

## **Activity Report**



# 2009 - 2012



Activity Report 2009-2012

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### Verein Deutscher Zementwerke Forschungsinstitut der Zementindustrie

Dear Activity Report Reader,

The German Cement Work's Association's (VDZ) Activity Report traditionally provides information on the activities of the Research Institute of the Cement Industry. We have again summarised the important events from our research for the reporting period from 2009 to 2012. They are the result of the joint efforts of the German cement industry, which have now been in place for over 135 years and which are still well-established to this day.

Cement remains a building material without which modern society could not function. The forecast is for a further increase in the global demand for cement – not least due to population growth in many countries which has resulted in a huge demand of infrastructure projects.

In view of this development and the global availability of the basic materials for cement production, particularly limestone and clay, there is currently no other building material that could adequately replace cement or concrete. This especially also applies as concretes produced with cement are extremely robust and durable in their applications.

Nevertheless, the cement industry faces enormous challenges. Given the huge demand for cement-bound building products, the energy requirement and use of resources as well as the associated  $CO_2$  emissions need to be further optimised. As no binding agent is available in the short term that even comes close to replacing the type and quantity of the established cements, the current Portland cement clinker-based systems must continue to be improved.

Against this background, this Activity Report summarises the activities of the Research Institute of the Cement Industry in the area of cement production and application. The research continues to focus on process technology and environmental protection in production as well as the characteristics of cement in mortar and concrete – with regard to application. Occupational health and safety and quality assurance are of utmost importance in all areas.

The VDZ research activities are not just based on the joint effort and the exchange of experiences with its members. Knowledge gained from the VDZ's extensive range of services constantly provides new impetus. Integrated in international research projects, in particular as a founding member of the European Cement Research Academy, the VDZ and its Research Institute will continue to contribute to a competitive, environmentally friendly and sustainable cement production well into the future.

On behalf of the VDZ I hope we have provided a stimulating read for all readers.

Dr. Martin Schneider Chief Executive Verein Deutscher Zementwerke Düsseldorf, September 2012

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The Research Institute of the Cement Industry in Düsseldorf



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#### The Verein Deutscher Zementwerke (German Cement Works Association)

The Verein Deutscher Zementwerke (VDZ), with its registered office in Düsseldorf, is the technical and scientific association of the German cement industry. It continues the tradition of the Verein Deutscher Cement-Fabrikanten (Association of German Cement Producers) founded on 24 January 1877. Differing views between the Portland and slag cement industry on the issue of adding granulated blast furnace slag led to the Verein Deutscher Eisenportlandzementwerke (German Iron Portland Cement Works Association) (from 1901) and the Verein Deutscher Hochofenzementwerke (German Blast Furnace Cement Works Association) (from 1907) representing the technical and scientific interests of German cement producers apart from the Verein Deutscher Portland-Cement-Fabrikanten (Association of German Portland Cement Producers) founded in 1877. They merged in 1948, initially under the name of Verein Deutscher Portland- und Hüttenzementwerke e.V. In 1952 the association adopted the name Verein Deutscher Zementwerke e.V. In January 2012 the non-profit part of the technical and scientific work was transferred to VDZ gGmbH, whose sole shareholder is the Verein Deutscher Zementwerke e.V.

With its Research Institute, the VDZ promotes the development of the production and application of hydraulic cement-type binders. The tasks include, in particular, the promotion of quality assurance measures, environmental protection and occupational safety. Publications, symposia, seminars, meetings and congresses serve to transfer the scientifically or practically acquired know-ledge. The VDZ also supports the training and development of young managers. In pursuit of this object, the Association has been administering the "Gerd Wischers Foundation", a scientific foundation of the German cement industry without legal capacity, since 1995. The training and development programme for employees in the members' works serves the same purpose.

#### Membership in the VDZ

Any natural person or legal entity, which produces cement or cement-type binders standardised or officially approved in the Federal Republic of Germany, can become an ordinary member. Cement producers outside Germany and other organisations close to the cement industry may be accepted into the VDZ as extraordinary members The previous Baden-Württemberg Environment Minister Tanja Gönner and VDZ CEO Dr. Martin Schneider during the annual cement meeting 2011 in Düsseldorf



without voting rights. 25 German cement companies with 50 cement works currently belong to the VDZ as ordinary members, as well as 25 foreign cement companies as extraordinary members.

## Committees, working groups and commissions

**Concrete Technology Committee** Working groups: Transport Engineering, Cement and Admixtures; Ad-hoc working groups: European Standardisation, ASR Studies, Sulphate Resistance

The Concrete Technology Committee is concerned with the current issues of concrete production and application. It supports the corresponding research activities conducted by the Institute on the proper and quality-conscious application of cement and concrete in practice.

The progress report "Thin asphalt layers on concrete surfaces (DAB)" was prepared and published under the leadership of the Transport Engineering Working Group. Various concrete constructions were tested and measured in practice in order to test the effectiveness of noise-reducing measures. Apart from experience with porous concrete test surfaces, the working group also compiled their experiences with the grinding process, in which longitudinal grooves are cut into road surfaces, and experiences with exposed aggregate concrete construction. The grinding process is a measure that reduces noise emissions by up to 3 dB(A) compared to the exposed aggregate concrete construction.

The Cement and Admixtures Working Group works closely together with representatives of Deutsche Bauchemie in the VDZ/Deutsche Bauchemie Coordination Committee on behalf of the committee. The Interface Issues project group within the Coordination Committee developed core principles on the interactions between cement and admixtures. The objective, to represent the status quo with the help of these core principles and to improve the communication between the cement industry and the concrete additive industry, was thereby achieved. Furthermore, the working group also facilitated and discussed the Gefahrstoff-Informationssystem der Berufsgenossenschaft der Bauwirtschaft (GISBAU - Hazardous Substances Information System of the Construction Industry Trade Association) investigating dust-reduced / dust-free products.

In an effort to extend the standardised fields of application of CEM II/B-M cements with up to 20 mass % limestone, the European Standardisation Ad-hoc Working Group developed a proposal for supplementing DIN 1045-2. As the cement standard DIN EN 197-1 does not provide for any class/limitation of limestone content, it was proposed to adopt a regulation in the standards series DIN 1164 in this regard. In the course of discussions in the Cement Standards Committee, the Deutsche Institut für Bautechnik (DIBt) presented an evaluation of the results of durability tests in technical approval processes. Based on this evaluation, the formation of a class of CEM II/B-M cements with a minimum clinker content of 70 mass % and a maximum limestone content of 15 mass %, with regard to the sum

of the main components, would be possible. These cements could then be approved for application in concrete for all the exposure classes in the concrete standard.

During the reporting period the Committee focussed its work on the revision of the European concrete standard EN 206. Members of the Working Group were actively involved in improving the draft standard in various CEN working groups (e.g. CEN / TC 104/SC 1/TG5) and superior committees CEN/TC 104 and CEN/TC 104/SC 1. As questions regarding the regulations and the durability of the concrete arose for these and other issues; in future, the European Standardisation Ad-hoc Working Group will conduct their tasks as the Regulation and Durability Working Group.

The Alkali-Silica Reaction Ad-hoc Working Group was dissolved. Their tasks are now performed by the Alkali-Silica Reaction (ASR) commission. The committee supported the revision of the DAfStb alkali directive in close cooperation with the ASR commission. The working committee and the commission also support the research projects regarding a possible alkali sensitive class E-II-S and the evaluation of the damage potential of ASR with regard to concretes in moisture classes WF and WA in performance tests.

Another major topic in the reporting period was the analysis of the results of the DAfStb special research project "Detailed examinations of the sulphate resistance of concrete" (three work packages - collaborative research). The majority of the research activities were concluded in 2011. The results will be published in the DAfStb series of publications. The examinations determined that for cement-fly ash mixtures with 20 mass % fly ash, relating to (c+f), low magnesium concentrations in soils and water containing sulphates accelerated the development of damage at consistently low temperatures in laboratory and field tests. The accelerating development of damage at considerably lower magnesium concentrations had already been determined, as they are classified in DIN 1045-2. The combination of sulphate attack, low magnesium concentrations and lower temperatures is currently not recorded in a classification. The introduction of a new classification system would complicate the application of the concrete standard. In addition, class boundaries cannot be derived from these investigations. An increase of the currently prescribed minimum fly ash content from 20 to 30 mass %, where DIN 1045-2:2008-08, section 5.2.5.2.2, subsection 7, third bullet point, applies must therefore be provided as a preventative measure. All investigations (laboratory and field tests) have shown that an increase of the fly ash content in the cement and fly ash mixture by this amount clearly improves the sulphate resistance of concretes that reach the sulphate property of up to 1500 mg SR/l by adding fly ash. This regulation is a precautionary measure against sulphate attack, regardless of whether small amounts of magnesium are present or not. The benefit of this regulation is that, firstly, it is easy to handle and, secondly, that additional specifications for new impact classes with (currently unknown) limits in the area of lower magnesium concentrations in DIN EN 206-1 are unnecessary. This regulation will be incorporated into the new edition of DIN 1045-2 in connection with the revision of EN 206 (Source: DAfStb).

The committee also deals with the communication of environmental data of cement and concrete in environmental product declarations (EPD). In the reporting period, an EPD was prepared based on a generic cement, characteristic for domestic shipments in Germany. The publication of the environmental product declaration will take place in the first quarter of 2012. This collective EPD can be used in further calculations on the ecological assessment of components or buildings. Environmental product declarations should also be generated for construction concretes of various strength classes based on the EPD of an average German cement. The VDZ has held the necessary coordination meetings with the Bundesverband der Deutschen Transportbetonindustrie e.V. and the Fachvereinigung Deutscher Betonfertigteilbau e.V.

Another project dealt with investigating the effects of the extended basic European requirements of the building products regulation on harmonised building product standards. These effects were investigated in a research project led by the VDZ on behalf of The Federal Institute for Research on Building, Urban Affairs and Spatial Development.

#### Environment and Process Engineering Committee

Working Groups: Occupational Safety, Refractory Materials (until 2009), Monolithic Refractory Linings (from 2010), NO<sub>x</sub> Reduction, Rotary Kiln Burners; Training Advisory Board; Ad-hoc Working Groups: Alternative Raw Materials and Fuels

Apart from the current issues of thermal and mechanical process engineering, the committee focussed on safety, environmental and energy issues. The primary focus were issues such as the improvement of occupational safety, NO<sub>x</sub> reduction using SCR processes, the impact of emissions trading, possible waste heat utilisation concepts and the continued optimisation of alternative raw materials and fuels. Furthermore, the committee also provided intense support for the Institute's research activities on the separation of CO<sub>2</sub> from the clinker burning process, on the reduction of corrosion damage, on burner optimisation and on optimising the charge of ball mills and the related investigations in largescale plants.

The 100th meeting of the Working Group in the spring of 2011 means that it can now look back on 50 successful years of safety work of the Verein Deutscher Zementwerke and its member companies. The Working Group's activities focussed on developing safety data sheets, the industrial safety regulation, the European machinery directive and other conditions for protecting people at the workplace. A testing guideline in accordance with BetrSichV (Occupational Health and Safety Regulation) and a recommendation for action on the implementation of the European machinery directive were prepared and published in order to support the plants.

In addition the "Work safety when handling hot meal" memorandum was completely revised and provided to the member companies.

With the publication of the process engineering leaflet Vt 16 "Refractory Materials" at the end of 2009, the Working Group compiled a document that is tailored to the special requirements of the practitioners in the cement plants and which includes all the necessary information regarding refractory linings and formed products. The memorandum focussed on the lining in the rotary kiln. It covers the following topics:

- Incoming inspection of rock
- Status diagnosis techniques (refractory materials)
- Lining techniques
- Drying and heating procedures
- Influence of the operating conditions on the consumption of refractory products
- Damage to refractory materials in cement plants
- Measuring and adjusting the rotary kiln
- Occupational safety when completing refractory tasks

The practical experiences of the Working Group members and knowledge from the supplier industry was considered when preparing the memorandum.

After the successful publication of memorandum Vt 16, the Working Group assumed the tasks of updating the process engineering memorandum Vt 11 "Monolithic refractory linings in cement works" from 1994, as many aspects of the memorandum no longer applied to current practices. The updated memorandum will contain the following issues:

- Monolithic masses for the cement industry
- Fields of application of monolithic masses
- Construction of monolithic linings
- Lining techniques and processing monolithic masses
- Drying and heating procedures
- Monolithic lining damage

The NO<sub>x</sub> Reduction Working Group predominantly dealt with the two SCR demonstration projects (SCR = Selective Catalytic Reduction) in the Mergelstetten cement works (high-dust process) and in the Rohrdorf cement works (low-dust/tail end process). Furthermore, all international developments in connection with SCR technology were also tracked. Another demonstration project that started at the Mannersdorf/ Austria cement works was also supported by the Working Group.

Apart from the technical issues regarding  $NO_x$  reduction, the environmental requirements were also an important issue in the Working Group. The implementation of the IED directive and the preceeding amendment of the 17th BImSchV (Federal Emission Protection Regulation) were also intensely discussed.

The German plant operators now have many years of operating experience with large quantities of solid alternative fuels, but knowledge of the optimal operation of rotary kiln burners with a large quantity of fuel is not clear or generally substantiated. The Rotary Kiln Burner Working Group therefore discussed an "optimal" burner design and "optimal" burner operation with eight burner manufacturers. Modern rotary kiln burners are characterised by a number of lances, pipes and ring channels that enable the flexible burning of coarse and ground fuels as well as liquid and viscous and gaseous fuels. Turbulence systems aligned specifically to the fuel, mix the fuel directly into the flame. Initial experiences with oxygen application in the clinker burning process were also exchanged with the plant operators. Knowledge of burning processes in rotary kiln flames when burning alternative fuels was also expanded in discussions with burning experts from research and practice. The results of the Working Group's activities were summarised in a memorandum. The memorandum focusses on the issues of rotary kiln burners, alternative fuels and rotary kiln furnaces. Other issues include electrical equipment, wear, kiln operation and clinker quality as well as emissions.

In 2009 and 2010, the Training Advisory Board primarily supported the development and implementation of the VDZ learning platform (www.vdz-elearning.de) into further operational training. Since 01.01.10 the platform has been successfully applied by many members for internal training. Since 2011, the focus has been on the further development of the VDZ learning platform in the knowledge areas of lime and concrete and the integration of a reference book and a communication platform. The objective of the project is to investigate the approach to knowledge in the non-metallic minerals industry and optimise this with Web 2.0 technologies.

In October 2010 an Ad-hoc Working Group was appointed to revise and update the German cement industry literature on the application of alternative fuels and raw materials. The backdrop to this is that, firstly, energy and resource efficiency is becoming increasingly important. And secondly, that the VDZ "Hard-strong-fair" brochure is over ten years old and therefore no longer current. The following issues were dealt with in the Working Group:

- Energy efficiency: The particular application aspects of alternative fuels and their impact on the energy efficiency of cement rotary kiln burner systems. This should also be viewed together with CO<sub>2</sub> emissions trading.
- Waste policy: The issues of the evaluation of industrial coincineration with regard to waste policy were again raised by the European Commission. It is to be assumed that the availability of the relevant quality of alternative fuels and raw materials will reduce considerably in the future. Competition with waste incinerations plants, which are now largely classed as recycling plants, is of primary importance. They are therefore competing with the cement industry for the same input materials on the alternative fuel market.

- Environment/Emissions: The impact of the application of alternative fuels on the emissions of cement rotary kiln systems is a constant topic of discussion, in particular compared to waste incineration plants. Furthermore, the biogenic content of the applied alternative fuels represents an important form of relief with regard to CO<sub>2</sub> emissions trading for many cement works.
- Product quality/Environmental compatibility: Although the environmental compatibility of the application of alternative fuels and the unchanged high product quality has been repeatedly scientifically verified, discussions that raise this issue still continue. The relevant arguments will therefore be updated and compiled.
- Resource efficiency: Resource efficiency is a particular success story for the cement industry as a result of the high rates of application of alternative fuels and raw materials as well as the main cement constituents. However, the cement industry remains reliant on domestic raw materials such as limestone, marl and clay, without which the industry could not exist in Germany.

The key Working Group results will be summarised in a presentation and a brochure. All member companies will receive these once they have been completed.

