mg/m³ (in normal operation) would also have far-reaching consequences. This emission level could not be implemented in every plant.

The implementation of the IED in Germany will lead to much tighter requirements for the cement industry and major efforts will be required in order to maintain the economic application of waste as an alternative fuel in cement works.

### Use of replacement fuels in the German cement industry

The production of cement is both energy and raw material-intensive. One possibility to sustainably reduce the consumption of primary resources exists in the utilisation of suitable alternative materials. The German cement industry recognised this opportunity very early on. In particular, German cement producers lead the world in the use of suitable alternative fuels. In Germany, replacement fuels substituted more than 60 % of the required fuel en-

| Table II-1: International and national emission limit values (daily averages) for cement works with waste co-incineration in mg/m³ (in normal operation) |
|---------------------------------|---------------------------------|---------------------------------|
|                                | New directive on industry emissions | 17th BImSchV | BMU proposal: Revised 17th BImSchV |
| Total dust                      | 30                               | 20 (14–10) |
| HCl                             | 10                               | 10           |
| HF                              | 1                                | 1            |
| NOx                             | 500 (1)                          | 500 (320–200) |
| NH₃                             | –                                | –            |
| Hg                              | 0,05 (MPZ)                       | 0,03 (2) |
| ΣCd, Tl                        | 0,05 (MPZ)                       | 0,05 (MPZ) |
| ΣSb, As, Pb, Co, Cu, Mn, Ni, V, Sn | 0,5 (MPZ)                       | 0,5 (MPZ) |
| Dioxins and furans mg/m³ (in normal operation) | 0,1 (MPZ) | 0,1 (MPZ) | 0,1 (MPZ) |
| SO₂                             | 50 (2)                           | 50 (2)       |
| TOC                             | 10 (2)                           | 10 (2)       |
| CO                              | 3 (3)                            | 5 (5)        |

MPZ: Average over the sampling period

1) Exceptions of up to a maximum of 800mg/m³ (in normal operation) are possible for lepol kilns and long kilns until 01.01.2016
2) Raw material-related exceptions possible
3) Emission limit values may be determined by the responsible authority
4) Weighted limit value determination by the responsible authority for waste utilisation > 60 %
5) Responsible authority to set a limit value; raw material-related exceptions possible
6) From 01.01.2016
7) No later than from 01.06.2018
8) Raw material-related exceptions possible; average daily value of maximum 0.05 mg/m³ (in normal operation)
ergy in 2011 (Fig. II-1). This corresponds to an energy equivalent of almost 2.4 million tons of hard coal.

The undisputed ecological benefits of the responsible use of alternative materials in the clinker burning process has been clearly demonstrated in numerous studies in previous years. Not least, the classification of suitable materials as a measure that corresponds to the state of technology in the current BAT reference of the European Commission is also based on these findings.

Regardless of this, from the cement industry’s perspective, it would be sensible to publish the previous reasoning at a predominantly technical level with regard to the positive properties of the use of waste in the production process as feedstock and energy to make it available to a wider audience. In light of this a task force was established by the Environment and Process Engineering Committee in 2011. The interdisciplinary participation in this group ensures that the feedstock as well as the process engineering and environmental technology aspects can be taken into account. This task force also evaluates the extremely successful development of the use of alternative materials in previous years and the derivation of suitable messages for the public.

A significant component and a specific feature of using alternative substances for clinker burning is represented by the fact that both the energy content as well as the feedstock components of the material used can be incorporated into the end product. For all the other, predominantly energy recovery measures, ash or slag is produced that then has to undergo further processing (Fig. II-2).

Furthermore, the task force was able to determine that the energy consumption of alternative fuels provides the benefit of being able to dry these materials in the rotary kiln. This means that the additional use of upstream drying apparatus is no longer required. The energy efficiency of this integrated drying with simultaneous energy utilisation is well above 80 %.

The cement industry also achieved a high degree of efficiency with regard to the use of material properties. This was at 99 % with regard to the overall amount used.

Given that all the cement works that use alternative fuels have also determined their biogenic carbon content over the past years, potential energy-related CO₂ savings could also be estimated. Based on the figures obtained in 2010 as part of the emission reporting, the average CO₂ reduction for the energy-related use of alternative fuels in the clinker burning process was 0.74 t CO₂/t fuel used. This value clearly displays the high ecological benefits of using suitable alternative materials in the clinker burning process.

The task force also dealt with the phenomenon that the specification of various requirements results in increasing conflicts of interest, especially in the area of environmental protection (e.g., higher energy efficiency, reduced CO₂ emission, lower limit values for NOₓ). For example, the political requirement for reduced cement-specific CO₂ emissions led to increased substitution of the energy-intensive intermediate product clinker with other suitable hydraulic materials for cement production. However, in order to be able to ensure the same product properties with these CEM II cements, they had to be ground more finely, which in turn led to increased power consumption during cement milling.

The strict German requirements in relation to the reduction of nitrogen oxide emissions will inevitably lead to the increased use of electrical energy by the plants as additional units and, in most cases, more powerful fans will have to be installed. The task force agrees that, given the already high environmental protection level that has been reached, such conflicts of interest will become more frequent.
this point political decision makers are also urged to reach conclusions in favour of a target value in case of uncertainty.

The task force will continue its activities. The objective is to provide the overall positive properties of the use of alternative raw materials and fuels to the cement industry in the form of a position paper once they have been clearly established. Furthermore, it is intended that key messages will be published in a brochure. Due to modern plant engineering, it can always be ensured that alternative raw materials and fuels in the cement industry are used in an environmentally compatible and harmless manner. In addition, its use often even leads to reduced environmental impacts. Moreover, this also enables the use of natural resources to be considerably reduced.

**Climate protection**

**Development of CO₂ emissions**

**Fuel-related CO₂ emissions**

The global warming potential of the cement industry emissions comes almost exclusively from carbon dioxide. Other greenhouse gases specified in the Kyoto protocol (e.g. N₂O) are not generated during cement production or only in extremely low amounts. In the clinker burning process, fuel-specific CO₂ emissions are generated by the conversion of fuel energy into process heat in the rotary kiln. Furthermore, the fuel energy is also used to dry other main cement constituents such as blastfurnace slag. The specific fuel-related CO₂ emissions of the German cement industry reduced from 0.117 to 0.104 t CO₂/t cement in the period from 2008 to 2011. In absolute figures this relates to a reduction from 4.05 to 3.41 million t CO₂/a. The CO₂ emissions from the use of alternative fuels—in line with the voluntary commitment system—is not taken into account in this figure, as they completely replace traditional and pure fossil fuels. As the waste would otherwise release its carbon content as CO₂ at another point, the use of alternative fuels results in an overall reduction of CO₂ emissions.