#### **Cement Chemistry Committee** Working Groups: Analytical Chemistry, Performance of Cement Constituents

The committee activities were focussed on current analytical issues, product-related occupational health and safety and on-going research projects by the Research Institute in the reporting period. Research activities, in particular on the application of cements with several main constituents and cements with low clinker content were carried out together with the Performance of Cement Constituents Working Group. Issues such as Rietveld and trace analyses and isothermal heat flow calorimetry were processed together with the Analytical Chemistry Working Group. Other issues such as classification and identification according to the CLP regulation, new safety data sheets for clinker, kiln dust and cement, fine quartz dust, low dust cement and cementitious preparations as well as the REACH regulation were processed together with the REACH Working Group. Furthermore, issues regarding concrete durability - such as the alkali-silica reaction

and the sulphate resistance of cements – were deliberated and activities by the international research consortium NANOCEM, of which VDZ is a member, were reflected upon. Many of the issues were presented and discussed with a broad expert community in two plenary committee meetings. They took place in Düsseldorf on 01.04.2009 and 05.04.2011 and were attended by more than 200 participants.

The Analytical Chemistry Working Group remained focussed on the analytics of secondary fuels, the selection and suitability testing of various reference materials, in particular for trace analysis, the determination of water-soluble chromate in cements and investigations of the storage stability of chromate-reduced cements. It became clear that the previously tested fluff and PVC samples could not be used as reference materials due to the lack of homogeneity. The Trace Analysis Ad-hoc Working Group worked intensely on developing an interactive expert system on the methodology of trace analysis based on a "Wiki" in the reporting period. After completion, this is expected to provide analysts with a practical as well as current working aid.

The Capability of Cement Components Working Group primarily discussed the results of the on-going AiF research projects. This included the following research topics: The impact of burning and cooling conditions on Portland cement clinker, joint use of slag sand, hard coal fly ash and Portland cement clinker to produce optimised cements and concretes, improving the capability of fly ash-containing binders, application of naturally tempered clays as main cement constituents, the interactions between plasticisers and main cement constituents including clinker, limestone and slag sand (see Sections III and V).

The REACH Working Group primarily focussed on the results from the two new European regulations on chemical legislation, the REACH and the CLP regulations, in the reporting period. This required that dusts from the production of cement clinker, so-called flue dust, had to be registered with the new European Chemicals Agency (ECHA) by 01.12.2010. Portland cement clinker had to be registered by 03.01.2011. This means that all cement clinker producers had to register in ECHA's classification and identification directory. The new sample safety data sheet for Portland cement clinker, flue dust and cement was created based on the new regulations. The second reporting period for the European Social Convention "Crystalline Silica" concluded in the first half of 2010. With almost 100 % representation of their sites, the cement industry was again better represented than most of the other sectors. The issue of preventing dust, especially fine quartz dust, was a top priority in the plants (see Section VI).

#### VDZ Commission Alkali-Silica Reaction

The Commission supported the revision of the alkali directive and the preparation of the WS basic and confirmation testing concept in close cooperation with the Concrete Technology Committee in the reporting period. The objective of all the activities is to prevent damage to concrete buildings as a result of an alkali-silica reaction (ASR).

Damage to existing concrete pavements, which were constructed prior to the inception of the General Circular on Road Construction no. 15/2005, occurred during the reporting period. Reporting on these and other alleged cases under the heading "Concrete cancer" led to further uncertainty in dealing with the risks of damaging ASRs. The Commission therefore compiled an information brochure "Practical experiences and current regulations" under the leadership of the VDZ, together with the BDB, BTB and MIRO associations. The brochure was simultaneously directed at journalists, building owners, contractors and building authorities and provided an overview and orientation on the issue of ASR.

The road construction (ZTV Beton-StB) and structural engineering (e.g. ZTV-ING) areas were separated from each other under the regulations with the 1st amendment to the alkali directive. The measures for concrete pavements of moisture class WS (construction classes SV and I to III pursuant to RStO [Directive for the Standardisation of Road Surface Superstructures]) were determined by the TL Beton-StB and by General Circulars on road construction. The Commission supervised the draft of the WS basic and confirmation testing and discussed this with the aggregates industry in the MIRO/VDZ Contact Working Group. The WS basic and confirmation testing set the requirements for aggregates for concrete in moisture class WS. It is expected that this will be introduced by way of a General Circular on road construction.

The Commission also documented the developments in the field of AKR over the

previous year in the MIRO/VDZ Contact Working Group. It determined that important aspects that were discussed ten years ago, in cooperation with the VDZ and the member companies, had been implemented (e.g. enhancement of NA cements according to DIN 1164).

The Commission supervised the IGF project to determine a new alkali sensitivity class E II-S and the testing of the ASR damage potential of concretes in moisture classes WF and WA. Relevant concrete-related measures will become necessary if a new alkali sensitivity class E II-S can be defined.

Further IGF projects on fly ash-containing low alkali cements and the impact of alkali supply by de-icing agents on binding agents for concrete with alkali-reactive aggregates are part of the Commission's work program.

#### VDZ Emissions Trading Commission

The revision of the EU emissions trading directive in 2009 set the framework conditions for CO<sub>2</sub> emissions trading from the period after 2013. According to this, a free allocation based on benchmarks is received by all industry sectors for which the EU Commission determined a risk of production relocation (carbon leakage) in 2009. This determination initially applies until 2014. After the publication of the McKinsey study on the issue of carbon leakage in 2008, an important task will be the re-specification of the effects on the cement industry at the upcoming risk assessment in 2013. The European CO<sub>2</sub> benchmarks for the production of grey and white cement clinker were determined based on the emissions data of the top 10 % of the most efficient plants in Europe. This means an 11 % reduction of free certificates for the average specific CO<sub>2</sub> emissions of the European cement industry per produced ton of grey cement clinker in 2007 and 2008. In Germany the EU emissions trading directive was transformed into national law by an amendment to the Treibhausgasemissionshandelsgesetz (TEHG -Greenhouse Gas Emissions Trading Law) in 2011 and a new Allocations Ordinance (ZUV 2020). The Emissions Trading Commission could therefore clarify special issues, in particular with regard to product and plant segregation, with the German Emissions Trading Authority in advance. At the end of 2011 the German clinker producers compiled their application for the free allocation of emission certificates for the third phase of EU emissions trading 2013 to 2020.

The  $CO_2$  monitoring with regard to the self-commitment of the cement industry to  $CO_2$  reduction from 2000 was continued and summarised accordingly in the reporting period.

#### VDZ Ready-Mix Concrete Commission

The Ready-Mix Concrete Commission focussed primarily on the revision of the European concrete standard EN 206-1 and the new Grundwasserverordnung (Groundwater Regulation) in the reporting period.

The three-year EN 206-1 revision process started in September 2010 with a corresponding CEN/TC 104 (concrete and related products) resolution. A table of basic requirements for aggregates, a reference to a technical report for the prevention of damaging alkali-silica reactions and a reference to the principles of the "Equivalent concrete performance concept" (ECPC) and the "Equivalent performance of combinations concept" (EPCC) were new additions in the current draft. A comprehensive report on the revision of EN 206-1 can be found in the "Regulations" subsection of section V.

Another important issue considered by the Ready-Mix Concrete Commission during the reporting period was the potential impact of the inception of the Grundwasserverordnung (Groundwater Regulation) for building with concrete. The contents of the regulation were analysed and possible actions were discussed. A supplementary section to the concrete standard "Concrete groundwater compatibility" was not considered expedient by the Commission, as this would likely trigger a systematic test order in the DIBt in which all building material standards would have to be tested with regard to groundwater. Rather the objective should be to continue to pursue the "on average, limits will not be exceeded over a short period and in a regionally limited volume" approach and the possible "suspension" of critical parameters. To support the argument, the Commission referred to a position paper by the Deutscher Ausschuss für Stahlbeton (BAfStb - German Committee for Reinforced Concrete) titled "DAfStb explanation on the current state of regulation for the environmental compatibility of concrete", compiled with the participation of the Research Institute of the Cement Industry and which can be accessed on the DAfStb internet site.

Other issues tackled by the Commission were environmental product declarations for concretes, the current state of regulation for alkali-silica reactions and safety data sheets for Portland cement clinker, cements and concretes.

One focus of the Commissions future activities will be the formulation of suitable requirements for the provision of more robust concretes. The basis for further considerations in this regard would include a research project by the Research Institute titled "Framework conditions for the targeted attainment of projected concrete properties in the modern 5-susbtance system of various concrete raw materials". This is a joint project between the Research Institute of the Cement Industry (FIZ) and the Ruhr University, Bochum (RUB), chair for building material technology. The research project will run from 01.05.2012 to 31.10.2014. The research project should also determine which influencing parameters are primarily responsible for the fact that fresh concrete produced over long periods occasionally displays unexpected characteristics, such as a changed consistency, signs of sedimentation or accelerated or retarded strength development. In addition, criteria are to be developed for designing concrete compositions that must be met so that no undesired fresh concrete characteristics appear in the economically optimised 5-substance system and so that the vulnerability regarding material and product-related fluctuations is as low as possible; even under the variety of influences that can occur when manufacturing concrete and its raw materials.

This issue is particularly important as undesired fresh concrete properties such as sedimentation or unexpected changes in consistency can have a negative impact on the outer zone of the concrete. The quality of the outer zone is particularly important for ensuring the durability of the concrete. This applies for properties relevant for durability with regard to reinforcement corrosion (carbonation and chloride penetration) as well as for frost and resistance to de-icing salt.

The project will be executed in two stages:

In the first stage, previously determined cement-admixture combinations will be investigated with regard to how the composition of a fresh concrete in the 5-component system impacts the occurrence of undesired aspects under set manufacturing conditions. This will identify concrete compositions that react "sensitively", with regard to their fresh concrete properties, under defined influencing parameters such as temperature, grainsize or mixing time, i.e. that already exhibit a tendency to display one or more of the undesired properties but which can still be assessed as suitable for application in practice. In addition, concrete compositions that do not display these undesired properties and which can be described as "robust" will also be identified.

The second stage is to systematically investigate how changing various parameters, on which the concrete producer generally has no influence, influences the wet cement properties investigated in the first stage. This will highlight the impact of process-related parameters, such as the starting weight tolerances, as well as the impact of production-related fluctuations in the properties of individual raw materials (cements, plasticiser and aggregate). Concrete compositions assessed as both "sensitive" and "robust" will be investigated.

All the considerations will require the qualified processing of the concrete within the scope of the applicable regulations on the construction site.

Another commission work package relates to the analysis of the quality assurance measures of the production and processing of concrete along the entire value chain. This includes a review of the conformity control and evaluation systems and the external monitoring of ready-mix concrete.

## Cooperation with other organisations

The VDZ and its Research Institute work closely together with authorities, universities, material testing offices and a number of professional associations, standards committees and organisations of related industries at the national, European and international level in numerous fields. This cooperation generally takes place among employee members of the Institute or member companies in the committees of these organisations. This cooperation continued to lead to extremely good results in many areas during the reporting period.

#### Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF – German Federation of Industrial Research Associations)

The AiF, of which VDZ is a founding member, promotes joint industrial research, in particular that of medium-sized industry, financed by funds from the Federal Ministry of Economics. One condition of the funding is that the research associations have to match the funding amount provided by the Ministry. In previous years the VDZ has once again received AiF funding for several large research projects. The AiF and the Federal Ministry of Economics are to be thanked for their support.

## Cement production and environmental protection

In the area of cement production as well as environmental protection the VDZ is in close professional contact with the Federation of Germany Industry (BDI) and the German Building Materials Association (BBS) with a focus on energy and climate policy, emission control and issues of sustainability. Given the broad scope of their professional activities, the VDZ also works together with a number of other organisations. These include the Association of German Engineers (VDI), the Deutsche Vereinigung für Verbrennungsforschung (DVV-The German Association for Combustion Research), the Vereinigung der Großkraftwerksbetreiber (VGB PowerTech The Association of Major Power Plant Operators), the Verein Deutscher Eisenhüttenleute (VDEh - German Steel Institute), the FEhS - Institut für Baustoff -Forschung (Institute for Research on Building Materials), the Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall (ATV-DVWK - The German Association for Water Management, Waste Water and Waste) and the Deutsche Vereinigung des Gas- und Wasserfachs (DVGW - The German Technical and Scientific Association for Gas and Water). The cooperation with the Bundesverband der Deutschen Kalkindustrie (BV Kalk - Federal Lime Industry Association) and its research community primarily relates to the jointly operated training and further education of industrial foremen in the field of lime and cement, and the various activities in the area of environmental and health protection and occupational safety. The cooperation with the Bundesverband der Deutschen Kalkindustrie developed in an outstanding manner on issues regarding CO2 emissions and its capture in the reporting period.

The VDZ is in regular contact with many federal state ministries and the federal government on issues regarding the environmental compatible application of alternative materials, CO<sub>2</sub> reduction and the trade of emission certificates. VDZ representatives are also actively involved in various committees of the Deutschen Instituts für Normung (DIN). This primarily includes the construction (NABau), water (NAW) and the fundamentals of environmental protection (NAGUS) standards committees.

#### **Cement application**

The VDZ is represented on the board and in the steering committees of the Deutschen Ausschuss für Stahlbeton (DAfStb) and on the Advisory Board and in various working groups of the Construction Standards Committee, on boards of the Materials Testing Standards Committee and in the Forschungsgesellschaft für Straßen-und Verkehrswesen (FGSV - The Road and Transportation Research Institute). On issues of road surfaces and concrete the VDZ is actively involved in the concrete road surface quality association. In addition, employees from the Research Institute of the Cement Industry are involved in various committees of the Deutschen Instituts für Bautechnik (DIBt) or are appointed as experts in the relevant committees. The cooperation in external committees also extends to advising, coordinating and assessing research projects, to the development of standards, directives and leaflets and to advising on the provision of building approvals.

A traditionally strong and trusting cooperation exists with the technical and scientific associations of cement consumers, especially with the Deutsche Beton- und Bautechnik Verein (DBV - German Concrete and Construction Technology Association) and the Bundesverband der Deutschen Transportbetonindustrie (BTB - Association of the German Ready-Mix Concrete Industry). Regular contact also exists with the Fachvereinigung Deutscher Betonfertigteilbau e.V. (fdb), with the Betonverband, Straße, Landschaft, Garten e.V. (SLG), with the Bundesverband Estrich und Belag e.V. (BEB) and with the Institut für Baustoffprüfung und Fußbodenforschung (IBF - Institute for Building Material Testing and Flooring Research). The VDZ also has a close professional exchange with the manufacturers and producers of additional raw materials for cement-bound building materials, such as the Vereinigung der Großkraftwerksbetreiber (VGB PowerTech), the Deusche Bauchemie (DBC) and the Bundesverband Mineralische Rohstoffe (MIRO - Federal Association of Mineral Raw Materials). For applications of cement-bound building materials in the area of drinking water supply and waste water removal professional contact exists with the Deutschen Vereinigung des Gas- und Wasserfachs (DVGW), the DIN water standards committee (NAW) and the Deutschen Vereinigung für Wasserwirtschaft, Abwasser und Abfall (DWA). Close professional contact also exists with the Verband Deutscher Betoningenieure (VDB - Association of German Concrete Engineers).

Issues on the application of cements in ready-mix concrete have been deliberated for many years in a contact committee with the Bundesverband der Deutschen Transportbetonindustrie (BTB) and common ground has been sought on overarching issues. The Concrete Admixture Coordination Committee was founded with the Deutschen Bauchemie e.V. as early as 1990, and a contact working group exists with the Bundesverband Mineralische Rohstoffe (MIRO).

#### Gemeinschaftskreis Beton (Concrete Community)

One of the key tasks of the Gemeinschaftsarbeitskreis Beton (GAK - Concrete Community Working Group) is the preparation of joint initiatives in the area of standardisation - with the strategic objective of promoting concrete construction. The Bundesverband der Deutschen Transportbetonindustrie (BTB), the Deutsche Beton- und Bautechnik-Verein (DBV) and the Verein Deutscher Zementwerke (VDZ) are represented in the Gemeinschaftsarbeitskreis. The head of GAK changes on an annual basis. Jointly initiated research projects, for example, on the issues of fair-faced concrete and sulphate resistance were financed and extensively supported by the associations, in part also by public donors, in the reporting period. In the area of standardisation, a position had to be taken on a number of interpretation enquiries regarding the concrete standards. In particular, GAK will pursue further standardisation activities at a European level in the coming years. These include the revision of the European concrete standard EN 206-1 by the CEN/ TC 104 and the activities of the CEN/TC 351 "Building products: Evaluation of the approval of hazardous substances" and the CEN/TC 350 "Sustainability assessment of construction works".