In this evaluation of alternative fuels there is a significant difference to reporting as part of emissions trading. Emissions trading includes all fossil fuels and the fossil fractions of alternative fuels. Only the biogenic fractions of the fuel are given an emission factor of zero. A substitution of the traditional fossil fuels of lignite and hard coal by other fuels with lower specific CO₂ emissions, such as natural gas, is not possible for reasons of cost. As fuel costs have a considerable effect on cement production costs, the efforts of the cement industry also continue to target the increased replacement of fossil fuels with alternative fuels from waste. The use of biogenic waste fuels and fuels with biogenic fractions is therefore playing an increasing important role.

The emission factors agreed and applied as part of the voluntary commitment also differ from the values prescribed in emissions trading. Quantitatively, the values only differ slightly, but they are subject to greater differentiation in emissions trading. The electrical energy use accounts for about 10 % of the overall energy use. If, however, electrical energy consumption is regarded as the primary energy, its share—and the resulting indirect CO₂ emissions—is larger.

The CO₂ emissions resulting from power consumption were between 0.066 and 0.073 t CO₂/t cement from 2008 to 2011. The electrical power consumption rose slightly in absolute and specific terms. Only a low level of independent power generation currently takes place in the German cement industry.

**Raw material-related CO₂ emissions**

The calcination of the key raw material limestone (CaCO₃) for clinker production releases CO₂. The raw material-related CO₂ emissions for every ton of clinker produced depends on the raw material composition, but only varies slightly for each plant. In Germany this amounts to approx. 0.53 t CO₂/t clinker or between 0.383 and 0.398 t CO₂/t cement between 2008 and 2011. The total raw material-related CO₂ emissions of the German cement industry initially fell

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**Table II-2: CO₂ emissions of the German cement industry from 2008 to 2011**

<table>
<thead>
<tr>
<th>Year</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>4.05</td>
<td>3.40</td>
<td>3.19</td>
<td>3.41</td>
<td>0.117</td>
<td>0.110</td>
<td>0.104</td>
<td>0.100</td>
</tr>
<tr>
<td>Electrical</td>
<td>2.30</td>
<td>2.11</td>
<td>2.23</td>
<td>2.51</td>
<td>0.066</td>
<td>0.068</td>
<td>0.074</td>
<td>0.073</td>
</tr>
<tr>
<td>Raw material-related</td>
<td>13.44</td>
<td>12.31</td>
<td>12.19</td>
<td>13.13</td>
<td>0.388</td>
<td>0.398</td>
<td>0.398</td>
<td>0.383</td>
</tr>
<tr>
<td>Energy-related</td>
<td>6.35</td>
<td>5.51</td>
<td>5.42</td>
<td>5.92</td>
<td>0.183</td>
<td>0.178</td>
<td>0.178</td>
<td>0.173</td>
</tr>
<tr>
<td>Total</td>
<td>19.79</td>
<td>17.82</td>
<td>17.61</td>
<td>19.05</td>
<td>0.571</td>
<td>0.575</td>
<td>0.575</td>
<td>0.556</td>
</tr>
</tbody>
</table>

1) Without alternative fuel from waste

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**Table II-3: Specific CO₂ emissions of the German cement industry (in t CO₂/t cement)**

<table>
<thead>
<tr>
<th>Year</th>
<th>From thermal power consumption</th>
<th>From electrical power consumption</th>
<th>From limestone</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>0.280</td>
<td>0.072</td>
<td>0.450</td>
<td>0.802</td>
</tr>
<tr>
<td>1994</td>
<td>0.252</td>
<td>0.072</td>
<td>0.450</td>
<td>0.775</td>
</tr>
<tr>
<td>1995</td>
<td>0.254</td>
<td>0.071</td>
<td>0.451</td>
<td>0.776</td>
</tr>
<tr>
<td>1996</td>
<td>0.245</td>
<td>0.072</td>
<td>0.451</td>
<td>0.768</td>
</tr>
<tr>
<td>1997</td>
<td>0.231</td>
<td>0.070</td>
<td>0.453</td>
<td>0.754</td>
</tr>
<tr>
<td>1998</td>
<td>0.218</td>
<td>0.070</td>
<td>0.444</td>
<td>0.732</td>
</tr>
<tr>
<td>1999</td>
<td>0.199</td>
<td>0.068</td>
<td>0.427</td>
<td>0.694</td>
</tr>
<tr>
<td>2000</td>
<td>0.195</td>
<td>0.068</td>
<td>0.431</td>
<td>0.694</td>
</tr>
<tr>
<td>2001</td>
<td>0.179</td>
<td>0.067</td>
<td>0.415</td>
<td>0.661</td>
</tr>
<tr>
<td>2002</td>
<td>0.168</td>
<td>0.069</td>
<td>0.413</td>
<td>0.650</td>
</tr>
<tr>
<td>2003</td>
<td>0.156</td>
<td>0.067</td>
<td>0.401</td>
<td>0.624</td>
</tr>
<tr>
<td>2004</td>
<td>0.155</td>
<td>0.068</td>
<td>0.428</td>
<td>0.651</td>
</tr>
<tr>
<td>2005</td>
<td>0.132</td>
<td>0.068</td>
<td>0.406</td>
<td>0.606</td>
</tr>
<tr>
<td>2006</td>
<td>0.123</td>
<td>0.067</td>
<td>0.383</td>
<td>0.573</td>
</tr>
<tr>
<td>2007</td>
<td>0.128</td>
<td>0.067</td>
<td>0.419</td>
<td>0.614</td>
</tr>
<tr>
<td>2008</td>
<td>0.117</td>
<td>0.066</td>
<td>0.388</td>
<td>0.571</td>
</tr>
<tr>
<td>2009</td>
<td>0.110</td>
<td>0.068</td>
<td>0.398</td>
<td>0.575</td>
</tr>
<tr>
<td>2010</td>
<td>0.104</td>
<td>0.074</td>
<td>0.398</td>
<td>0.575</td>
</tr>
<tr>
<td>2011</td>
<td>0.100</td>
<td>0.073</td>
<td>0.383</td>
<td>0.556</td>
</tr>
</tbody>
</table>

1) Without alternative fuels from waste
2) Base year of voluntary agreement of 2000
to 12.2 million t CO₂/a in the years 2009 and 2010 due to declining production, before again rising to slightly above 13 million t CO₂/a. The specific and absolute CO₂ emissions for the reporting period are represented in Table II-2. A reduction of the raw material-related CO₂ emissions – per ton of cement – is only possible to a limited extent by the increased production of cements with several main constituents. A reduction is practically impossible per ton of clinker.

In summary this provides the specific CO₂ emissions of the German cement industry compiled in Table II-3 for the period from 1990 to 2011. The base year for the voluntary commitment of the cement industry for the specific energy-related CO₂ emission is 1990.