#### VDZ/Deutsche Bauchemie Coordination Committee

The Coordination Committee, with specialists from the cement and admixture industry, was led by the VDZ in the reporting period. The chairmanship changes every two years. The committee focussed intensely on issues regarding the interaction of cement and concrete admixtures. At the fore during the reporting period was the effect of natural and synthetic air-entraining agents and the interactions between air-entraining agents and plasticisers based on polycarboxylatether (PCE). An intensive exchange also took place regarding the environment product declaration of cement and admixtures, the safety data sheets and the low-dust mortar products. The committee also provides regular information on the current standard. The contact working group intensely discussed the interactions between cement and contents of building chemical products. Key principles on the interactions between cement and retardants and between cement and air-entraining agents were prepared.

#### Universities

The VDZ has always been involved in promoting university activities in the field of construction research and structural engineering. In the reporting period the VDZ again provided funds for research activities at university institutes. The VDZ is participating in the "Binding agents and building materials" professorship together with the Bundesverband der Deutschen Kalkindustrie at the Clausthal University of Technology. Furthermore, employees of the Research Institute are lecturers at various universities of technology.

#### International cooperation

CEMBUREAU is the European umbrella association in which 26 national cement associations are involved in a transnational cooperation. The VDZ has been providing its technical and scientific expertise in this community work for many years. The focus in the reporting period was on environmental protection and CO<sub>2</sub> reduction issues. The VDZ was involved in the revision of the BREF documents on best available techniques (BAT), and the determination of the benchmarks for the allocation of emission certificates as part of European emissions trading was intensely supported by VDZ employees. The joint European work on the possible impact of cement processing on human health was continued and cement producers were also supported in implementing the REACH regulation.

The VDZ has been heavily involved in European standardisation activities. At the forefront are the activities of the CEN/TC 51 (cement standardisation), the CEN/TC 104 (concrete standardisation) and the CEN/TC 178 for pre-cast road construction products. A particular highlight is the completion of the new "cement standard" EN 197-1, which now also regulates cements with high sulphate resistance (socalled SR cements - sulphate resisting cements). In addition, standards EN 413-1 for plaster and wall binders, EN 15743 for supersulphated cement, EN 15368 for hydraulic binders for non-structural applications and draft standard EN 13282 for hydraulic base course binders were compiled and revised in the reporting period. Standardisation activities spanning across all types of materials are also constantly gaining in importance. The European Commission draft mandate M 366, that targets potential environmentally relevant releases from building materials has led to extensive research activities and an intense exchange of experiences at the European level. The VDZ established their cooperation in the mirror group to the CEN/TC 343 in the reporting period. This group is expected to establish quality standards for processed fuels from waste not requiring special supervision.

The European umbrella association of building material producers (CEPMC) is also an important platform for the cement industry in order to be able to recognise European developments at an early stage. In particular, there are common interests for all building material producers on issues regarding the environmental impact of building materials. The experiences of the VDZ flow into the activities of the CEPMC. Research Institute employees are therefore directly involved in activities at a European level. The German Building Materials Association works together with the VDZ on developing German positions for discussion in Brussels.

The VDZ remains involved in scientific projects that provide synergies with transnational cooperation. VDZ has been a part of the European research and training consortium NANOCEM since its foundation. NANOCEM consists of 30 partner organisations. This includes universities, national research institutions and industrial partners. More than 120 researchers collaborate in NANOCEM. The objective is to improve our knowledge of the nano and microstructures of hardened cement paste in order to better understand the macroscopic properties of cement-bound building materials.

In addition to the previously mentioned international organisations, the VDZ and its Research Institute also maintain contact with other European and international organisations. These include the partner associations of the cement industry and their technical and scientific organisations in neighbouring foreign countries. The cooperation takes place in many different forms, in particular in the committees of the European Committee for Standardisation (CEN) and the European cement association CEMBUREAU. Furthermore the VDZ maintains good contacts with the Indian National Council for Cement and Building Materials (NCB), the China Building Material Federation (CBMF) and the China Building Materials Academy (CBMA). The VDZ was also actively exchanging ideas with the US Portland Cement Association (PCA) in the reporting period. Additional exchanges of experience took place in the field of concrete road construction and on the issues of cement application and environmental protection. The VDZ maintains additional contacts with the International Organisation for Standardisation (ISO), with the Fédération Internationale du Béton (fib) and with the International Union of Laboratories (RILEM), the International Flame Research Foundation (IFRF), the American Concrete Institute (ACI) and with the American Society for Testing and Materials (ASTM). VDZ is also in contact with many other research institutes worldwide.

#### European Cement Research Academy

The VDZ is one of the founding members of the European Cement Research Academy (ECRA) that will celebrate ten years of joint activities in 2013. ECRA now has over 40 members, including cement producers and cement associations as well as companies that are related to cement producers in various ways. Seminars and workshops are held on various cement manufacturing and application issues. In most cases these are held on site at the plants of ECRA members. Furthermore, ECRA also develops expertise on important individual issues. ECRA works together in extremely close cooperation with the Cement Sustainable Initiative (CSI) and the CEMBUREAU in this regard. Research activities to determine the biogenic CO<sub>2</sub> content using <sup>14</sup>C methods continued in the reporting period. Final reports of the three project phases are now available for the research project to separate CO<sub>2</sub> from exhaust gases (CCS). The extent to which the post-combustion process and the oxyfuel technology can be implemented in the cement industry was investigated. Various work packages were jointly processed by cement producers, industrial partners from plant construction and gas production and other research and consulting companies for the first time.

ECRA is headed by a Technical Advisory Board in which leading German and European cement producers are represented. These include the companies Aalborg Portland, Buzzi, Cemex, CRH, HeidelbergCement, Italcementi, Lafarge, Holcim, Schwenk, Titan Cement, Vicat, CEMBU-REAU and the VDZ.

#### Knowledge transfer

Specialist publications, symposiums, seminars and lecture programs are a welcome platform for communicating the numerous activity results from the committees, working groups and commissions as well as the Institute's research activities to members and interested experts. Most of the publications are available on the VDZ internet pages or from the Betonshop (concrete shop) of BetonMarketing Deutschland GmbH at www.betonshop.de.

#### Publications

The environmental data of the German cement industry (annual update) continues to be recorded and published along with the CO<sub>2</sub> monitoring report.

A multitude of research topics were processed and published during the reporting period. This resulted in no less than five new dissertation volumes in the cement industry series. Eberhard Eickschen focussed on the action mechanisms of air-entraining concrete admixtures. Jürgen Bokern contributed to the improvement of testing results in evaluating alkali-silica reactions. Stefan Seeman summarised the results of his work on the impact of the grinding atmosphere on the properties of cements containing granulated blastfurnace slag. Vera Tigges focussed on the possibilities of influencing the hydration of granulated blastfurnace slag with regard to optimising blast-furnace cements. Sören Eppers presented the ring test as a proven process for determining the autogenous shrinkage cracking propensity. Apart from these issues, a number of diploma theses and student research projects, which dealt with various cement production and application issues, were also supported in the Research Institute of the Cement Industry.

The tri-annual VDZ communications included current information on well-known issues such as  $CO_2$  emissions trading, ASR, REACH as well as process engineering and road construction aspects. The energy transition and  $CO_2$  reporting were also referred to, among other things. Since integrating with the cement communications, the range of issues has extended to current contributions from the areas of architecture and statistics.

In addition to the VDZ communications, numerous safety information sheets and test lists once again proved to be valuable aids on the issues of occupational safety and risk prevention. Besides the recognised publications, the VDZ bulletins, which form a section of the "Cement International" magazine, have since the end of 2011 provided an insight into various research areas and general VDZ issues with one DIN-A4 page dedicated to each issue.

#### Training and further education

The VDZ has provided successful further education measures for the cement industry and related industry sectors for over 50 years. The offer extends from the teaching of technical fundamentals through to imparting specialist knowledge and long-term further education courses for managers. Besides the recognised international courses for further education to become industry foremen and production controllers, individual and tailored one-day and multiday seminars on the topics of clinker and cement production, quality assurance, environmental protection and concrete technology are also offered. Since 2010, the VDZ online courses have also offered cost-effective multimedia further education on the internet, which can be flexibly applied for individual and company-internal training.

The lime/cement industry foreman course has been provided together with the Bundesverband der Deutschen Kalkindustrie since 1958. The courses, which are divided into theoretical and practical training components, last 18 months and finish with an exam at the Düsseldorf Chamber of Commerce and Industry. The first section of the 24<sup>th</sup> industry foreman course commenced in September 2009. 19 participants from the lime and cement industry were given theoretical and practical preparation for the final exam that took place in Düsseldorf on 15.03.2011.

Apart from foreman training and further education, control-room operators are also trained as part of the VDZ training system. The training includes a 7-week theoretical section at the VDZ and a practical section at the respective plant. During the course, participants are taught the fundamentals of plant technology, kiln burning, processing technology, measurement and control technology as well as environmental technology. Three internet courses took place in the reporting period. More than 350 control-room operators have been trained in 17 courses since 1990.

#### **Scientific foundations**

The Gerd-Wischers foundation founded in 1995 supports the training and further education of young scientists. The founda-

tion has assets of EUR 1,533,875. The interest income allows four to five scholarships to be granted in parallel.

In the reporting period, three dissertations on the topic of increasing energy efficiency and reducing  $CO_2$  emissions, optimising the charge grading in ball mills and interactions between main cement components and plasticisers were supported. In addition, various scholarships with shorter terms were awarded for internships, masters and diploma theses in the area of cement chemistry and processing and concrete technology.

The Dyckerhoff foundation, which originated in 1994, has supported the activities of young scientists in the Research Institute of the Cement Industry for many years. In the reporting period for example, activities to optimise grinding plants, on corrosion mechanisms in cement works and on assessing the low-alkali property of cements were supported.

#### Research Institute of the Cement Industry

The VDZ maintains the Research Institute of the Cement Industry in order to carry out its duties. The Institute's management provides a detailed specification of the tasks in coordination with the Technical and Scientific Advisory Board and with the approval of the Board. The VDZ's Research Institute is a renowned and internationally recognised scientific facility. It covers all the areas of cement production and application.

The Research Institute has modern equipment and is also well-equipped for sophisticated fundamental investigations. The Institute can also act for third parties, e.g. by performing public service tasks as an official emission measuring station or as an officially recognised testing office. In addition, the Research Institute also increasingly provides expert and advisory support in specialist matters as part of the association's purpose. The Institute is organised into five specialist departments.

The "Cement chemistry" department of the Research Institute is concerned with the overall life cycle of cement, starting from the production through to application and the recycling of cement-bound building materials. The characterisation of the raw materials and fuels and the reactions when burning cement clinker is also a primary focus as well as the processes during the setting and hardening of cements. The



Karl von Wedel receives the Dyckerhoff prize at the annual cement conference in Düsseldorf in 2011 for his work in clinker cooler development. The picture shows the prize winner with the two benefactors Dr. Klaus and Dr. Edith Dyckerhoff.

interactions between the various main cement components or with admixtures/additional materials and the concrete-damaging reactions are intensely investigated. Apart from classic application-related research in this department, the service sector has also become increasingly important in the past few years.

The production of cement starts with the extraction of raw materials in quarries and the subsequent clinker burning and grinding process in the cement work. This is the focus of the activity and research of the "Environment and Plant Technology" department. In line with the complexity and diversity of the environmental and processing aspects that are taken into account for the environmentally friendly, energy efficient and yet still economical production of cement, the Environment and Plant Technology department comprises scientists from various disciplines, supported by technicians and laboratory assistants with extensive theoretical and practical experience. Both an environmental and process-oriented laboratory and modern measuring equipment for investigations and optimisations in cement works form the basis of the extensive research. In addition, the department also offers a diverse range of services in the area of environmental reporting, environmental consulting and education.

The "Environmental Measuring" department is identified as an independent measuring body. This notification allows work to be performed in areas regulated by law. For example, the environmental measuring body is therefore also authorised to perform statutory acceptance measurements. Given the increasing internationalisation of the cement industry, the services of the environmental measuring body are also increasingly asked for on a global level.

The environmental measuring station consists of an interdisciplinary team of engineers, natural scientists, laboratory assistants and technicians with extensive practical experience. This allows the Institute to provide services in all environmental areas. This primarily includes areas relating to emissions measurements that arise from the relevant regulations.

The "Quality Assurance and Analytics" department provides testing, monitoring and certification services and is responsible for the chemical and physical investigations that the Research Institute provides for third parties. Quality monitoring and quality assurance of cement and cementitious binding agents by the monitoring organisation are part of the traditional core competencies of the Verein Deutscher Zementwerke. The department assumes the tasks of the VDZ monitoring organisation as a legally recognised testing, monitoring and certification office for building products.

The "Concrete Technology" department deals with current issues in the field of concrete raw materials as well as concrete technology and concrete application. Based on the findings from the research activities, the department offers a comprehensive service package regarding the application of concrete and other cement-bound building materials, the all-important testing as well as consultation and complex reports including structural condition analyses. Due to the leading role of the Research Institute on issues regarding alkali-silica reactions, a large number of reports are compiled and aggregate evaluations are performed. The service program also covers all the levels of approval processes for new building materials, such as the application, preparation and implementation of the test program as well as the preparation of test reports and reports on product suitability. The service range also includes the preparation of ecological assessments and environmental product declarations (EPD).

The general services in the Research Institute include the areas of management, information and data processing with a data centre and library, documentation and publishing activities and the mechanical and electronic workshop. The Research Institute laboratories are accredited, while the Institute also has a certified quality and environmental management system. The organigram on page 6 shows the structure of the Institute with the individual departments and the certification office for management systems, FIZ-Zert. At the time of reporting, about 180 staff were employed at the Research Institute. The Institute currently provides 6 apprenticeship positions in various departments. In the reporting period, 4 chemical lab technician apprentices and 1 apprentice administrator for office communication successfully completed their studies.

#### Information centre - library

The central task of the central information centre is to provide timely and comprehensive information for employees of the Research Institute of the Cement Industry. The provision of electronic documents plays a key role in this regard. As a result, the literature database that has existed for over 25 years is being increasingly upgraded with additional information such as indexes. The provision of electronic documents ensures quick access to available information regardless of time or place.

Besides the rapidly increasing electronic inventory, the classical stock of conventional media also continues to grow. The Institute's library currently stocks approx. 41,000 volumes, comprised of monographies, series of volumes and periodicals as well as standards. About 140 constantly updated magazines ensure an up-to-date insight into the central topics of the Institute and these are evaluated by research assistants for relevance of content. Relevant specialist literature finds its way into the literature database, making the content accessible, which currently contains about 78,300 researchable records to books, articles and standards.

In order to constantly expand the inventory beyond the classical literature, the information centre also maintains intensive loan connections with other libraries, documentation centres and information facilities as well as an extensive and lively document exchange with many domestic and overseas research centres and libraries. This provides access to literature from its relevant fields of cement chemistry, plant technology and environmental protection that would otherwise be difficult to access.

The information centre is involved in the production, issuing and the dispatch of VDZ publications. Besides the timely information of members through the automatic dispatch of new publications, the VDZ publications are also provided in the BetonMarketing Deutschland GmbH Betonshop at www.betonshop.de.

Besides the classical activities in the library and information area, the information centre is also responsible for the administration of the VDZ website. A comprehensive update of the public site was undertaken at the start of 2012. The internal intranet and extranet will continue to be constantly updated and extended for members.

#### **IT service**

In the past three years the IT infrastructure in the VDZ has been brought up to standard through the targeted replacement of hardware and software and the extension of the internet connection bandwidth at all three sites. Furthermore, various IT security measures have also been planned and implemented (e.g. physical protection of the server room). The 180 PC workstations at the Düsseldorf, Berlin and Erkrath sites use the Windows XP operating system. Microsoft Office is used as the standard office application. The ERP program and various special applications in the measurement data acquisition systems or in laboratory management complete the range of applied software.