**Determination of biogenic carbon in replacement fuels**

The alternative fuels used are still examined for the biomass content to determine the biogenic fraction of CO₂ emissions in clinker production. The method of direct determination from the flue gas is currently still in the standardisation process and has no practical relevance to date.

In contrast, the technical specification CEN/TS 15440 was transferred to DIN EN 15440 in 2011 for directly determining the biogenic fraction of CO₂ emissions in clinker production. The method of direct determination from the flue gas is currently still in the standardisation process and has no practical relevance to date.

What is important for CO₂ emissions trading is that both the selective dissolution method as well as the I°C method have now been standardised as determination methods for solids and they may now be applied to determine performance characteristics for European emissions trading. The same restrictions with regard to the selective dissolution method, as described in the previous technical specification, continue to apply. For example, the materials that are examined by way of selective dissolution may not contain more than 5 mass % rubber. Impurities in fossil fuels may also lead to incorrect results. In general, improper application may produce results that are either too high or too low. For materials that are suited to both methods, these can be checked for conformity of the analysis results so that considerably more cost-effective, selective dissolution methods can be applied without any issues.

However, the analysis according to the selective dissolution method should always be performed by an experienced laboratory. Evaluations of interlaboratory tests have shown that extreme precision is required for the selective dissolution method in order to achieve comparable and reproducible results. The set initial weights and chemical volumes and concentrations must be precisely complied with. Also of particular importance is that room temperature must be maintained during the dissolution method. The heat generated during the reaction may otherwise lead to excessive dissolution and the reported biogenic fraction being too low.

**Measurement of biogenic CO₂ emissions in rotary kiln exhaust gases**

As part of emissions trading, the ratio of biogenic material to fossil CO₂ emissions represents a relevant value that is also indicated in the CO₂ reporting by rotary kiln plants of the cement industry. By definition, an emission factor of zero is provided for CO₂ from biogenic carbon, so no CO₂ certificates have to be purchased for this part of the CO₂ emissions.

The biogenic fraction in the (alternative) fuels is currently established by way of input analyses. The fraction of biogenic CO₂ emissions is determined based on the fuel mass flow and a regular determination of the biogenic carbon fraction in the fuel used. Given the annual reporting obligation, a period of twelve months must be considered for each analysis. While the fuel mass flow is comparably easy to determine based on the fuel weights, the fractions of biogenic carbon are determined differently depending on the fuel type. For some alternative fuels, such as used tires, sewage sludge or animal meal, standard values have been determined by the responsible authority for the fraction of biogenic carbon, which may be used without further analysis. In contrast, other alternative fuels, such as fractions from industrial and commercial waste or treated fractions from municipal waste, have to be analysed regularly to determine the biogenic carbon fraction.

As the composition of these alternative fuels can fluctuate and the samples are generally removed from block materials, the exact determination of the biogenic CO₂ emissions as the total monthly or annual emission requires correspondingly high test expenses.

A process in which the fraction of biogenic CO₂ emissions will be determined by way of a long-term measurement in the chimney of the rotary kiln plant is currently being developed as an alternative method. This is a 3-phase process:

1. Representative long-term sampling of the CO₂ emissions in the chimney
2. Analytical determination of the relationship between the biogenic and fossil CO₂ in the aggregate sample
3. Continuous measurement of the exhaust gas volume flow and the total CO₂ concentration to calculate the total biogenic CO₂ emission

The prototype of a long-term sampler suitable for this measurement is currently installed in the chimney of a cement work for test purposes.

The sampling takes place proportional to speed via a sampling probe, with several measuring openings across the chimney cross-section. This should ensure that the gas sampling records both a possible inhomogeneous distribution of the CO₂ concentration in the chimney as well as the fluctuating gas velocities due to the changing operating conditions and differing plant performance.

The system is set up so that the gas sample is collected over a period of up to four weeks on absorption material suitable for separating CO₂. Various materials can be used in this respect, but solid absorbers are preferred as they are easy-to-use. The suitability of soda lime, which ensures an effective CO₂ separation, is being trialled in the current tests. The long-term sampling is set up so that an initial main gas flow of approx. 2.5 l/min is removed via the sample gas probe in order to keep the retention times in the probe system as short as possible. A partial volume flow of approx. 10 ml/min is then branched off from this main gas flow and fed into the solid absorber.

As an entire long-term average value (e.g. for a month) would immediately be lost if the sample is damaged or in the event of an incorrect analysis in the laboratory, a duplicate determination on two solid absorbers takes place at intervals of 60 s in order to secure the results. Fig. II-3 displays the prototype of the long-term sampler.

The duration of the sampling may be varied over a wide range of periods as required. Sampling periods of a day, week or month are possible. The solid absorbers are replaced with new collection cartridges at the end of the sampling period. This is a
very simple procedure that can, in principal, also be performed by plant employees after they have received relevant instructions.

The samples are suitably prepared in the laboratory prior to analysis (Fig. II-4). The collected sample is first mixed with phosphoric acid, which completely converts the CO$_2$ bound to the soda lime into the gas phase, and subsequently collected in a container. This provides an undiluted, homogeneous average sample of the carbon dioxide emitted by the rotary kiln plant in the sampling period. A sub-quantity of this sample is then analysed.

Various methods are available for the analysis, in which the fraction of the $^{14}$C isotope is determined in the sample matrix. The following methods are available:

- AMS (Accelerator Mass Spectrometer)
- BI (Beta Ionisation measurement)
- LSC (Liquid Scintillation Counting)

The methods differ with regard to their accuracy and with respect to the costs associated with the analysis. As the biogenic CO$_2$ content in the exhaust gas is about 8 to 15 % of the total CO$_2$, comparatively high demands must be placed on the measuring uncertainty of the analysis method. For AMS and Beta Ionisation, the measuring uncertainty of the analysis method is well below ±1 %, while this is ±5 % for Liquid Scintillation Counting.

This information shows that the use of the LSC technique is currently not precise enough for this type of investigation on rotary kiln plants of the cement industry. However, as this relates to the most broadly used method of analysis, for reasons of cost, one focus of the current developments is on optimising this method of analysis with the aim of reducing the measuring uncertainty in order to potentially include it as an alternative to AMS measuring or $\beta$ Ionisation.

The results of the $^{14}$C analysis are indicated in “percentage modern carbon” (pmC) and can be converted into “% biogenic carbon” with regard to a (year-dependent) reference value. As additional measured values, the exhaust gas volume flow and the total CO$_2$ concentration must be constantly measured with sufficient accuracy in order to finally determine the biogenic emission level. Further improvements to measuring technology are required in order to comply with the accuracy needed in emissions trading.

The on-going activities are oriented towards an ISO Standard PrEN 13833 Stationary Source Emissions - Determination of the Ratio Biomass (Biogenic) and Fossil-derived Carbon Dioxide – Radiocarbon Sampling and Determination, which is currently available in draft form. This standardisation process is expected to be completed in the coming years.