New challenges are provided by the increasing use of mobile end devices. The use of these devices in the company required a compromise between security and the "simple" use of the device. This has been an outstanding success due to the relevant guidelines and raising of employee awareness.

A client backup solution was introduced in the reporting period in order to protect laptops, which are also used in the field, against data loss and which has now been applied across the board.

The old files archive is being digitalised as part of an on-going process. Several thousand folders have already been transferred to a digital archive.

For the future, the focus is on further investment in IT security and system availability.

#### Services

The Research Institute of the Cement Industry provides expert and advisory services in all areas of the production and application of cement, cement-bound building materials and many other building materials from the construction materials industry. This includes performing tasks under public or private law, e.g. activities as a test, monitoring and certification office, as an environmental measuring office or as a certification centre for management systems (environment and quality). With its five departments of Cement Chemistry, Concrete Technology, Environment and Plant Technology, Environmental Measuring and Quality Assurance and Analytics, the Research Institute covers all the areas of cement production and application. The Institute is accredited and certified according to ISO 9001, ISO 14001, DIN EN ISO/ IEC 17025, EN 45011 and DIN EN ISO/ IEC 17021.

The services are provided separate from the non-profit activities of the VDZ's joint research. The individual projects are billed separately and are subject to strict internal and external confidentiality requirements. Consulting services are provided and invoiced based on fixed daily rates. Standardised activities are provided as fixedrate services.

Research Institute customers include cement and building material producers, construction companies and construction administrations in Europe and, increasingly, worldwide. The Research Institute offers solutions on increasing efficiency and reducing costs as well as competitive measures to improve environmental protection, durability or quality assurance. It provides answers to questions on cement manufacturing, chemistry and mineralogy, concrete and mortar production, environmental issues, issues relating to the certification of building materials and management systems as well as the issues of knowledge management and further education, which are becoming increasingly important.

The Research Institute of the Cement Industry therefore offers its customers a service package that includes all the important tests and consultations through to complex reports. The combination of current research and competent service leads to synergies that are reflected in high quality and performance in practice.

#### Mortar and concrete

The Research Institute of the Cement Industry offers a comprehensive service package with regard to the application of concrete and other cement-bound building materials: Consultations, material tests, reports, self and third party monitoring concepts during construction, monitoring of concrete production and concreting. All of the service modules help to ensure the quality of the raw materials and the building materials and to comprehensively prevent damage to concrete buildings.

Building material acceptance tests are managed across all the process steps from application through to the trial program and reporting. The Research Institute also prepares ecological assessments in accordance with DIN EN ISO 14040 – according to the regulations of the standards developed for the building sector by CEN/TC 350 on request – and environmental product declarations (EPD).

#### Material testing

- Fresh concrete and mortar (e.g. consistency, bleeding)
- Hardened concrete and mortar (e.g. compressive strength, tensile splitting strength, e-module)



The management circle: Volker Hoenig, Martin Schneider, Martin Oerter, Christoph Müller (back row from left) and Jörg Rickert, Silvan Baetzner, Stefan Schäfer, Sascha Vogts (front row from left)

- Durability investigations (e.g. frost and de-icing salt resistance tests, chloride migration coefficient, carbonation, alkali-silica reaction (ASR))
- Aggregate investigations
- Admixture investigations
- Special processes for investigating the shrinkage of concrete

#### Consultation/Reporting/Monitoring

- Preparation of ASR reports (incl. performance tests, WS basic test)
- Self and third party monitoring concept during construction
- Monitoring the production and placement of concrete
- Ecological assessments (DIN EN ISO 14040 and DIN EN 15804), environmental product declarations (EPD), sustainability certification of buildings
- Acceptance tests for attaining general building approval (abZ), European Technical Approval (ETA) and KOMO attestation with product certificate pursuant to CUR 48
- Damage analysis and damage prevention reports

#### Zement.art

The Zement.art program includes all of the services regarding the optimisation, production and application of cements with several main components:

- Recording and evaluation of the status quo (manufacturing, properties)
- Concept for large-scale implementation
   Supervision and evaluation of operating trials
- Execution of pretrials for obtaining approvals (national and international)
- Execution of approval tests
- Execution of company training measures
- Supervision of practical implementation

#### **Chemistry and mineralogy**

Understanding chemical and mineralogical processes in cement production and application is a key requirement for optimising the clinker burning process and the product properties. The activities in the area of cement chemistry are oriented towards current issues and include both the assessment and optimisation of the main cement components as well as the development of test processes and measuring methods. The Institute has a powerful analytical laboratory with extensive technical equipment for this purpose. The lab is accredited according to ISO/IEC 17025. Due to its long-term cooperation with cement producers and concrete users, the Research Institute of the Cement Industry has vast experience in consultancy, analysis and method development in the area of chemical and mineralogical tests on raw materials, cements and the products produced from them. The service range focuses on the following contract investigations:

- Characterisation of Portland cement clinkers
- Quantitative phase analysis using Rietveld refinement
- Reference investigations on cements and concrete raw materials according to the applicable standards
- Characterisation of new binders
- Determination of hydration heat
- Sulphate optimisation of cement
- Determination of heating and calorific values
- Structural analysis of cementitious systems
- Environmental analysis, e.g. trace analyses of metals and metalloids
- Determination of water-soluble chromate according to EN 196-10 and the former TRGS 613
- Thermoanalysis (DSC and TG/DTA)
- Sulphate resistance of cement
- Hygienic properties of cement-bound building materials (e.g. in the area of drinking water)
- Effects of concrete admixtures

#### **Environmental reports**

The great importance of environmental protection in the cement industry is reflected by the numerous activities of the Research Institute of the Cement Industry. Given the Research Institute's extensive experience, particularly useful synergy effects are established in plant evaluations and approval management as all the necessary services can be provided under one roof, even for more complex projects. The Research Institute employees are provided with constant training. Their integration in current research topics also ensures that they can constantly refer to the latest knowledge when preparing reports. The service offer includes the following contract investigations:

- Emissions forecasts
- Emissions dispersion conditions/chimney height calculation
- Recommendation of measures to improve the emission situation
- Environmental compatibility studies
- Plant considerations (state of technology/best available technology)
- Complex dispersion calculations
- Soil investigations
- Noise reports

#### **Technical audits**

VDZ employees have extensive experience in the area of thermal and mechanical process technology as well as environmental technology. This experience was gained as part of consultations on process optimisations and energy efficiency increases of cement works at both a national and international level. This has allowed for numerous projects, which comprised of the planning and organisation of process investigations, to be successfully implemented. These investigations included the entire production process, with a particular focus on the clinker burning process and the comminution of raw material and clinker in grinding plants. Furthermore, complex environmental issues, such as the impact of the use of alternative fuels and measures to reduce emissions, were also processed. Material aspects, such as the development of recirculating material systems or product quality, were naturally also always taken into account and evaluated.

#### Process optimisation measures

Optimisation measures are developed as part of technical audits. Here, the focus is primarily on the kiln and grinding operation. Kiln and mill audits deal with issues and problems such as fuel technology for alternative fuels, effects of the use of alternative fuels on the kiln operation, reduction of recirculating material systems, primary and secondary emission reduction measures, reduction of CO<sub>2</sub> emissions, process modelling of kiln plants and grinding plants and operational optimisation of rotary kilns and grinding plants.

These technical audit services are adapted to the relevant customer's wishes and plant requirements. Important issues in times of rising energy costs and increased environmental requirements include the reduction of emissions and the reduction of thermal as well as electrical energy requirements.

VDZ employees are able to apply all of their know-how and experience in the area of process measurements and sampling, which are performed on site as part of the audit. The equipment of the Research Institute of the Cement Industry is also available for the preparation and analysis of samples. By using modern measuring and analysis processes, process measurements on kiln plants and pulverising mills can be rapidly assessed and the results can be compared with the VDZ database. The extensive knowledge of the cement manufacturing process and structured processes enables a systematic potential analysis regarding energy consumption (see top image on the following page).

In addition to the daily challenges faced during plant operation, the production process also need to be constantly reviewed with regard to efficiency and competitiveness. If necessary, the plant and spare parts have to be improved so that they meet the future requirements and correspond to the latest technological developments. VDZ experts diagnose weak points in the plant operation, provide solutions and help to remedy problems.

An example is the execution of a kiln audit to investigate the stability of the rotary kiln operation. Key components include the analysis of the composition and homogeneity of the raw meal, the recirculating sulphur and chlorine systems, the bypass, the degree of sufatization, the flame stability and the alternative and primary fuels used. The kiln and cooler equilibriation provides further information on possible improvement measures.

In the area of grinding technology, experience has shown that, in many cases, ball mills have a high potential for efficiency improvement. The evaluation of the grinding plant takes place based on a mill audit, which includes the evaluation of the mechanical state of the grinding plant, the filling level of each grinding chamber, the state of the liner plates and the grinding media (see bottom image). The progress of comminution in the grinding chambers is determined based on regularly spaced samples. Furthermore, sampling of the feedstock, coarse material and fine material also takes place.

#### Energy efficiency analysis

VDZ services on energy efficiency analysis were developed in order to identify potential energy savings in the cement production process and to improve the energy efficiency of the entire production line. Recorded energy data is compared with the VDZ database and evaluated, which enables a neutral evaluation of the electrical and fuel efficiency. The extent of the energy efficiency analysis is always customised to the specific customer requirements and either includes the entire manufacturing process or selected subprocesses. Individual expert visits are also available in order to identify possible energy saving potentials.

Entire companies with several cement works, individual works or plant units can be evaluated as part of the energy efficiency analysis. The investigations focus on, for example, the optimisation of energy requirements for drying processes, the evaluation of surplus thermal capacity for further application – such as heat and energy recovery – or the improvement of heat recovery in the clinker cooler. In addition, the improvement of electrical energy efficiency during cement grinding is also a particular focus. Recommendations on the reduction of  $CO_2$  emissions are also part of the energy efficiency analysis.

The specific fuel energy requirement is the decisive figure for evaluating energy efficiency in the cement industry. First the actual state of the kiln plant is determined from the energy analysis of the thermal process. Optimisation potentials are derived by comparing the actual data with modelled values. A process model helps to simulate modern precalciner plants, where the specific production conditions such as clinker capacity, raw material basis and fuel mix are individually applied.

For example, the minimum energy requirement is increased by 160 to 320 kJ/kg of clinker in order to take the actual operating conditions, such as operating fluctuations or start-up and shut-down processes, into account (see BREF document for the cement industry). The comparison of the determined actual fuel energy requirement with the modelling results provide the relevant savings potentials.

The significant operational optimisation potentials of grinding plants with ball mills lie in improving the classifier separation efficiency and optimising the comminution by adapting the charge grading to the existing comminution task. As per the fuel energy requirement, the data for the clinker production are compared with a reference plant from the VDZ database in order to determine the savings potential.

#### **Environmental measurements**

The Research Institute of the Cement Industry has been recognised as an independent measuring and testing institute by environmental authorities for many years. This notification requires an accreditation based on the international standard DIN EN ISO 17025 which, in this special case, also includes the emission protection module. In a testing process lasting more than one year the Institute was able to extend this special accreditation for a further five years in mid-2012. This also includes the extension of the official announcement by the environmental authorities. This means that not only can customers from the



Energy balance of a rotary kiln plant as the basis for an energy efficiency analysis



Reviewing a ball mill as part of a mill audit.

non-metallic minerals industry draw on the extensive practical experience of employees (natural scientists, engineers and technicians); but the independence of the measuring and testing activities, particularly when sampling in the area regulated by law, can continue to be ensured. The service offer continues to include areas relevant for companies in the cement industry and the non-metallic minerals industry:

Planning and competent processing of emission measurements

- Development of measuring plans
- Determination of noise emissions
- Noise reduction concepts and plant noise maps
- Determination of emissions caused by blasting vibrations
- Functional testing and calibration of constantly operating measuring equipment
   Assessment of measuring stations
- Assessment of measuring st
   Immission measurements
- Infinitission measurements

Due to the increasing internationalisation of the cement industry, all of the above-

mentioned services are now also being offered overseas.

#### **Product certification**

Quality monitoring and quality assurance of cement and cement containing binders by the testing, monitoring and certification centre (PÜZ centre) are part of the traditional core competencies of the Research Institute of the Cement Industry. About 580 cements and 58 plants are tested and monitored according to national and international legislation. As a result of existing agreements with foreign centres, the monitoring can also be performed in accordance with regulations under private law. The national and European recognition as a PÜZ centre by the responsible building control authorities extends to:

- Cement and cementitious binding agents
- Concrete additives
- Concrete admixtures
- Mortar and concrete
- Aggregates
- Cement-containing preparations

Furthermore, the PÜZ centres and the associated laboratories are also accredited under private law according to EN 45011 and EN ISO/IEC 17025.

#### System certification

The FIZ-Zert certification office certifies and monitors management systems (quality, environment, energy, occupational and health protection). FIZ-Zert is accredited pursuant to EN ISO/IEC 17021. Companies from the non-metallic minerals industry or similar industry sectors that deal with the production and application of building materials (especially cement, binders, concrete, concrete goods and finished parts) are primarily certified. The basis of the system certification are the standards EN ISO 9001, EN ISO 14001, EN 16001, EN ISO 50001 and OHSAS 18001. FIZ-Zert customers can take advantage of synergies as system certification is also possible in combination with the legally regulated product certification (e.g. according to EN 197).

#### Verification of CO<sub>2</sub> emissions

In the past few years FIZ-Zert has verified  $CO_2$  emissions in connection with the European emissions trading on a recurring basis. Customers have therefore been able to benefit from both the high technical competency as well as the comprehensive legal knowledge of our experts. Individuals acting on behalf of FIZ-Zert either have appropriate approval as tested experts or they are recognised EMAS verifiers. This

ensures that the testing of emission reports and the assessment of allocation applications performed by FIZ-Zert meet the highest standards. The same experts from the Research Institute of the Cement Industry also tested and verified the data for benchmark determination of the European cement industry for the EU Commission in 2010.

## Process technology of cement manufacture



Cleaning work at the kiln inlet

Photo: Steffen Fuchs / Heidelberg Cement

#### Plant operation

## CFD simulation of coincineration in the calciner

Alternative fuels (AF) such as prepared fractions of industrial, commercial and municipal waste, shredded tires and animal meal are used in the cement industry precalcining plant for reasons of cost. Precalcining plants therefore offer a special flexibility, as alternative fuels can be added to several hearths at different temperatures. Besides the economic criteria, the physical and chemical properties also play a decisive role as they may impact the kiln operation. For example, particle size, volatility, heating performance and the content of chlorine, sulphur, alkalis and nitrogen in the fuel impact the heat release progression, and therefore the deacidification process and emissions, e.g. due to changes in the formation of NO<sub>x</sub>. These changes are currently difficult to predetermine. As a result, experimental tests or optimisations and, in some cases, conversion activities are currently considered to be usual.

To better predict potential process changes in the calciner the Research Institute took part in an AIF research project with the objective of better analysing the processes in calciners using CFD simulation (computational fluid dynamics). Building on the knowledge from the simulation of combustion processes for coal, the processes with the application of fractions that are capable of becoming airborne from industrial and commercial waste, which constitute the majority of fuels applied in the calciner, were investigated. FIZ supervised this project in cooperation with the chair for energy plant and energy process technology (LEAT) of the Ruhr University, Bochum, and the chair for environmental process technology and plant technology (LUAT) of the University of Essen/Duisburg.

This involved the new development and adaptation of key submodels to describe the process. Individual submodels on the fluid-dynamic behaviour and the burnout of alternative fuels were verified based on the results of laboratory tests and unified under a single methodological concept. The results of the simulations were compared with actual results based on extensive operational measurements at an industrial plant. This showed that the gas concentration profile of O<sub>2</sub>, CO<sub>2</sub> and CO in the calciner, as calculated by the simulation model, was in the values range of the measured data and that the NO<sub>x</sub> value was broadly correct (Fig. I-1).