### Emissions trading

**European climate policy**

On 23.04.2009 the European Union decided on a package of measures that specified their climate policy for the period from 2013 to 2020. The key instrument for the industry remains CO$_2$ emissions trading. A
Emissions trading 2013 to 2020
The 3rd period of EU emissions trading (2013 to 2020) started with numerous innovations in the allocation process for free emission rights. In Germany, the amendment to the greenhouse gas emissions trading law and the Allocation Order (ZuV 2020), which entered into force on 27.07.2011, applies for the implementation of the EU emissions trading directive. The application process by the plant operators concluded on 23.01.2012. The German Emissions Trading Authority (DEHSt) compiled a list of the reviewed preliminary allocations after evaluating all the applications and transmitted this to the European Commission. After reviewing all of the figures submitted by the European member states, a cross-sectoral correction factor will be determined, which may lead to an annual allocation reduction. The DEHSt expects to prepare the final allocation notification for every plant on this basis by the end of 2012.

The number of EU certificates is restricted throughout the EU and is reduced by 1.74% every year in order to achieve the EU-wide emissions reduction target by 2020. This reduction factor does not apply directly for plants that are allocated free certificates based on benchmarks. However, challenging benchmarks on allocation and possible cross-sectoral allocation reductions will result in more certificates having to be auctioned in the future.

Special rules apply for capacity changes. These are to be reviewed for their materiality with regard to a technical change and the actual production quantity. An amended capacity concept is relevant for the allocation with respect to BImSchG (German Federal Pollution Control Act) approval. The capacity is determined based on the average of the two highest monthly productions, standardised for 30 days, over a certain period. The resulting value is then projected for one year.
Benchmark determination

The allocation of the emission adjustments is subject to uniform regulation in the CO\(_2\) emissions trading system from 2013. The free allocation of certificates to companies from the production industry is based on production figures from base years 2005 to 2008 and 2009 to 2010 as well as on product-specific CO\(_2\) benchmarks. For clinker this is 766 kg CO\(_2\)/t grey cement clinker and 987 kg CO\(_2\)/t of white cement clinker.

These challenging benchmarks are derived based on the CO\(_2\) emissions of the top 10 % most efficient plants in Europe in 2007 and 2008 (cf. Fig. II-6). With respect to the average specific CO\(_2\) emissions of the European cement industry in the same period, this relates to an 11 % reduction of free allocation with regard to all plants. A key opportunity for reducing the specific CO\(_2\) emissions in cement clinker production, and thereby to at least partially offset this lower allocation, exists in the use of suitable alternative fuels with proportionate fractions of biogenic carbon. Reporting will also become more challenging from 2013 given that the EU allocation rules will include specific heating systems, etc. in the product-related benchmark. It is expected that certificates will also have to be submitted for the operation of these low additional emission sources from 2013.

Carbon leakage evaluation

The term “carbon leakage” describes the transfer of industrial production and the related CO\(_2\) emissions to countries outside the EU ETS due to EU emissions trading. This is problematic for several reasons:

1. CO\(_2\) emissions escape the control of the emissions trading system, which then loses its effectiveness
2. A specific competitive disadvantage is established for industrial locations in Europe and economic value creation is shifted outside of Europe.
3. The production transfer to countries outside of the emissions trading system is often less CO\(_2\) efficient, as additional CO\(_2\) emissions are generated during the transport and import of the products to Europe.

In order to prevent this carbon leakage effect, in 2009 the EU Commission compiled a list of energy-intensive industry sectors that receive free certificates. This list is reviewed every five years. According to the EU guideline, there is a risk of transferring the CO\(_2\) emissions if the cost of the CO\(_2\) certificates to be purchased effect an increase in the production costs of at least 5 % of the gross value added and if the intensity of trade with non-EU ETS countries is more than 10 % of the total volume of the Community market. Alternatively, there is also a risk of transfer if the CO\(_2\) certificate costs effect a particularly high increase in production costs of at least 30 % of the gross value chain, or the intensity of trade with external states exceeds 30 %.

The cement industry is on the list of industries facing a risk of carbon leakage as they fulfil the second criteria (production cost increase of at least 30 %).

In a 2008 study commissioned by the CEMBUREAU, the risk of carbon leakage for the European cement industry was presented in the event of a full auctioning of certificates. In this case 81 % of the clinker production would be at risk of production relocation and import of clinker from non-EU ETS countries at a certificate price of 25 EUR/t CO\(_2\).

A re-evaluation of the CL status and the free benchmark allocation to certain industry sectors will take place in 2014. A re-analysis of the influencing factors is currently taking place in the CEMBUREAU for an updated evaluation of the risk of carbon leakage to the European cement industry for the next 5-year period from 2015.

CO\(_2\) reporting

The cement industry companies are required to provide an annual report on their direct CO\(_2\) emissions from raw materials and fuels in the clinker production as part of the EU emissions trading (EU ETS). Apart from the applicable reporting requirements, the globally applied Cement CO\(_2\) and Energy Protocol (CSI protocol) is a tool also available to the cement industry, with which direct and indirect CO\(_2\) emissions from power consumption and clinker purchases in cement production can be determined on a voluntary basis.

Both methods require knowledge of the relevant material flows in a cement plant (cf. Fig. II-7), the material and production quantities and the applicable material parameters such as the calorific value and emission factor.
Cement CO₂ and Energy Protocol

The CSI protocol was developed by the Cement Sustainability Initiative (CSI) of the World Business Council for Sustainable Development (WBCSD) in cooperation with its member companies and the VDZ, with the objective of harmonising the reporting of CO₂ emissions with the EU regulations, among other things. Version 3.04 has been available online since December 2011 (www.cement-co2-protocol.org). Important changes include, for example, the consideration of the biogenic fractions of CO₂ emissions from alternative fuels and newly implemented methods for power generation in cement works from waste heat or separate power plants. Methods of determination for process-specific CO₂ emissions from the calcination of raw material, according to either the material input or output method, were enhanced. The raw meal (klin feed) and additional raw materials (klin intake) are considered for the input method. In contrast, the produced clinker and the organic carbon content of the raw materials are taken into account for the output method. Both approaches consider possible CO₂ emissions from the calcination of dusts that are removed from the clinker burning process (cement kiln dust, CKD and bypass dust). Furthermore, all fossils and alternative kiln flows and other fuel flows (e.g. for dryers, heating systems, work vehicles, power production plants) are also included.

Specific emission data is collected as part of the CSI Getting The Numbers Right (GNR) project based on the CSI protocol in order to create a global CO₂ energy information system for clinker and cement production. The GNR report published in 2009 covers the period from 1990 to 2006 (data to 2010: www.wbcsdcement.org/co2data).

This CSI protocol currently serves as starting point for a task force for developing an EU standard for the reporting of direct and indirect CO₂ emissions in energy-intensive industry sectors established by the European Committee for Standardisation (CEN) in 2011.