Fig. I-1: Comparison of the measured and simulated  $\rm NO_x$  concentrations for 100 % lignite resp. 80 % AF utilization



Overall it became clear that the fundamental process values were correctly predicted as part of the measuring and modelling uncertainties. The developed simulation approach is therefore suitable to broadly predict various operating conditions for changed framework conditions, fuel changes or modifications to the plant geometry. Apart from comparing the values that can be measured, the simulation also offers additional possibilities for predicting and analysing process changes by changing the fuel mix. For example, **Fig. I-2** displays the calculated flow rate in the lower area of the calciner up to the tangential input of the tertiary air in the conic area. It is evident that speeds of up to 50 m/s can occur in the riser duct. The average flow rate is approx. 30 m/s. This high speed leads to an extremely short retention time of the input materials in the reduction zone of less than one second.

The tangential inflow of the tertiary air constricts the rising particle-containing flow in the conical section and pushes it against the side wall across from the tertiary air inflow. A stagnation point is formed on the opposite side before the oxygen-rich tertiary air is also diverted upwards and it slowly mixes with the fuel-rich streaks. The high flow rate in the lower part of the calciner means that predominantly heavier particles remain here (in the reduction zone), while lighter particles are rapidly transported to the upper oxidation zone, due to the fluid-dynamic forces, where they burn out (**Fig. I-3**).

Overall, it is evident that the combination of measuring and simulation enables a more detailed and further-reaching analysis of the processes in the calciner under realistic conditions than would be the case solely by measuring. In addition, the developed methodology provides a tool for evaluating improvements in existing calciners as well as for new designs.

Possible starting points for optimisations with the aid of CFD simulations are provided in the following points:

- Calculation of the optimal degree of preparation (fineness) of the fuels with regard to the rate of descent and flight properties
- Determination of the optimal feed location for the various fuels with regard to retention time and burnout
- Optimisation of the constructive design of calciners with regard to streak formation and improved mixing

The specified optimisation criteria must be subjected to individual testing by the plant operators, given the fluctuating raw material and fuel qualities and various designs and modes of operation of the kiln plants. Detailed fuel characterisation is essential in this regard. The investigation of the interaction of the SNCR process with staged combustion and the investigation of a preferred location for buildup formation in the calcinator are planned in the medium term as further developments of the CFD simulation for the calcinators.

#### **Refractory material**

The knowledge of refractory linings in rotary cement kilns compiled by the VDZ "Refactory Materials" task force and documented in VDZ code of practice Vt 16 (**Fig. I-4**) is a valuable guideline for industry practitioners. In particular, the detailed representations and descriptions of the applied methods and processes for the application of formed refractory products in rotary cement kilns and the exemplary representa-





tion of typical lining damage and aspects of occupational safety are valuable in practice. Furthermore, recommendations for incoming inspection are provided as well as a description of the techniques for diagnosing the status of refractory linings.

The durability of refractory linings in rotary kilns mainly depends on three different parameters, these are:

- The general operating conditions of the plant,
- The mechanical condition of the rotary kiln, in particular of the kiln shell ovality in the area of the kiln tires as well as the heating and cooling of the kiln, and
- The selection of refractory materials and their proper installation as well as their application in the relevant zones.

In view of the requirements and stresses to which the refractory material is exposed in a rotary cement kiln, the proper installation of the refractory lining helps to ensure a longer service life and exclude some of the stresses that usually cause premature wear. The lining methods used during installation play a key role in this regard.



Fig. I-5: Transition of dual blocks in the bonded brickwork

The installation methods generally have to fulfil three requirements:

- The safety of the installation personnel must be ensured.
- The installation quality must be suitably high so that the lining is firmly positioned against the kiln shell and so that subsequent loosening or turning is prevented to the greatest possible extent.
- An acceptable speed of lining construction must be realised in order to keep the plant's down-time as short as possible.

The installation of bricks in the rotary kiln is either performed according to the spindle method or the bonding methods, with mortar, grating, sheeting or with the aid of wooden bows, pneumatic or hydraulic bow "pogo sticks". In order to prevent spiralshaped lining twisting in the rotary kiln, the bricks are bonded in the relevant area in some rotary kilns (**Fig. I-5**). The segments laid in the bonded area are a maximum of 5 m long. Longer bonded sections are not recommended in order to allow partial sections to be renewed in the event of damage.

The ridge lining is installed in the kiln inlet and outlet area and in satellite coolers. The ridge lining is a lining that is constructed of various brick strengths. It is tasked with mixing the kiln feed, thereby enlarging the surface area of the kiln feed in order to improve the heat transfer when heating the raw material as well as when cooling the clinker.

Kiln heads of precalcining plants, which have very large areas to be lined with refractory material due to the connection to the tertiary air line, are constantly subject to premature wear of the lining. In order to prevent this, highly abrasion-resistant brick qualities with Al<sub>2</sub>O<sub>3</sub> components of at least 50 % must be used in the lower area and approx. 60 to 65 % or 80 to 85 % in the upper area. The use of magnesia spinel bricks is also adequate in this area. Particular attention should be paid to the anchor points. Adequately high refractory steel qualities and a sufficient amount of anchors (at least 6 to 9 anchors per m<sup>2</sup>) should be used. Furthermore, the number, width and design of the expansion joints must be sufficiently dimensioned to prevent the premature failure of the lining segments.

It is important to decide on the right drying and heating procedure whether a completely newly lined kiln is to be heated or if refractory bricks have been exchanged just in sections of the rotary kiln. Drying and heating refractory materials in a completely new lined kiln plant is started by heating the preheater, tertiary air duct and clinker cooler. Special gas or light oil burners, which are supplied and operated by special companies, are used in this regard. The heating curves of the applied monolitic refractory, as provided by the manufacturer, must be complied with when heating. The gas temperatures after the plant part to be heated, are measured for this purpose. A temperature measurement is required for every cyclone stage.

Modern refractory linings are adapted to the changed firing conditions with the application of alternative fuels. An extension of the sintering zone must include the extension of the zone with highly refractory bricks that predominantly consist of magnesite-based materials. Today, kilns that consume a high amount of alternative fuel are generally lined with magnesite-based bricks. Due to continued research and new developments, the manufacturers of refractories offer today brick qualities that resist thermal, chemical, mechanical stresses and even combinations of these. The increased durability is provided by adjusting the pore quantity and size and the application of high-quality raw materials and mixtures thereof.

#### Causes and reduction of corrosion damage in the exhaust gas path of rotary kiln plants

Corrosion causes millions of euros worth of avoidable damage in the cement industry every year. The entire clinker firing process plant is affected, with different types of corrosion arising in the various production process areas. The additional maintenance expense for the plant caused by corrosion represents an economic strain on the operation. This is primarily due to the additional material costs, the increased deployment of personnel and increased production losses due to unplanned and drawn-out downtimes. However, the removal of corrosion damage is still seen as an unavoidable cost factor in the area of general maintenance in many parts of the cement industry.

After constructive discussions with the industry, VDZ, in cooperation with the Department of Ferrous Metallurgy of RWTH Aachen, initiated a research project in order to investigate the causes of the corrosion phenomenon in the exhaust gas path of rotary kiln plants, the so-called low temperature corrosion. The results provided in this research project will help to formulate solution proposals to reduce corrosion, which will then be provided to the industry. These recommendations should provide operators with a basis for suitable site-specific corrosion protection plans.

In practice, the problem of low temperature corrosion is well-known for the constant repair work it generates (**Fig. I-6**). Based on the operating experiences of the works, the kiln gas filter was identified as the most severely affected unit in the exhaust path. For this reason, the planned investigations will focus on this plant component.

The corrosion damage observed in the plants frequently displays the hallmarks of wet or acid corrosion. The cause generally involves a discussion on the occurrence of sulphuric acid, which arises when the acid dew point is reached or when it condenses from gaseous phase. However, to date, no reliable investigations have been carried out that clearly establish, either qualitatively or even quantitative, amounts of SO<sub>3</sub> or  $H_2SO_4$  in raw gas and clean gas. Furthermore, there is also the fundamental question of whether acids can even have a damaging effect in the prevailing environment and whether they are not immediately neutralised by the high quantities of available alkaline dusts. A new measuring technology to determine SO<sub>3</sub> in raw gas was therefore developed as part of the research project (Fig. I-7). The measuring method corresponds to VDI directive 2462, sheet 2 (dated 2010) and is designed for use in gases with high dust contents. This should enable us to measure the SO<sub>3</sub> and  $H_2SO_4$  content in raw gas correctly for the first time. In addition, laboratory tests will be performed in order to investigate the acid absorption potential of various dusts.

A cooperation with the Department of Ferrous Metallurgy at the RWTH Aachen was established in order to process the metallurgic aspects of the research project. This will involve investigating plant parts that are already damaged as well as performing laboratory and exposure trials. The trials will test the corrosion resistance of various steel alloys with regard to the specific corrosive stresses occurring in the exhaust gases of rotary kiln plants. The long-term exposure trials will be performed in various cement plants with different exhaust gas conditions. The corrosion samples will be exposed to particularly severely affected areas of kiln exhaust filters and then, on expiration of a defined exposure time, investigated for their material loss. The compilation of the results of the Research Institute and those of the Department of Ferrous Metallurgy should provide a complete picture of the represented problems.



Fig. I-6: Severely corroded side wall of a kiln exhaust filter



Fig. I-7: SO<sub>3</sub> measuring in the clean gas of a rotary cement kiln plant according to VDI directive 2462, sheet 2 (dated 2010)

Even if metallic corrosion in rotary cement kilns is ultimately not able to be prevented based on material or operational measures, the objective will be to considerably reduce corrosion rates, which will lead to significantly increased lifetimes of the individual plant units.

## Rotary kiln firing systems for the use of alternative fuels

More than 25 years ago the German cement industry started using substantial quantities of alternative fuels to cover the thermal energy demand of the clinker burning process. Due to their economic and envir-





Fig. I-8: Heterogeneous composition of solid alternative fuels



onmental advantages, these "new fuels" are nowadays used to a growing extend.

These alternative fuels differ remarkably in consistency and combustion characteristics from conventional fossil fuels, especially from coal dust. The operational experience of the plants points out that high quantities of alternative fuels used in the rotary kiln firing system reduce the maximum flame temperature and can lead to higher temperatures in the kiln inlet. At high rates of these fuels used in the rotary kiln firing system, therefore, the demands on burner and on kiln operation increase.

With the technical evolution of rotary kiln burners some significant changes have taken place due to their adaption to the respective fuels used. Today, the widely used multi-channel rotary kiln burners enable the simultaneous combustion of several fuels with different combustion properties. Modern rotary kiln burners are characterized by a variety of lances, tubes and annular channels that flexibly allow the combustion of coarse, ground, liquid, viscous and gaseous fuels. Swirling systems individually designed to the used fuels mix the alternative fuels into the flame.

Conventional fuels are retrieved from naturally resources like coal, mineral oil or natural gas. After an appropriate conditioning, these can be directly used as coal dust, fuel oil or heating gas. Alternative fuels often retrieved from materials that were produced or used for other purposes and that are thermally utilized at the end of their useful life. Alternative fuels are typically graded as waste-derived fuels consisting of fossil and organic materials or as biofuels retrieved from biomass. In contradiction to coal dust, which has homogeneous properties and a high specific surface, solid alternative fuels are characterized by a comparably higher heterogeneity (Fig. I-8), a higher moisture content, a lower specific surface and a considerable distribution of physical and chemical properties affecting the combustion. Fig. I-9 displays exemplarily the fluctuation of the moisture content of a solid alternative fuel (fluff) in a rotary kiln firing system over the course of a day. The heterogeneity of the fuels should vary within certain limits. Typical requirements for the consistency of fluffy alternative fuels have been proven to be successful for the use in rotary kiln firing systems:

- Calorific value (fuel mix): 19 to 25 MJ/kg
- 19 to 25 MJ/kgMoisture content: 10 to 25 % by weight
- Particle shape: preferred 2-dimensional particles
- Particle size:
- 2-dimensional material: max 30 mm edge length 3-dimensional material: max. 20 mm
- diameter
- Bulk density: 0.1 to 0.2 t/m<sup>3</sup>

The rotary kiln firing system setting has to be adapted to the used fuel or the used fuel mix, respectively. By means of adjustable burner air, in many burners divided into several air flows, the flame shape and the fuel combustion can be actively controlled. The geometry of the emanation system at the burner tip and the adjustment of the burner air enable a dedicated setting of the length, divergence and twisting of the flame which in turn influence the combustion by mixing the fuels with the secondary air.

#### Gasification of heterogeneous fuels

The pyrolysis of the fuel using a plasma burner offers one possibility for stabilising the kiln operation when using low-calorific, inhomogeneous alternative fuels. Ionised gas molecules - the plasma created by an electric arc - can be used to achieve extremely high temperatures in order to pyrolyse alternative fuels, as well as other materials. This creates a combustible gas that contains a large amount of carbon monoxide and hydrogen due to the lowoxygen atmosphere. This combustible gas can be used in the calciner of a rotary cement kiln at temperatures of up to 1000 °C. This operation is more stable and has lower process fluctuations than the direct application of heterogeneous fuels in the calciner, as the differences in composition and moisture content are homogenised. The generation of an arc requires a relatively high supply of electrical energy. This expense must be considered in light of the positive benefits; the homogenisation of the kiln operation and the fuel and CO<sub>2</sub> saving.

Extensive simulation studies based on a process model developed at the FIZ for evaluating the application of combustible gas originating in the clinker process have been carried out at the Research Institute of the Cement Industry as part of a European research project (abbreviation EDE-FU). Experimental investigations on gasification using plasma were performed on fuel samples of sewage sludge, animal meal and RDF by a project partner. The combustible gas compositions and temperatures determined as a result form the input data for the process modelling. The simulations therefore allow specific statements to be made on the effects of the generated combustible gases on the plant operation.

In principle it is possible for the calciner's entire energy requirement to be provided by the combustible gas from the plasma burner due to its lower temperature level with regard to the sintering zone. The combustible gas has a lower calorific value than the original fuel but it has a high amount of sensible heat due to the plasma energy input. A lower fuel amount therefore needs to be gasified in order to generate the same energy level of direct combustion. Based on this, a theoretical reduction of 7 % of the CO<sub>2</sub> emissions arising in the process was generated compared to the combustion of fossil fuels. This recorded positive effect predominantly depends on the inlet temperature of the combustible gas, as more than 40 % of the energy is supplied to the calciner by sensible heat. The required energy quantity (and therefore gas quantity) can no longer be ensured at combustible gas temperatures under 750 °C. The fuel ash that cannot be fed directly into the kiln feed for this technology can be added to the raw material from the separate gasification. An extremely good burnout is required in this regard.

This study showed that the energy requirement of calciners can be covered by a combustible gas of corresponding quality with the simultaneous reduction of process fluctuations and  $CO_2$  emissions. The overall result depends on the electrical energy requirement of the plasma burner and the resulting indirect  $CO_2$  emissions. The evaluation of the benefits will be determined in the following project sections.

## Modelling the grinding media movement in ball mills

The electrical energy expense for cement production averages at approx. 110 kWh/t cement in Germany, where about 38 % is used for grinding clinker and cement additives. Ball mills are usually used for cement grinding. Despite their comparably lower efficiency, they are distinguished by higher operational safety as well as a broader grain size distribution of the







ground cement. For this reason it is not expected that the ball mill will be fully replaced by another grinding process even in the long term. The use of all of the available optimisation potentials is therefore considered expedient. However, the interaction of the various operating parameters and their impact on the mill filling is difficult to estimate as, in particular, the mill interior cannot be accessed for measurement. However, direct particle simulation represents a promising tool for the energetic optimisation of cement grinding.

Efficient methods for calculating and visualising bulk material have existed since the end of the 1990s. These are generally summarised under the heading "Discrete element methods" (DEM). This allows complex systems, such as the filling of a ball mill, to be simulated. A two and three dimensional model were applied at the FIZ in order to facilitate a detailed investigation of the processes in the ball mill interior. **Fig. I-10** provides an example visualisation of results of the three-dimensional model.

The simulation enables sizes to be determined that could not be measured in reality. Of particular interest are velocity and pressure distributions, which allow conclusions to be drawn about the comminution process.