CO₂ reporting in the EU ETS

In the 2nd trading period (2008 to 2012), the annual CO₂ emission reports required as part of the EU ETS must be compiled according to the monitoring guidelines of the EU and the guidelines and FAQ of the German Emissions Trading Authority (DEHSt). Work-specific methods are specified in the Monitoring Concept (MK), which have to be approved by the local authority. A central point in this regard is the determination of, and compliance with the required accuracy levels in determining the CO₂ emissions of individual material flows. At the start of the 2nd trading period, the works faced the challenge of subjecting their assessment methods and relevant measuring equipment (e.g. process balances) to a comprehensive uncertainty evaluation. The regular review and adjustment must be documented and must ensure that the accuracy of the measuring instruments comply with the regulations.

For the 3rd trading period (2013 to 2020), the regulations for the monitoring and reporting of CO₂ emissions (Monitoring and Reporting regulation, M&R regulation) adopted by the EU Commission in 2012 contain a number of alterations. As an EU regulation, it must be directly applied by the member states and establishes binding requirements, in particular, on the preparation and implementation of the inspection plans (UP), which replace the monitoring concept. In Germany, these inspection plans will be prepared online in a Form Management System (FMS) in the future and must be submitted to the German Emissions Trading Authority (DEHSt) for approval prior to the start of a reporting year.

CO₂ capture and storage

The reduction of CO₂ emissions is a global issue that will continue to increase in significance in the years to come. The industry must therefore make a considerable contribution in order to achieve the challenging climate objectives. In the past few years a series of so-called “roadmaps”, recording a possible path towards achieving the emission targets, have been published. A portfolio of different measures is fundamentally required. The separation of CO₂ from flue gas streams and the subsequent permanent storage in deep geological layers, i.e. the so-called CCS process (carbon capture and storage) will play a decisive role.

After the power station sector, the cement industry is one of the largest CO₂ emitters. The International Energy Agency (IEA) has therefore compiled its own “Technology Roadmap” for the cement sector, in which possible reduction measures including the current research requirement as well as the associated political and economic conditions are described.

The application of CCS technologies is extremely significant in view of the possible measures for reducing CO₂ emissions in the cement industry. This particularly ap-
plies, as around 60 % of the CO₂ emissions are raw material-related in the clinker burning process, i.e. they arise from the calcination of the raw material. This means that there are practically no other measures available to reduce the specific CO₂ emissions.

The International Energy Agency postulates that in 2050 about 50 % of the cement kiln plants in Europe, North America, Australia and Japan will have to be equipped with CCS technologies. Accordingly, this figure will have to be at least 20 % in the large emerging markets of China and India.

Research and development as well as the implementation of pilot and demonstration projects are required in order to meet these challenging objectives. Currently, however the high costs of the CCS process are a huge obstacle to the introduction of the necessary steps. And finally, it is still completely uncertain whether this process will even be technically and economically viable.

Another factor in Germany and many other member states of the EU is that the European CCS guideline had not been converted to national law as at spring 2012. This lack of legal certainty has resulted in the cancellation of various CCS projects in the power plant sector.

In order to address the challenges of climate protection and expansive CO₂ reductions, the European Cement Research Agency (ECRA) started a CCS research project in 2007 that is divided into five phases – from the initial literature work, through to laboratory and pilot trials and the implementation of a demonstration project. Phase III of the project was completed at the end of 2011 and phase IV was prepared in the first half of 2012. Phase IV fundamentally aims to investigate the oxyfuel process and the post-combustion process in parallel. However, the focus is on the application of the oxyfuel process, while the post-combustion activities are restricted to the supervision of a CCS project in the Norwegian cement work Brevik by the ECRA.

Apart from the ECRA CCS project, additional R&D projects on CO₂ separation are being implemented in the Research Institute of the Cement Industry, which are being supported by the German Federation of Industrial Research Associations (AiF).

**Oxyfuel technology**

The separation of CO₂ from the process is a significant step for CCS technology. One method that is comparable with regard to energy is oxyfuel technology. The process is based on the idea of operating industrial processes, such as the clinker burning process, with pure oxygen. This results in a drastic reduction of the exhaust gas volume and the simultaneous increased concentration of CO₂ due to the absence of atmospheric nitrogen, otherwise also included in the burning process. This increased concentration of CO₂ in the exhaust gas considerably simplifies its separation. CO₂ also has to be recirculated to set the temperature profile in the kiln plant. In addition, the application of this technology would influence both the plant operation as well as the chemical and mineralogical kiln feed reactions.

Experiences with the implementation of the oxyfuel technology as part of the CCS process are currently only available in pilot trials in the power plant industry. These cannot be fully transferred to the cement industry due to the process engineering and the product. Only minor increases in oxygen concentrations are currently applied in the cement industry for production increase or to optimise the co-incineration of alternative fuels. The Research Institute is investigating the technological effects and the CO₂ reduction potential of the oxyfuel technology as part of a project with the aid of process modelling and laboratory experiments.

No negative effects of varying burning and cooling atmospheres could be determined on the clinker phase formation based on the experimental investigations at a laboratory level. The analysis of the cement properties (hydration heat, strength development, etc.) showed minor divergences below 3 % between the reference cement...
and the cement produced under oxyfuel conditions. The improved cooling by the CO₂-containing gas had a particularly stabilising effect on the clinker phases.

There was no change in colour for any of the cements. Based on this experiment it can be assumed that an appropriately adapted oxyfuel operation will not have a negative impact on the product quality.

A plant formula was developed, which is most efficient from a thermotechnical perspective with regard to the requirement for the maximum possible prevention of CO₂ (Fig. II-8). A separation of the cooler into two units is planned, as the recuperation of heat in the clinker cooler is decisive for a good energy balance. A mixture of oxygen and recirculated exhaust gas, which forms the burning gas, will be added to the hot part of the cooler. The second stage is operated with ambient air, which is subsequently used to dry the raw material. The alignment of all the waste heat flows is decisive for the energy optimisation, due to the differing composition of the incidental gas flows. Firstly, sufficient energy to dry the raw material must be available. If necessary, the requirement can be fulfilled with a heat transfer plant between the drying air and the CO₂-containing exhaust gas. The oxyfuel technology provides for the operation of an energy-intensive air separation plant (LZA) and a CO₂ processing installation (CPU). The energy integration of these units via power generation using waste heat is therefore also a priority. In addition, an Organic Rankine Cycle (ORC) may also be continuously operated, depending on the energy required to dry the raw material. This results in a direct correlation between the waste heat utilisation units.