Fig. I-12: Crushing results after stressing cement clinker in the test device according to Zeisel and in a open-circuit mill



Fig I-13: Grinding bowl of the test device for measuring the grindability according to Zeisel

While simulations theoretically enable access to systems that cannot be measured, they always represent a simplification of reality. The prediction quality therefore ultimately depends on the precise validation of the applied model. The simulation calculations (numerical experiments) are therefore always performed in combination with extensive trials on a demonstration mill with armoured glass walls (**Fig. I-11**) and the semi-technical FIZ closed circuit grinding plant.

Apart from the kinematic simulation of the grinding media fill, the comminution process, depending on the material properties of the milled product, is also decisive for an effective optimisation. This requires a connection between the calculated energy distributions and the measurable comminution results to be established. Extensive investigations to determine the material characteristics were carried out for this purpose. Besides fracture tests, the grindability tester according to Zeisel proved itself to be a suitable measuring apparatus. Fig. I-12 shows the parameters of the RRSB distribution for cement clinker, which was stressed under various conditions in grindability testers according to Zeisel and in a ball mill in continuous operation. A generally good conformity of the crushing results can be identified in the considered range. The broader distribution of values during grinding in the ball mill can be explained by the influence of various operating parameters such as retention time for example. These parameters are explicitly investigated by systematic trial series in mills in discontinuous operation. Furthermore, a process to precisely determine the specific energy expenditure of the comminution in the test device according to Zeisel was also developed. The measurement of the power consumption was performed by a load cell rather than a protractor. The comminution progress is determined by laser granulometry.

The determined results form a promising basis for the complete description of comminution in ball mills. The development of an optimisation tool for increasing the energy efficiency of operating mills is planned based on these results.

#### Grindability testing according to Zeisel

A new testing apparatus for determining grindability according to Zeisel was installed at the Research Institute in 2010.

The test equipment manufactured by the TU Clausthal according to the "Tonindustrie" design replaced an apparatus from the 1960s that worked on the same principles. The device fundamentally consists of a grinding bowl in which seven steel balls are rotated by a die (Fig. I-13). The balls crush the added sample material through pressure and friction. The targeted fineness and the required energy are determined during the test. Significant differences between the new and old device are particularly apparent in the measurement data acquisition. The integral power value is no longer measured by an electric meter, rather the angle of deflection created by the rotation of the die against a spring force is measured, which can then be converted into the initiated torque by a preceding calibration.

Numerous comparison measurements were performed in order to ensure the conformity of the two testing facilities. Furthermore, investigations with regard to the machine parameters and additional variables on grindability were also performed, whereby the quantity of the feed material, the die load, the influence of the calibration and the fraction of the feed material were varied. In addition, numerous additional comparison measurements were performed with regard to the reproducibility of the grindability determinations according to Zeisel.

Another measuring process, which eliminated the inertia arising from the pivoted grinding dish, was established as part of the research activities on grinding media movement in ball mills. The torque measurement using an angle sensor was replaced by a force sensor. Fig. I-14 shows the load cell that is connected to the grinding dish by way of a lever arm. This enables a considerably higher resolution observation of the triggered torque and therefore the power demand. The mostly inertia-free measuring method no longer shows the uniform torque progression influenced by the spring, but short, clearly delineated force impacts against the direction of rotation that could not be recorded previously. A large number of grindability tests performed using both processes have provided a possible dependency between the two measuring processes, which is to be investigated in more detail. Overall, the results provide a number of starting points for the further development of the entire process and for determining the parameters of comminution models.

#### Energy efficiency

The issue of energy efficiency is on the political agenda at both the European as well as at the national level. During the introduction of CO<sub>2</sub> emissions trading, energy efficiency was cited as a measure to reduce CO2 emissions of energy-intensive sectors of industry. This has gained additional momentum with the European strategies for resource and energy efficiency. In Germany these strategies are being implemented by way of various legal undertakings as part of the new energy strategy. Energy efficiency and the introduction of energy management systems in the industry, together with the renewable energies law and the revision of the eco-tax legislation, therefore play a vital role.

For energy-intensive industrial sectors such as the cement industry this discussion is not without problems: Energy consumption has always been optimised for economic reasons, so remaining potentials are very low. In 2010 the "Cement Technology Roadmap" of the International Energy Agency (IEA) showed that, at a global level, energy efficiency can only



Fig. I-14: Modified measurement of power using a load cell



Fig. I-15: Specific energy consumption of the German cement industry 2010 in kWh/t cement



Fig. I-16: Cement production energy efficiency index

<sup>10</sup> Non-usable waste heat = waste heat < 100 °C, radiation losses <sup>21</sup> AF = Alternative fuels

contribute a maximum of 10 % towards the reduction of  $CO_2$  emissions of the global cement industry. This estimate corresponds with the earlier considerations of the Research Institute of the Cement Industry as, even the new construction of all kiln plants in Germany "on greenfield sites", would only lead to a maximum 7 % saving of the fuel requirement of German rotary kiln plants.

Fig. I-15 shows the distribution of energy consumption in the German cement indus-

try in 2011. This shows that – with regard to the total energy consumption – alternative fuels now contribute considerably more than 50 % to the energy requirement. In contrast, electricity only contributes about 12 % to overall energy consumption. Although the energy optimisation of plant units such as cement grinding displays certain potentials for optimisation with regard to the electrical energy requirement, this is only of limited use as an energy efficiency parameter.

	Dated 01.01.2010		Dated 01.01.2011			Dated 01.01.2012				
		Number	Capacity		Number	Capacity		Number	Capacity	
			t/d	%		t/d	%		t/d	%
Kiln with cyclone preheater		41	103 700	93	41	104460	94	39	100 460	94
Kiln with grate preheater		8	6 500	6	6	5350	5	6	5 500	5
Shaft kilns		8	1 200	1	8	1 200	1	8	1 200	1
Total		57	111 400	100	55	111010	100	53	107 160	100
Average kiln capa- city in t/d	Rotary kilns		2 2 4 9			2336			2355	
	Shaft kilns		150			150			150	
Clinker production (year)			(2009)			(2010)			(2011)	
In million t/a			23.2			23.0			24.8	
Capacity <sup>1)</sup> in %			65			65			72	

Table I-1: Number and capacity of the kilns with operating permits in the Federal Republic of Germany in 2009 to 2011

1) Assumed availability of 320 d/a

The reason for this is that:

- The increasing requirements of the performance of cement and concrete generally requires finer grinding and therefore a higher demand for electrical energy.
- The targeted reduction of CO<sub>2</sub> emissions by reducing the clinker-cement ratio requires the increased use of blastfurnace slag which is difficult to grind.
- The improved environmental situation requires an increasing demand for electrical energy for exhaust gas cleaning, e.g. for NO<sub>x</sub> or dust abatement.

Cement companies have no direct access to this increased demand.

The key variables for thermal energy efficiency in cement production have been the subject of many investigations. Plant technology, plant operation, raw material and fuel properties as well as the cement-clinker ratio play an important role in this regard. The Research Institute of the Cement Industry had already referred to the difference between guaranteed values of energy efficiency, which relate to short-term performance tests, the average annual specific energy requirement of kiln plants, the operating fluctuations, kiln stoppages, etc., in the period before 2010 during the preparation of the BAT Reference Documents for the cement industry (BREF). This was considered in the current BREF calculation by an increase of 160 to 320 MJ/t clinker in the BAT area of 2900 to 3300 MJ/t clinker, which took this difference into account. On the other hand, the specific fuel energy requirement is not suitable for the kiln plant comparison in all cases. For example, if the use of waste heat, e.g. for drying the raw material or other main cement constituents is included. If you also include the fact that alternative fuels are dried in a process-integrated manner then, based on the data for 2010, the total efficiency of the German cement industry is over 80 % (**Fig. I-16**). This efficiency index is not to be directly compared with physical efficiency but takes the specific boundary conditions of the sector, including all energy uses, into account.

#### Energy requirement

#### **Kiln plants**

The approved kiln capacity of the German cement industry was reduced from 111 400 t/d (2009) to 107 160 t/d in 2011. The operating permits of four kiln plants expired and the total number of approved kiln plants was reduced from 57 to 53. The overwhelming majority are operated using the dry and semi-dry process. Permits for eight shaft kilns also currently exist. The average kiln capacity of the rotary kilns rose slightly from 2 249 t/d in 2009 to 2 355 t/d in 2011. Table I-1 provides an overview of the available kiln plants and their capacities. This means that 98.9 % of the approved total capacity is used by plants with cyclone and grate preheaters. The share of cyclone preheater plants remained almost constant at 94 % (with regard to capacity) in 2010 and 2011. The number of precalcining plants remained steady at 12. Nine of these plants have a tertiary air duct. Precalcining plants represent more than a quarter of the installed approved clinker capacity of German cement works due to their comparably larger kiln capacity.

The capacity utilization of the kiln plants rose slightly from the low level of 65 % in 2009 and 2010, due to the economic crisis, to 72 % in 2011. The capacity utilization information was based on an assumed availability of 320 days per year.

#### Fuel energy demand

Fuel energy for cement production is predominantly expended on burning the cement clinker. Low quantities of thermal energy are used for drying additional main cement constituents such as blastfurnace slag. To produce a cement clinker with its characteristic properties, the raw materials, primarily limestone marl and clay, are burnt at temperatures of 1400 to 1450 °C. Due to the product requirements which require a high-temperature process the cement industry is one of the energy-intensive sectors in Germany. The cement industry has constantly attempted to lower its energy demand in order to reduce the high fuel energy costs. This is reflected in the development of the fuel energy consumed per kg clinker from 1950 to 2011 (Fig. I-17).

A small temporary rise in 1987 was due to the addition of the new federal states. Until about 1990 the burning process has been optimised to such an extent that the fuel demand has remained almost constant since then.

#### Initial voluntary commitment to climate protection fulfilled

In 1995 the German cement industry, together with other energy-intensive industry sectors, committed to making a contribution to the reduction of  $CO_2$  emission in Germany. This initial voluntary commitment of the cement industry included a reduction of the specific energy demand by 20 % in the period from 1987 to 2008. The cement industry achieved this objective in 2005, with 2786 kJ/kg cement (Fig. I-18). In 2011 a ton of cement was produced with an average of 2759 kJ.

The Research Institute of the Cement Industry has been collecting the production and energy demand data of the German cement industry since 1995. A summarised version of this data is submitted to the Rheinisch-Westfälisches Institut für Wirtschaftsforschung (RWI) for plausibility testing.

Over the past decades the German cement industry has constantly improved its specific fuel energy demand by modernising its kiln and grinding plants. This endeavour received a particular push after the German reunification as the East German cement works were brought into line with the current state of technology in just a few years. But also several old plants were replaced in the old Western German states. Another key measure in the reduction of the fuel energy demand per ton of cement was the production of cements with several main constituents, which led to a reduction in the clinker ratio.

The absolute fuel energy demand of the German cement industry fell from 1987 to 2011 due to a severely reduced cement production by about a fifth in the period under review. Another reason for this steep fall was the reduction of the specific thermal energy demand per ton by about 20 % during the same period (Fig. I-18). While the specific thermal energy demand of rotary kiln plants was at 3500 kJ/kg cement in 1987, this reduced to only 2759 kJ/kg cement in 2011. This was primarily the result of the reduction of the clinker/cement factor. This was 86 % in 1987 and was reduced to 73 % by 2011.

#### Fuel mix

The proportions of the various fuels used in the German cement industry have continued to undergo considerable changes in previous years. The overall fuel consumption was reduced from 119.9 million GJ/a in 1987 to 94.4 million GJ/a in 2011 due to the sharp fall in production, among other things. This corresponds to an absolute reduction of 21.2 %. The proportion of alternative fuels continued to rise in the reporting period (Fig. I-19) and amounted to 61.1 % in 2011 compared to 23.0 % in 1999. The increased use of alternative fuels predominantly replaced lignite in the reporting period. The consumption of other









Fig. I-19:

tion in the

1987



Table 1-2: Application of	alternative fuels	s in the German	cement industry
---------------------------	-------------------	-----------------	-----------------

2009 in 1 000 t/a 245 73 1 652	2011 in 1000 t/a 286 66
73	
	66
1652	
1052	1 643
175	63
556	474
1	0
9	10
911	1 0 9 6
204	187
188	336
13	8
81	104
0	0
263	304
78	125
	556 1 9 911 204 188 13 81 0 263



Fig. I-20: Specific electrical energy demand of the Germany cement industry (old Western German states until 1987, then the entire Federal Republic)

fossil fuels (fuel oil EL, fuel oil S and natural gas) remains low. They are primarily used for kiln start-up.

The break-down of the consumption of alternative fuels in 2009 and 2011 shows that the quantities of used tires applied again increased, while the consumption of traditional waste oil fuel continued to decrease (**Table I-2**). The consumption of used tires rose from 245 000 to 286 000 t/a, while the amount of waste oil consumed fell from 73 000 to 66 000 t/a. The consumption of fractions from industrial and commercial waste remained practically unchanged at 1 643 000 t/a (2011) compared to 1 652 000 t/a (2009). In contrast, the consumption of treated fractions of municipal waste at 336000 t/a in 2011 was considerably higher than the 188000 t/a in 2009. The consumption of animal meal and fat is also falling due to competing consumption in other co-firing plants such as power stations. This fell from 204000 t/a in 2009 to 187000 t/a in 2011.

#### **Electricity consumption**

Electrical energy is primarily used in cement production for preparing the raw material (about 35 %), for burning and cooling the clinker (about 22 %) and for cement grinding (about 38 %). The development of the specific electricity input per ton of cement for a German cement work reached a peak of 110 kWh/t in 1987 after rising for many years (**Fig. I-20**). This trend was reversed after the reunification of Germany until electricity consumption stabilised between 100 and 102 kWh/t cement in about 2005. The electricity consumption once again rose to about 110 kWh/t cement in 2010 and 2011. The key reason for this is likely to be the increased demand of the building materials industry for finely ground strong cements.

For cement with additional main constituents besides clinker, such as blastfurnace slag or limestone, the grinding power consumption depends on the grindability of these materials. For example, blastfurnace slag is more difficult to grind while limestone is easier compared to clinker. This requires increased grinding power consumption as these substances have to be ground more finely than clinker in order to achieve the same cement quality. On the other hand, it saves the equivalent electrical energy demand to produce the substituted clinker (raw material preparation, burning process). The application of more energy efficient mill types, such as highpressure grinding rolls, has been largely implemented in the cement industry. However, as the performance characteristics of cements from these mills do not correspond to those of conventional ball mills, secondary grinding in ball mills is generally still required. This means that the potential energy saving can still not be fully harnessed.

Also separate grinding of the various main constituents and their subsequent mixing in mixing plants does not seem to enable a significant reduction in energy demand within the scope of normal operating possibilities.