The oxyfuel technology doesn’t just influence the plant operation, it also provides additional degrees of freedom in the form of the recirculation rate and the resulting oxygen content, which differ from the previous conventional process design. The changed gas composition of the kiln atmosphere triggers a fundamental energy transfer in the plant. The flow profile in the preheater cyclones is also influenced by the changed exhaust gas composition, which in turn influences the dust separation efficiency and thereby effects an additional energy displacement. The substitution of nitrogen with CO₂ is manifested in a falling preheater capacity flow ratio and increasing cooler capacity flow ratio.

Two states were selected as the basis for the process modelling in order to optimise the operation. An operating state should model an upgrade, whereby the modifications to the plant must be kept to a minimum. In this regard, the optimal operating area lies at 23 vol.-% oxygen enrichment for a BAT plant in order to compensate for the negative effects of CO₂. However, the problem of a lack of space due to the additional installations arises, in particular for upgrades.

If the opportunity existed to completely redesign a work with no restrictions, then the objective would not only be thermal energy efficiency but a global energy minimum across all units. Restrictions include the variation of the recirculation rate above the maximum permitted thermal loading of the sinter zone, or the gasket on the cooler due to a reduced recuperation zone. The thermal energy demand falls to a minimum as a consequence of the reduction of the recirculation rate (Fig. II-9). Another reduction is caused by a rise in energy demand due to a capacity flow ratio that does not permit adequate preheating of the material in the preheater. As a controlling parameter, the recirculation rate is not just limited to the kiln operation. Furthermore, it is also suited to control the incidental heat in the external balance area. The reduction of the recirculation rate effects a transfer of the maximum waste heat from the exhaust gas through to the cooler exhaust air, which may, in turn, benefit the raw material drying. The targeted controlling of the waste heat with the recirculation rate can be individually coordinated by the operation for the specific conditions of the relevant plant and the material deposits.

Also important is the influence of the exhaust gas composition on the energy demand of the CPU. The CO₂ enrichment in the exhaust gas is predominantly determined by the fuel selection, the excess burning oxygen, the oxygen purity of the air separation plant and, in particular, the fraction of false air in the plant. An adequate CO₂ enrichment in the exhaust gas to be treated is determined based on a false air infiltration of 6 %. The process separation rate is predominantly and independently determined by the recirculation rate of the CO₂ preparation plant.

Based on the results previously achieved, it can be assumed that the oxyfuel technology can fundamentally be applied. However, according to the current level of knowledge, an increase of the cement production costs by about 40 % is expected due to the doubling of the electricity demand, which means that the process is currently not economical.
Post combustion carbon capture

The term post combustion carbon capture includes all the processes that separate CO₂ from flue gas. These processes are therefore generally suited for retroactively equipping existing cement works with CO₂ separation. Key processes in this group include amine scrubbing, cooled ammonia scrubbing, the regenerative carbonate cycle and various membrane technologies. Until now, key research projects primarily focussed on amine scrubbing, but the other processes have also been discussed for use in the cement industry. One thing that they have in common is that they are not yet available for industrial use. The development of the processes is either in the pilot or the demonstration stage.

While the CO₂ reacts with an aqueous solution in the amine scrubbing and ammonia scrubbing processes, the regenerative carbonate cycle uses finely ground CaO, which reacts with the CO₂ at temperatures of about 700 °C. However, this is still an extremely recent process, similar to the use of CO₂-selective membranes that enable the separation of CO₂ without liquid or solid recirculating material systems. However, these types of membranes have not reached industrial maturity at this stage.

The Research Institute of the Cement Industry has established a model in order to describe carbon dioxide separation in more detail. This numeric simulation calculates the physical and chemical processes during the CO₂ absorption. An exemplary absorption column has also been designed on this basis.

The computer-assisted calculations show that the high CO₂ concentration in the exhaust gas of cement works has a favourable impact on the required plant size (Fig. II-10). Compared to a power station, the absorption column dimensions for a cement work can be considerably smaller with a comparable CO₂ emission. The required package volumes fall accordingly as well as the related investment expense.

Depending on the plant size, a cement work requires an absorption column with a diameter of between 6 and 12 m. These dimensions are currently not commercially available. The height of the column is between 20 and 35 m, regardless of its diameter, as the absorbent used is the decisive factor in this regard.

The high carbon dioxide concentration in the exhaust gas leads to increased heat release, especially in the upper part of the absorption column, which also impairs absorption. The process could be further improved in the future by the use of an intermediate cooler.

Apart from the high amount of energy used for carbon dioxide separation, the chemical degradation of the absorption solution is the main problem for large-scale application. As the required chemicals cost several euros per kilogram, even small losses in the vicinity of 1 kg/t of separated CO₂ would lead to significant additional costs.

Literature studies and practical trials are therefore investigating which absorbents are fundamentally suitable and how significantly they are affected by degradation on contact with cement work exhaust gases.

Laboratory and work trials confirm that, in particular, amines with high reactivity, such as monoethanolamine (MEA), are subject to increased degradation. Sulphur dioxide, hydrogen chloride and hydrogen fluoride as well as oxygen and, to a small extent, nitrogen oxides contribute to this degradation. The high CO₂ concentration reduces
these effects to some extent, as the CO₂-rich absorption solution reacts less sensitively. This moderating effect increases with increasing CO₂ concentrations.

Other absorption solutions, such as methyltriethanolamine (MDEA) or aminomethylpropanol (AMP), react less strongly to impurities in the exhaust gas. However, these amines also react more slowly with CO₂ which is why activators, whose degradation then has to be separately considered, are added in industrial application.

Cement works with low SO₂ emissions offer benefits, especially for the use of amine scrubbing. Additional flue gas desulphurisation is required in works with an annual average of more than 30 mg/m³ SO₂.

The result shows a clear sensitivity of the degradation depending on the absorption solution applied. It is therefore also possible that the ideal amine composition could vary depending on the work specifications.

Environmental data

The VDZ has been publishing the “Environmental data of the German cement industry”, based on a survey of almost all the German cement producers, every year since 1998. The current edition is available to be downloaded as a PDF file at www.vdz-online.de. Printed copies can also be requested from the VDZ literature reference.

The brochures document the use of raw materials and fuels for clinker and cement production. In particular, a detailed representation of the quantities of alternative fuels used is provided. In 2010 the fraction of alternative fuels with regard to the total fuel energy use was 61 %. The focus as regards content is on emissions from the kiln exhaust gases of the cement plants, which can be used to represent the German cement industry.

Besides dust, exhaust gas components NOₓ (Fig. II-11) and SO₂ are considered, as well as all the relevant trace elements and organic exhaust gas components. Their concentrations in clean gases have been graphically represented for all of the clinker kilns operated in Germany, as well as the associated material quantity, i.e. the emitted quantities in kg/year. If a component can be determined by a measurement, then clear details on both the concentration as well as the annual emissions can be provided, whose accuracy can be described by the measuring uncertainty. However, this is not possible if measurement values are not secured or measurements are below the detection limit. In these cases no emission concentration is provided in the images. Only a theoretical upper limit of the emitted quantity can then be provided. It is calculated based on the assumption that the concentration of the substance in the clean gas reaches the detection limit.