A forward-looking possibility for saving power from the public network is provided by the utilisation of waste heat from the clinker burning process for conversion into electricity. The first plant applying energy recovery from kiln exhaust gas became operational in Germany in 2012. A large number of modern cement kiln plants have been equipped with this technology in some Asian countries, where uncertain power supply and/or high energy prices frequently force cement companies to supply their own power.
### **Environmental protection in cement production**



Insight into a preheater tower

### 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, NO<sub>x</sub>, mercury) than those to be complied with Table II-1: International and national emission limit values (daily averages) for cement works with waste co-incineration in mg/m<sup>3</sup> (in normal operation)

when wuste eo memeration in ing/in	(	-)	
	New directive on industry emissions	17th BImSchV	BMU proposal: Revised 17th BImSchV <sup>6)</sup>
Total dust	30	20 (14-10) 4)	10
HCl	10	10	10
HF	1	1	1
NO <sub>x</sub>	500 <sup>1)</sup>	500 (320-200) 4)	200 7)
NH <sub>3</sub>	-	-	30 2)
Hg	0,05	0,03 2)	0,02 8)
$\Sigma Cd, Tl$	0,05 (MPZ)	0,05 (MPZ)	0,05 (MPZ)
$\sum$ Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn	0,5 (MPZ)	0,5 (MPZ)	0,5 (MPZ)
Dioxins and furans mg/m <sup>3</sup> (in normal operation)	0,1 (MPZ)	0,1 (MPZ)	0,1 (MPZ)
SO <sub>2</sub>	50 <sup>2)</sup>	50 <sup>2)</sup>	50 <sup>2)</sup>
TOC	10 <sup>2)</sup>	10 <sup>2)</sup>	10 2)
СО	3)	5)	5)

MPZ: Average over the sampling period

<sup>1)</sup> Exceptions of up to a maximum of 800mg/m<sup>3</sup> (in normal operation) are possible for lepol kilns and long kilns until 01.01.2016

Raw material-related exceptions possible

<sup>3)</sup> Emission limit values may be determined by the responsible authority

<sup>4)</sup> Weighted limit value determination by the responsible authority for waste utilisation > 60 %

<sup>5)</sup> Responsible authority to set a limit value; raw material-related exceptions possible

6) From 01.01.2016

<sup>7)</sup> No later than from 01.06.2018

 $^{8)}$  Raw material-related exceptions possible; average daily value of maximum 0.05 mg/m<sup>3</sup> (in normal operation)

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/m<sup>3</sup> (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/m<sup>3</sup> (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  $30 \text{ mg/m}^3$  (in normal operation). The planned reduction of the mercury limit value to 0.02 mg/m<sup>3</sup> (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 energy 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 CO<sub>2</sub> savings could



Fig. II-1: Development of the use of alternative fuels in the German cement industry



Fig. II-2: Feed materials are selected, comprehensively inspected and the material and energy is completely used.

also be estimated. Based on the figures obtained in 2010 as part of the emission reporting, the average  $CO_2$  reduction for the energy-related use of alternative fuels in the clinker burning process was 0.74 t  $CO_2/t$  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 CO<sub>2</sub> emission, lower limit values for NO<sub>x</sub>). For example, the political requirement for reduced cement-specific CO<sub>2</sub> 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. At 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 CO<sub>2</sub> emissions** Fuel-related CO<sub>2</sub> 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 CO<sub>2</sub> emissions of the German cement industry reduced from 0.117 to 0.100 t  $CO_2/t$ cement in the period from 2008 to 2011. In absolute figures this relates to a reduction from 4.05 to 3.41 million t  $CO_2/a$ . The  $CO_2$ 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 CO<sub>2</sub> at another point, the use of alternative fuels results in an overall reduction of CO<sub>2</sub> 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  $CO_2$  emissions, such as natural gas, is not possible for reasons of cost. As fuel

#### Table II-2: CO<sub>2</sub> emissions of the German cement industry from 2008 to 2011

	At	osolute Co in 10	-	on	Specific CO <sub>2</sub> emissions in t CO <sub>2</sub> /t cement					
Year	2008	2009	2010	2011	2008	2009	2010	2011		
Thermal <sup>1)</sup>	4.05	3.40	3.19	3.41	0.117	0.110	0.104	0.100		
Electrical	2.30	2.11	2.23	2.51	0.066	0.068	0.074	0.073		
Raw material-related	13.44	12.31	12.19	13.13	0.388	0.398	0.398	0.383		
Energy-related	6.35	5.51	5.42	5.92	0.183	0.178	0.178	0.173		
Total	19.79	17.82	17.61	19.05	0.571	0.575	0.575	0.556		

<sup>1)</sup> Without alternative fuel from waste

Table II-3: Specific CO<sub>2</sub> emissions of the German cement industry (in t CO<sub>2</sub>/t cement)

Jahr	From thermal power consumption <sup>1)</sup>	From electrical po- wer consumption	From limestone calcination	Total
1990 <sup>2)</sup>	0.280	0.072	0.450	0.802
1994	0.252	0.072	0.450	0.775
1995	0.254	0.071	0.451	0.776
1996	0.245	0.072	0.451	0.768
1997	0.231	0.070	0.453	0.754
1998	0.218	0.070	0.444	0.732
1999	0.199	0.068	0.427	0.694
2000	0.195	0.068	0.431	0.694
2001	0.179	0.067	0.415	0.661
2002	0.168	0.069	0.413	0.650
2003	0.156	0.067	0.401	0.624
2004	0.155	0.068	0.428	0.651
2005	0.132	0.068	0.406	0.606
2006	0.123	0.067	0.383	0.573
2007	0.128	0.067	0.419	0.614
2008	0.117	0.066	0.388	0.571
2009	0.110	0.068	0.398	0.575
2010	0.104	0.074	0.398	0.575
2011	0.100	0.073	0.383	0.556

<sup>1)</sup> Without alternative fuels from waste

2) Base year of voluntary agreement of 2000

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 increasingly 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  $CO_2$  emissions – is larger. The  $CO_2$  emissions resulting from power consumption were between 0.066 and 0.073 t  $CO_2/t$  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 CO<sub>2</sub> emissions* The calcination of the key raw material limestone (CaCO<sub>3</sub>) for clinker production releases CO<sub>2</sub>. The raw material-related CO<sub>2</sub> 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 CO<sub>2</sub>/t clinker or between 0.383 and 0.398 t CO<sub>2</sub>/t cement between 2008 and 2011. The total raw material-related CO<sub>2</sub> emissions of the German cement industry initially fell to 12.2 million t  $CO_2/a$  in the years 2009 and 2010 due to declining production, before again rising to slightly above 13 million t  $CO_2/a$ . The specific and absolute  $CO_2$ emissions for the reporting period are represented in **Table II-2**. A reduction of the raw material-related  $CO_2$  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  $CO_2$  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  $CO_2$  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  $CO_2$  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 in fuels. Also integrated into this standard was the CEN/TS 15747, which describes the determination of the biogenic fraction using the <sup>14</sup>C method. The determination of the biogenic fractive dissolution method is described in Annex A8 and the <sup>14</sup>C method in Annex C.

What is important for CO2 emissions trading is that both the selective dissolution method as well as the <sup>14</sup>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 CO<sub>2</sub> emissions in rotary kiln exhaust gases

As part of emissions trading, the ratio of biogenic material to fossil  $CO_2$  emissions represents a relevant value that is also indicated in the  $CO_2$  reporting by rotary kiln plants of the cement industry. By definition, an emission factor of zero is provided for  $CO_2$  from biogenic carbon, so no  $CO_2$  certificates have to be purchased for this part of the  $CO_2$  emissions.

The biogenic fraction in the (alternative) fuels is currently established by way of input analyses. The fraction of biogenic CO<sub>2</sub> 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 weighers, 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  $CO_2$  emissions as the total monthly or annual emission requires correspondingly high test expenses.

A process in which the fraction of biogenic  $CO_2$  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 CO<sub>2</sub> emissions in the chimney
- 2. Analytical determination of the relationship between the biogenic and fossil  $CO_2$ in the aggregate sample
- 3. Continuous measurement of the exhaust gas volume flow and the total  $CO_2$  concentration to calculate the total biogenic  $CO_2$  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  $CO_2$  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 CO<sub>2</sub>. 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 CO<sub>2</sub> 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



Fig. II-3: Long-term sampler for determining the biogenic CO<sub>2</sub> emission in exhaust gas



Fig. II-4: Laboratory apparatus for preparing the solid absorber for the subsequent analysis

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 <sup>14</sup>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  $\pm 1$  %, while this is  $\pm 5$  % 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 <sup>14</sup>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

reduction target of -21 % (Cap, 2005 to 2020) has been set for this. Companies in industry sectors could apply for a free allocation of  $CO_2$  certificates pursuant to the uniform benchmarks until 23.01.2012. This value is 766 kg  $CO_2/t$  clinker for grey cement clinker production plants.

Following a fall in production in the years during the economic crisis and a considerable price decline of the CO<sub>2</sub> emissions trading certificates in 2011, the European Commission is currently discussing a retroactive reduction of the quantity of auctioned CO2 certificates (set-aside) or a possible tightening of the minimum target (cap). The directive to promote renewable energy sources contained in the package of measures also influences the development towards lower CO<sub>2</sub> prices, with objectives that overlap in some areas. The directive regarding the geological storage of carbon dioxide (CCS) has not yet led to the hopedfor development and introduction of CCS technology. Apart from the lack of tested separation techniques, this is certainly also due to the lack of public acceptance of the underground storage of separated carbon dioxide.

To date, international UN climate negotiations for a Kyoto follow-up agreement have not resulted in any update of binding climate protection objectives outside Europe. Regardless of this, the EU is discussing further strategies for achieving long-term reduction targets and for a competitive low-carbon economy under the title "Roadmap 2050".

#### Emissions trading 2013 to 2020

The 3<sup>rd</sup> 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.



Fig. II-5: Assignment of plant units and processes to allocation elements (ZE)

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.

From 2013, the allocation of free certificates will take place based on product-specific emission values (benchmarks) for industrial plants. This requires the assignment of plant units and processes to several allocation elements. Their allocation to a product emissions value for clinker, or to heat or fuel emissions value for clinker, or to heat or fuel emissions values as a so-called fallback solution, is decisive. **Fig. II-5** presents these assignments in a cement work. The clinker production with the quantity of calcined bypass dust is crucial for allocation according to the product emissions value. In addition, an allocation based on a heat emissions value may arise for the use of waste heat from clinker production, e.g. blastfurnace sand dryers, as hot gas producers in cement grinding cannot be assigned to the TEHG plant clinker. During the base periods (2005 to 2008 or 2009 to 2010), the operator was free to determine the applicable activity rate from the clinker production data for the allocation to existing plants.

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.



Fig. II-6: Specific  $CO_2$  emissions for the production of grey cement clinker in Europe (EU 27 and Norway) in 2007 and 2008

### 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

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<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> emissions from the calcination of raw material, according to either the material input or output method, were enhanced. The raw meal (kiln feed) and additional raw materials (kiln 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 CO<sub>2</sub> 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  $CO_2$  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  $CO_2$  emissions in energy-intensive industry sectors established by the European Committee for Standardisation (CEN) in 2011.

### CO<sub>2</sub> reporting in the EU ETS

In the  $2^{nd}$  trading period (2008 to 2012), the annual CO<sub>2</sub> 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  $CO_2$  emissions of individual material flows. At the start of the 2<sup>nd</sup> 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 3<sup>rd</sup> 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 (ÜP), 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.

### CO<sub>2</sub> capture and storage

The reduction of CO<sub>2</sub> 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 CO<sub>2</sub> 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  $CO_2$  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  $CO_2$  emissions in the cement industry. This particularly ap-



Fig. II-7: Material flows in the clinker burning process



plies, as around 60 % of the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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  $CO_2$  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. CO<sub>2</sub> 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 CO<sub>2</sub> 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  $CO_2$ -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 CO<sub>2</sub> (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 CO<sub>2</sub> 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 the CO<sub>2</sub>. 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  $CO_2$  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  $CO_2$  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  $CO_2$  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.



Fig. II-9: Fuel energy demand of a BAT plant dependent on the recirculation rate



Fig. II-10: Influence of the CO<sub>2</sub> concentration on the absorber size





### Post combustion carbon capture

The term post combustion carbon capture includes all the processes that separate  $CO_2$  from flue gas. These processes are therefore generally suited for retroactively equipping existing cement works with  $CO_2$  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  $CO_2$  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  $CO_2$  at temperatures of about 700 °C. However, this is still an extremely recent process, similar to the use of  $CO_2$ -selective membranes that enable the separation of  $CO_2$  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  $CO_2$  absorption. An exemplary absorption column has also been designed on this basis.

The computer-assisted calculations show that the high  $CO_2$  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  $CO_2$  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 interim 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  $CO_2$ 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  $CO_2$  concentration reduces these effects to some extent, as the  $CO_2$ rich absorption solution reacts less sensitively. This moderating effect increases with increasing  $CO_2$  concentrations.

Other absorption solutions, such as methyldiethanolamine (MDEA) or aminomethylpropanol (AMP), react less strongly to impurities in the exhaust gas. However, these amines also react more slowly with  $CO_2$  which is why activators, whose degradation then has to be separately considered, are added in industrial application.

Cement works with low SO<sub>2</sub> 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/m<sup>3</sup> SO<sub>2</sub>.

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.vdzonline.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  $NO_x$ (Fig. II-11) and  $SO_2$  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





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

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/m<sup>3</sup>. 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/m<sup>3</sup> for each measuring and analysis method (crossbar).

The concentration values of the vanadium emissions and the clean gas volume flow  $(m^{3}/year)$  can therefore only be clearly provided for one plant (triangle) in **Fig. II-13**.

For 37 plants the emissions have to be estimated for an assumed concentration value of  $0.005 \text{ mg/m}^3$  (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 NO<sub>x</sub> 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 NO<sub>x</sub> emissions were able to be reduced from about 560 mg/m<sup>3</sup> in 2000 to about 350 mg/m<sup>3</sup> in 2010. Almost all the kiln plants lie within the targeted emissions level of 200 to 450 mg/m<sup>3</sup> 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 NO<sub>x</sub> 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 NO<sub>x</sub> 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 NO<sub>x</sub> 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/m<sup>3</sup> (for 60.1 % substitution rate) and 200 mg/m<sup>3</sup> (for 100 % substitution rate) apply for the NO<sub>x</sub> components at substitution rates of over 60 %. While the application of the SNCR process frequently enables such low NO<sub>x</sub> limit values to be complied with, it is often connected with a rise in NH<sub>3</sub> emissions (NH<sub>3</sub> slip).

An amendment f the 17<sup>th</sup> Federal Ambient Pollution Protection Act, which will include a further tightening of the  $NO_x$  limit values, is in progress as part of the conversion of the European "Industrial Emissions Directive" (IED) into German law. According to this, an  $NO_x$  emissions limit value of 200 mg/m<sup>3</sup> will apply in the future for kiln plants for the production of cement clinker in the event of the coincineration of waste. An  $NH_3$  limit value of 30 mg/m<sup>3</sup> ( $NH_3$  slip) is also intended. Compliance with an extremely low  $NO_x$  limit value, connected with a limit value for  $NH_3$  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 NH<sub>3</sub> and NO, so that this results in only a minimum amount of NH3 emissions even at very high NO<sub>x</sub> 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  $NO_x$  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 NO<sub>x</sub> 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  $NO_x$  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 Mannersdorf 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/m<sup>3</sup>. Regular reports on the progress of the on-going SCR projects are provided in the VDZ  $NO_x$  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.

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 instruments onto 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 coincineration 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 HgCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub>, 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. SO<sub>2</sub>.



Fig. II-14: Possible conversion reactions of mercury in the clinker burning process



Fig. II-15: Filled adsorption tubes for the Dowex-iodised carbon process



Fig. II-16: Example of the use of various speciation methods in a rotary kiln plant with SCR-Denox catalyst

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 elemen-

tary 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 "Dowexiodised 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 (HgCl<sub>2</sub>), 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 as per the UBA process.

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.

### **Performance of cement**



Light-optical microscopic recording of a polished section of Portland cement clinker

# Chemical and mineralogical composition

The cements produced by the VDZ members are investigated on their chemical compositions by means of X-ray fluorescence analysis on a regular basis. **Table III-1** lists the average values, as well as the highest and lowest values of the chemical composition for the various strength classes of the Portland cements according to DIN EN 197. The shift of the market towards cements with several main constituents has resulted in a broad product range. Beside classical cement types increasingly Portland composite cements are produced as CEM II. Besides the dominant S-LL (blastfurnace slag and limestone) combination, main constituents such as fly ash from hard coal or burnt oil shale are being increasingly used. Due to the current standardisation status, technical application approvals from the German Institute for Building Technology are still required for the comprehensive use of these types of cements. **Table III-2** shows the average chemical compositions of Portland pozzolanic, Portland limestone and Portland composite cements produced by the German VDZ members in the reporting period.

Table III-3 summarises the chemical compositions of the Portland slag and blastfurnace cements (CEM II/A-S, CEM II/B-S, CEM III/A and CEM III/B). Cement types CEM III/C, CEM IV and CEM V are still of minor importance in the German market.