These types of estimates with upper limits are often inevitable when determining trace element emissions of cement industry rotary kiln plants. The concentrations of trace elements are frequently under the detection limit of the measuring process due to their behaviour in the clinker burning process and the high separating efficiency of the dedusting plant. Fig. II-12 provides an example of the emission concentrations of the trace element vanadium in mg/m³. For example, a total of 114 values for the vanadium concentration in the clean gases were determined by measurements at 38 kiln plants in 2010. However, only the two displayed values (points) were above or equal to the detection limit, which is between 0.005 and 0.008 mg/m³ depending on the measurement.

Fig. II-12: Measured value (2010) of the vanadium concentration in the clean gas of 38 rotary kiln plants

Fig. II-13: Vanadium emissions (2010 annual quantity) of 38 rotary kiln plants
For 37 plants the emissions have to be estimated for an assumed concentration value of 0.005 mg/m³ (line). The actual emissions only equal the displayed upper limit in the worst case scenario which must, in particular, be considered for an environmental evaluation of the figures.

Reducing gas and dust emissions

State of NOx reduction

The German cement industry has significantly reduced the NOx emissions of rotary kiln plants over the previous years. According to the measured values recorded for the VDZ environmental data, the sector average NOx emissions were able to be reduced from about 560 mg/m³ in 2000 to about 350 mg/m³ in 2010. Almost all the kiln plants lie within the targeted emissions level of 200 to 450 mg/m³ specified in the European BREF document for rotary kiln plants with cyclone preheaters. The SNCR process (selective non-catalytic reduction) is applied in 38 kiln lines as an efficient NOx reduction measure. Extensive operational experience has been available for this process for many years, so that it is now considered the “BAT” (Best Available Technique). With this state of NOx reduction, the German cement industry also takes account of the fact that it has to maintain extremely strict national limit values compared to other countries.

Predominantly secondary measures are applied in order to ensure compliance with this challenging NOx limit value. The emissions limit values of the 17th Federal Ambient Pollution Protection Act must be complied with if alternative fuels are used, which is the case in almost all kiln plants. Mixed limit values between 320 mg/m³ (for 60.1 % substitution rate) and 200 mg/m³ (for 100 % substitution rate) apply for the NOx components at substitution rates of over 60 %. While the application of the SNCR process frequently enables such low NOx limit values to be complied with, it is often connected with a rise in NH3 emissions (NH3 slip).

An amendment to the 17th Federal Ambient Pollution Protection Act, which will include a further tightening of the NOx limit values, is in progress as part of the conversion of the European “Industrial Emissions Directive” (IED) into German law. According to this, an NOx emissions limit value of 200 mg/m³ will apply in the future for kiln plants for the production of cement clinker in the event of the coincineration of waste. An NH3 limit value of 30 mg/m³ (NH3 slip) is also intended. Compliance with an extremely low NOx limit value, connected with a limit value for NH3 slip, could therefore become a limiting factor for the application of the SNCR process.

The SCR process (selective catalytic reduction), which is applied in a temperature window of about 250 to 400 °C, could provide a solution to this problem. As for the SNCR process, ammonia or urea solution is injected into the exhaust gas flow as the reducing agent. The exhaust gas is then fed through a reactor that is equipped with several catalyst layers. This allows an essentially stoichiometric reaction to be achieved between NH3 and NO, so that this results in only a minimum amount of NH3 emissions even at very high NOx reduction rates. However, the investment costs are considerably higher for this process than for the SNCR process.

Furthermore, catalytic reduction in the cement industry is currently not the “state of technology” or BAT. Two demonstration projects are being carried out in the German cement industry in order to gain insights and establish limiting factors on the application of the SCR process. From the perspective of the cement industry, it is essential that exemptions for determining the NOx limit values can be provided until both demonstration projects have been concluded, as the data base is currently insufficient for comprehensive investment decisions.

State of the SCR demonstration projects (Mergelstetten / Rohrdorf)

The SCR process for NOx reduction has been applied in power plants and waste incinerators for about 30 years. However, the operating experience gained as a result cannot be directly transferred to kiln plants of the cement industry as the exhaust gas boundary conditions and compositions vary considerably for each process. For example, the high dust concentrations in the exhaust gas of cement rotary kiln plants place special requirements on the catalyst material and the cleaning technology. Besides a few pilot plants, only three SCR plants were installed in cement works in 2010, which included one in southern Germany that was operational from 2001 to 2006.

Two demonstration projects were initiated in the German cement industry in order to further develop the promising SCR process for use in the clinker burning process with regard to further NOx reductions, and to minimise the existing uncertainties and risks. Both projects are supported by the Federal Ministry for the Environment and the Federal Office for the Environment and financed with public funds. A new SCR plant in a raw gas arrangement (high-dust SCR) started operation in the Mergelstetten cement work in the spring of 2010. The reactor, equipped with 3.5 catalyst layers, is fed directly by the dust-laden kiln exhaust gas escaping from the heat exchanger. Sootblowers operated using compressed air ensure regular cleaning of the catalyst plant.

Another SCR plant started operation in the Rohrdorf cement work in the spring of 2011. Unlike the plant in Mergelstetten, in this case the so-called low-dust or tail-end SCR was installed. In this case, the reactor is positioned after the exhaust gas filter. This has the advantage that the risk of catalyst blockages is much lower than for the high-dust version. A disadvantage is that the incoming exhaust gas first has to be reheated to the required reaction temperature by an external heat source. In the Rohrdorf cement work, the exhaust gas is reheated using several heat exchangers, both via the exhaust gas escaping from the catalyst as well as via the hot central exhaust air of the clinker cooler.

Both projects are supported by comprehensive measuring campaigns by the Research Institute of the Cement Industry. The focus of the investigations in Mergelstetten is the combined operation of the SCR with the existing SNCR plant. The aim is to determine whether the combination of both processes will enable the dimensions of the downstream SCR plant to be decreased in order to save investment and operating costs in future projects. Furthermore, investigations on cleaning and the loss of activity or deactivation mechanisms of the catalyst material will also be carried out.

In Rohrdorf the focus is on specific issues regarding the clean gas arrangement in combination with heat displacement. In addition, the impact of the catalyst on the concentration of organic compounds and additional exhaust gas components, e.g. mercury, will also be investigated.

Another SCR plant became operational in the spring of 2012 in the Austrian Mannsdorf cement work. In this case, a semi-dust configuration was realised in which the kiln exhaust gas is dedusted using a hot gas electrostatic precipitator at a concentration of 5 mg/m³. Regular reports on the progress of the on-going SCR projects are provided.
In the VDZ NOx reduction task force and current operating experiences are also exchanged.

However, reliable results will only be available on conclusion of the demonstration projects in 2013/2014.

**New developments in the field of mercury emissions technology**

Rotary kiln plants of the cement industry that are subject to the 17th Federal Ambient Pollution Protection Act must be equipped with continuously operating mercury measuring instruments based on the statutory requirements. This only relates to instruments that have previously undergone suitability testing pursuant to VDI 4203 and DIN EN ISO 14956 and have been recognised by the responsible authority. A current list of all instruments that have undergone suitability testing is provided at [www.umweltbundesamt.de](http://www.umweltbundesamt.de).

The continuously operating mercury measuring instruments currently approved for use in rotary kiln plants of the cement industry (as at May 2012) were developed in the 1990s and underwent their suitability tests between 1996 and 2001. The experiences in the following years have shown that, despite the successful completion of the suitability testing, difficulties constantly arose in practice with regard to the stable long-term operation of the measuring instruments. Instrument modifications based on experiences gained as part of a multitude of emissions measurements, calibrations and function tests enabled an improved adaptation to the features of the exhaust gas matrix of rotary kiln plants of the cement industry. Despite the efforts of instrument producers and operators together with the Research Institute of the Cement Industry, not all issues have been able to be conclusively clarified.

In light of this – but also due to the drastic tightening of the emissions limit values for combustion plants discussed in the USA since the end of 2011 – various instrument manufacturers brought various newly developed mercury measuring devices to the market. These instruments are currently still undergoing suitability testing in Germany – with one exception. Due to a revision of the relevant guidelines, it is now necessary to perform the suitability testing at various types of plants. A distinction is now made between single-material combustion plants and co-incineration plants for constantly operating mercury measuring instruments pursuant to the 17th Federal Ambient Pollution Protection Act. The single suitability announcement for a single-material combustion plant is not sufficient for the application of the relevant instrument in a rotary kiln plant of the cement industry. The conclusion of the suitability testing by the instrument manufacturers has been delayed until now due to this additional expense. The instrument type, whose suitability test was concluded in 2011, is only approved for single-material combustion plants – in contrast to the previous model. Despite the lack of suitability testing, in special cases and in coordination the responsible supervisory authority, the newly developed mercury measuring devices are already being used in some cement industry locations. This step was necessary for operators as the instrument types generally used at these locations in the cement industry were not able to inspect emissions with the required precision.

The constant measurement of mercury emissions is particularly challenging as mercury can arise in the exhaust gas of combustion plants in very different forms. Generally a distinction has to be made between elementary mercury [Hg(0)] and oxidised mercury [Hg(I) or Hg(II)]. Apart from the most important agents according to the previous state of knowledge, including HgCl2 and Hg2Cl2, a variety of other exhaust gas components must also be considered as bonding partners (Fig. II-14). While elementary and oxidised mercury is present in the exhaust gas in a gaseous state, the fraction of particulate mercury also needs to be considered depending on the exhaust gas temperature and the amount of dust emissions.

Constantly operating mercury measuring instruments must be in a position to completely record this complex mix of different components. The UV photometers used in all mercury measuring instruments only detect the elementary form of mercury [Hg(0)]. The prior reduction of the mercury compounds into elementary mercury is therefore essential for a complete measurement of the overall mercury emissions. This preparation step is decisive for the quality of the constant overall mercury measurement.

A distinction must be made between the two fundamentally different designs of the newly developed mercury measuring instruments. Instruments for which the reduction of the bound mercury takes place using a thermal catalyst continue to be used. Sample gas dilution takes place in the sampling probe in order to prevent the premature contamination of the catalyst and the associated loss of reactivity. This also reduces possible cross-sensitivity by other exhaust gas components, e.g. SO2.

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**Fig. II-14: Possible conversion reactions of mercury in the clinker burning process**
Some of these instruments are also equipped with a gold amalgamation in order to improve the sensitivity in lower emission concentrations.

High temperature conversion represents a fundamentally newly developed alternative to the instruments with thermal catalyst. For this type of instrument, the measured gas is fed into a quartz measuring cell that is heated to 1,000 °C. Mercury compounds are immediately reduced to elementary mercury at these temperatures and can be measured directly in the photometer.

All instruments can also be optionally equipped with automatic adjustment devices that ensure that a regular review is performed with elementary mercury testing gas or mercury compounds. This additional module enables the measuring instrument to undergo daily function controls. Furthermore, this allows the requirements of DIN EN 14181 to be fulfilled with regard to the regular quality control (QAL 3) to be performed by the operator.

The bonding structures of mercury are also decisive for constant mercury measurement as well as for mercury emission reduction measures. From the power plant industry it is known that great efforts are being made to transfer all of the mercury present in the exhaust gas to an oxidised form. While oxidised mercury compounds can be separated by adding adsorbents or in wet scrubbers, elementary mercury is not fully recorded by these reduction measures. On the other hand, the presence of larger fractions of mercury compounds in the exhaust gas places higher demands on the efficiency of the constant mercury measurement.

These associations mean that the measurement of various mercury species is constantly gaining in importance. Several methods are provided in the Research Institute of the Cement Industry that are constantly being improved and developed in this regard. All the methods enable the breakdown into particulate, elementary and oxidised mercury. The measurement of individual mercury species, with the exception of elementary mercury, is not possible for the time being.

The speciation may take place according to the “UBA method” or the “Dowex-iodised carbon process”. The UBA method relates to a modification of the standard reference process according to DIN EN 13211. In this case the sample gas volume flow is initially fed into a flat filter in order to separate the particle phases. The gas flow then flows through three wash bottles connected in series, of which the first is filled with diluted hydrochloric acid and the following two with a potassium permanganate solution. Water-soluble mercury compounds, primarily mercury chloride (HgCl₂), are thereby separated from the elementary mercury and both components can be analysed separately.

In the Dowex-iodised carbon process the measured gas is fed through two adsorbents with different properties with regard to the mercury separation (Fig. II-15). A specially pretreated adsorber resin is located in the first collection tube, which selectively separates oxidised mercury, while the elementary mercury is adsorbed in the next iodised carbon tube. Separate analysis allows the fractions of elementary and oxidised mercury to be determined separately.
An application example in which the two speciation processes were applied in parallel is represented in Fig. II-16. Relevant measurements were taken in a rotary kiln plant with installed SCR-Denox catalyst for this purpose. The measurements took place in the interconnected operation, immediately prior to entry into the SCR catalyst, after the 1st catalyst layer and after the SCR catalyst in the clean gas chamber. The measurements identified a very good consistency between the UBA method and the Dowex-iodised carbon process. This applies for both the total measured mercury concentration as well as for the breakdown into oxidised and elementary mercury. As already established from the power plant sector, a large amount of the elementary mercury converts to oxidised mercury compounds with the SCR-Denox catalyst.