### Table III-1: Chemical composition of Portland cements, data in mass %, containing the loss on ignition

	Portland cements												
Strength		32,5			42,5		52,5						
class	min	mean	max	min	mean	max	min	mean	max				
SiO <sub>2</sub>	19.04	20.73	22.92	18.64	20.63	23.18	18.96	20.86	23.53				
$Al_2O_3$	3.50	4.82	5.83	2.86	4.73	5.77	3.38	4.53	5.68				
TiO <sub>2</sub>	0.19	0.26	0.30	0.11	0.25	0.30	0.09	0.24	0.50				
$P_2O_5$	0.04	0.19	0.60	0.03	0.19	0.54	0.02	0.19	0.45				
Fe <sub>2</sub> O <sub>3</sub>	1.35	3.06	6.58	0.16	2.93	7.06	0.15	2.49	5.45				
Mn <sub>2</sub> O <sub>3</sub>	0.04	0.07	0.10	0.02	0.07	0.19	0.02	0.06	0.19				
CaO	60.41	63.20	65.91	59.72	63.56	66.37	61.41	64.44	67.82				
MgO	0.83	1.61	3.39	0.59	1.52	3.80	0.57	1.31	3.27				
SO <sub>3</sub>	2.34	2.99	3.77	1.96	3.03	3.79	2.22	3.20	3.98				
K <sub>2</sub> O	0.53	0.92	1.44	0.35	0.80	1.45	0.25	0.73	1.40				
Na <sub>2</sub> O	0.14	0.20	0.30	0.06	0.20	0.40	0.04	0.19	0.47				
Na2Oequiv.	0.51	0.81	1.17	0.35	0.73	1.21	0.25	0.67	1.26				
Loss on ignition	0.78	1.97	3.08	0.49	2.09	4.06	0.28	1.84	3.75				

Table III-2: Chemical composition of Portland pozzolanic, Portland limestone and Portland composite cements, data in mass %, containing the loss on ignition

	Portland pozzolanic, Portland limestone and Portland composite cements														
Cement type	С	EM II/B-	-P	CH	EM II/A-l	LL	CEM	CEM II/A-M (S-LL)		CEM II/B-M (S-LL)			CEM II/B-M (V-LL)		
	min	mean	max	min	mean	max.	min	mean	max	min	mean	max	min	mean	max
$SiO_2$	28.82	30.36	32.02	17.46	18.94	21.59	20.64	20.90	21.04	19.71	21.23	24.20	18.60	21.12	24.56
$Al_2O_3$	6.94	8.06	8.56	3.29	4.62	6.14	5.07	5.35	5.72	4.61	5.46	6.41	4.73	6.01	7.23
TiO <sub>2</sub>	0.33	0.40	0.46	0.18	0.24	0.41	0.25	0.27	0.28	0.26	0.32	0.44	0.20	0.28	0.33
$P_2O_5$	0.11	0.19	0.36	0.04	0.16	0.42	0.05	0.13	0.22	0.03	0.14	0.38	0.14	0.18	0.27
Fe <sub>2</sub> O <sub>3</sub>	3.25	3.58	3.93	1.21	2.51	3.76	2.17	2.43	2.70	1.62	2.32	3.02	2.54	3.15	4.26
$Mn_2O_3$	0.07	0.11	0.14	0.03	0.07	0.18	0.06	0.14	0.26	0.06	0.13	0.29	0.05	0.10	0.20
CaO	44.43	46.12	50.70	58.67	62.08	63.90	58.34	59.60	60.54	56.74	58.38	60.70	53.26	57.93	62.36
MgO	1.11	1.63	2.48	0.61	1.63	3.30	2.21	2.76	3.32	2.07	2.72	3.96	1.20	1.50	1.97
SO <sub>3</sub>	1.93	2.65	3.34	2.07	2.89	3.65	3.07	3.34	3.58	2.35	2.80	3.33	2.53	2.77	3.02
K <sub>2</sub> O	1.06	1.91	2.71	0.41	0.86	1.46	0.91	0.95	0.99	0.47	0.92	1.34	0.45	0.88	1.46
Na <sub>2</sub> O	0.53	0.84	1.20	0.08	0.17	0.32	0.19	0.30	0.37	0.13	0.21	0.32	0.16	0.21	0.28
Na2Oequiv.	1.23	2.10	2.98	0.35	0.73	1.14	0.83	0.92	0.97	0.44	0.82	1.08	0.48	0.79	1.24
S <sup>2-</sup>	n.a.	n.a.	n.a.	0	0.04	0.08	0.06	0.11	0.26	0.11	0.19	0.37	0.02	0.05	0.08
Loss on ignition	3.35	4.15	5.11	3.16	5.89	7.87	3.27	3.79	4.11	2.93	5.26	7.24	5.32	5.87	6.35

n.a. = not analysed

	Portland slag and blastfurnace cements												
Cement type	(	CEM II/A-S	5	(	CEM II/B-S		CEM III/A				CEM III/B		
	min	mean	max	min	mean	max	min	mean	max	min	mean	max	
SiO <sub>2</sub>	20.51	22.08	25.22	23.10	24.44	26.26	24.82	27.24	31.18	28.80	30.52	32.05	
$Al_2O_3$	4.79	5.73	6.51	5.30	6.31	7.94	5.46	7.57	9.34	7.82	8.84	9.80	
TiO <sub>2</sub>	0.26	0.35	0.53	0.31	0.43	0.60	0.33	0.61	1.10	0.41	0.78	1.25	
$P_2O_5$	0.04	0.18	0.46	0.03	0.12	0.25	0.01	0.09	0.27	0.01	0.07	0.50	
Fe <sub>2</sub> O <sub>3</sub>	1.25	2.50	3.56	1.19	2.19	3.33	0.83	1.62	2.72	0.65	1.14	1.50	
Mn <sub>2</sub> O <sub>3</sub>	0.07	0.13	0.33	0.07	0.16	0.52	0.07	0.21	0.91	0.06	0.25	0.58	
CaO	55.72	60.05	63.64	54.64	57.49	60.16	46.79	52.71	56.95	43.97	47.50	51.43	
MgO	1.41	2.42	4.36	1.93	3.00	4.25	2.50	4.09	6.05	2.00	5.42	7.71	
SO <sub>3</sub>	2.45	3.14	3.78	1.93	2.71	3.73	1.17	2.69	3.88	0.89	2.19	3.33	
K <sub>2</sub> O	0.43	0.88	1.36	0.44	0.73	1.23	0.47	0.75	1.16	0.44	0.71	1.08	
Na <sub>2</sub> O	0.11	0.23	0.42	0.15	0.24	0.39	0.14	0.25	0.44	0.19	0.28	0.49	
Na2Oequiv.	0.42	0.81	1.22	0.47	0.72	1.03	0.50	0.74	1.09	0.51	0.74	0.99	
S <sup>2-</sup>	0.07	0.20	0.41	0.13	0.35	0.61	0.28	0.59	0.99	0.48	0.85	1.12	
Loss on ignition	0.52	1.95	3.18	0.36	2.01	3.33	0.47	1.83	3.20	0.54	1.55	3.00	

Table III-3: Chemical composition of Portland slag and blastfurnace cements, data in mass %, containing the loss on ignition

# Quantitative phase analysis of cements

The quantitative X-ray diffraction analysis has continued to increase in importance in the cement industry over the past years. This method of investigation is now available in most plants and is also being increasingly installed in laboratory automation. The evaluation of the measured data is therefore no longer restricted to individual monitoring-specific parameters, such as the free lime content in clinker, but allows for a complete phase analysis.

### **Rietveld is the method of choice**

The Rietveld method, in which there is a comparison between the measured X-ray diffraction pattern and that calculated from the peaks of predefined mineral phases, has established itself as the method of choice. In addition, a multitude of measuring and structural parameters of the mineral phases are mathematically included in the calculations. This type of evaluation can still only provide approximate values of the real composition, especially in complex mineral mixes with various minerals, solids, degrees of crystallinity and textures.

The instrument manufacturers provide software solutions that include evaluation routines that are individually tailored for the plant and the material system to be measured. The constantly repeating measurement and evaluation of raw materials, clinkers and cements allow changes in the phase composition of the materials to be determined with high precision. In some plants, the data of the X-ray phase analyses is now no longer just used to monitor the ongoing production, but also for process control or for internal quality assurance in some cases.

Determining the absolute phase content remains challenging. Interlaboratory tests to determine the accuracy overwhelmingly provide unsatisfactory results. The German Chemical Society (GDCh) established a task force to evaluate the Rietveld method for X-ray diffraction measurements on Portland cements and Portland cement clinker. The exchange of experiences between specialists from the industry, service laboratories as well as associations and universities is expected to result in the formulation of a guideline to increase the interlaboratory accuracy. Starting with the sample preparation, the instrument parameters, the phase identification and the selection of the structural parameters, all important areas of a quantitative X-ray diffraction analysis are addressed using the Rietveld method. For reasons of practical proximity, only evaluation routines that require no manual post-processing will initially be considered. Initial task force internal investigations on Portland cements show that large ambiguities still occur based just on the sample preparation. However, in contrast, analyses that were performed under identical preparation, measurement and evaluation conditions, e.g. production controls, provided more precise data.

### Analysis of composite cements

Apart from the phase analysis of clinker or Portland cement, the quantitative X-ray diffraction analysis also principally enables the description of the mixture composition of composite cements. In order to achieve this objective, the already complex phase mixture of clinker and sulphate agents has to be extended by the additional main constituent components. It becomes particularly challenging when X-ray amorphous ("glassy") components are to be considered, for example, for blastfurnace slag or fly ash. The modern evaluation software also provides solution possibilities in this case, e.g. via so-called pseudo-structures. However, the results of these types of calculations must be carefully evaluated and calibrated to test results from conventional analysis. The Research Institute of the Cement Industry will comprehensively investigate the current application possibilities of quantitative X-ray diffraction analyses for quality control in cement production as part of an AiF research project (IGF no. 17397 N) that has just commenced.



Fig. III-1: Alite crystals partially decomposed to belite and free lime in the vicinity of a free lime cluster



Fig. III-2: Laboratory clinker nodule with dense belite rim, produced from raw meal nodules with Al(OH)<sub>3</sub> rim (schematic representation top left)



Fig. III-3: Laboratory clinker nodule produced from a raw meal nodule with Al(OH)<sub>3</sub> particles (schematic representation top left) containing belite clusters with pores (arrows) in the dimension of the Al(OH)<sub>3</sub> particles



Fig. III-4: Belite cluster with central pore, detail from Fig. III-3

### Impact of raw materials and fuels on clinker properties

Every raw material and fuel has an impact on the clinker burning process and the clinker properties. As the performance of cements is, to a large extent, determined by the Portland cement clinker, the continuous and detailed monitoring of the clinker properties is state-of-the-art in modern cement production. In recent years, the Research Institute of the Cement Industry has carried out a research project and various investigations on technical clinker in order to further improve the knowledge of the impact of alternative raw materials and fuels on Portland cement clinker. **Raw materials with fuel properties** The effects of a material, which was used as an alternative source of calcium and as a fuel in the clinker burning process, the microstructure of a technical clinker were examined.

The investigated clinker sample contained intergrown crystals of belite and free lime (**Fig. III-1**) that presented decomposed alite crystal. This phenomenon is a typical indicator for reducing burning conditions. However, the structure features unusually only occurred in the direct vicinity of clusters of free lime crystals.

Due to their high calcium content, coarse particles of the combined raw material and fuel in the clinker nodules led to the formation of free lime clusters in the clinker. Reducing conditions were present in the direct environment of the coarse particles in the clinker nodules due to the fraction of organic compounds, which were responsible for the fuel properties of the material. The unusual microstructural relationship of decomposed alite and free lime clusters was the result of the specific properties of the combined raw material and fuel.

The importance of rapid clinker cooling with regard to the impacts of reducing conditions on clinker was evident in the results of this investigation. Due to the available process technology, the described clinker sample was cooled slowly. No signs of reducing conditions were observed in another





clinker sample that was cooled much more rapidly.

The more rapid cooling prevented the decomposition of alite or other effects caused by reducing burning conditions.

### Al-rich ash

The effects of artificial fuel ashes on the microstructures of laboratory clinkers were investigated in an AiF research project (no. 15251 N). One objective was to simulate the inhomogeneous distribution of aluminium oxide in the kiln feed due to coarse Al-rich ash particles or due to the accumulation of Al-rich ash particles on the surface of clinker nodules. Al-rich ashes especially are introduced into the clinker burning process by certain alternative fuels.

Al(OH)<sub>3</sub> particles with a few hundred  $\mu$ m diameter were added to a raw meal in order to simulate a coarse grained aluminium-rich fuel ash. A layer of Al(OH)<sub>3</sub> powder was applied to the surface of raw meal nodules in order to simulate the accumulation of aluminium-rich particles on the nodule surface. Raw meal nodules with a homogeneous composition were also produced for comparison. The overall chemical composition of all three nodule types was identical.

The aluminium-containing clinker phases  $C_3A$  and  $C_4AF$  were homogeneously distributed in the microstructure of the clinker nodules produced from all nodule types. However, rims (**Fig. III-2**) and clusters of belite (**Figures III-3** and **III-4**) were observed in the clinkers produced from nodules with Al(OH)<sub>3</sub> rims or homogeneously distributed coarse Al(OH)<sub>3</sub> particles. The belite clusters had diameters that were comparable to those of the added Al(OH)<sub>3</sub> particles and generally had central pores. Comparable clusters or rims of belite were not observed in the laboratory clinker made from the homogeneous raw meal.

During the burning of the nodules, calcium aluminates and, finally, clinker melt had formed from the enriched  $Al(OH)_3$  and calcium from the raw meal. The melt distributed in the clinker microstructure. Hollow spaces remained in place of the former  $Al(OH)_3$  particles. However, a part of the calcium was also removed with the melt so that only the low-calcium silicate phase, the belite, but not the calcium-rich alite could form in the direct vicinity of the  $Al(OH)_3$ rims and the coarse  $Al(OH)_3$  particles.

The extent to which this effect observed in the laboratory also occurs in technical clinkers must still be investigated. However, the results indicate that belite clusters in clinker are not exclusively the result of local SiO<sub>2</sub> enrichments. Mechanisms that lead to local depletion of CaO can noticeably influence the clinker microstructure. X-ray diffraction investigations on the laboratory clinker showed no change in the mineralogical composition compared to the laboratory clinker produced from homogeneous raw meal. This is not surprising as the same total quantity of calcium aluminates is expected for a constant total quantity of Al<sub>2</sub>O<sub>3</sub>. The properties of the resulting laboratory cements were not affected.

#### Changing temperature profiles

How changes of the temperature profile and the burning temperature in the rotary kiln may affect the properties of Portland cement clinker and the Portland cement produced thereof was also investigated. Differences in the burn-out behaviour of various fuels can change these parameters when using new materials, as the flame shape and temperature may be influenced.

Laboratory clinkers of the same chemical composition were exposed to different sintering temperatures (1400 °C, 1450 °C, 1 500 °C) in a laboratory kiln or were burnt for different lengths of time at the same maximum temperature (5 min, 60 min) for the investigations. Furthermore, changes in the length of the precooling zone in the rotary kiln, which extends from the hottest point of the flame to the kiln outlet, were simulated. In some cases the laboratory clinkers were removed from the laboratory kiln at the burning temperature and cooled in air (rapid precooling). In other cases the laboratory clinkers were left in the kiln after burning until this had cooled to 1250 °C (approx. 30 min) and then removed and cooled in air (slow precooling).

Laboratory cements were produced from these laboratory clinkers by grinding them to comparable fineness and mixing them with a predefined quantity and composition of a sulphate agent. Small prisms (1.5 cm x 1.5 cm x 6 cm) were produced from these cements on which the compressive strengths were determined after 2 and 28 days. Despite the significant changes of the burning conditions that the laboratory clinkers were exposed to, there were no significant differences in the 28-day compressive strengths of the resulting laboratory cements (**Fig. III-5**).

However, the 2-day compressive strengths were noticeably lower for clinkers that were burnt for long periods and/or at high temperatures than for clinkers that were burnt for short periods at intermediate to low temperatures (Fig. III-5). The precooling variation did not have a significant effect on the 2-day compressive strengths.

However, the extreme test conditions must be considered when evaluating the practical relevance of the results. Fuel-related fluctuations in the burning temperature or sintering zone lengths are lower in practice than in the tests in which extreme conditions were supposed to be examined.

# Cement sulphate optimisation

The initial setting time of cements is defined by the reactive cement components and their interactions. The optimisation of the sulphate content, in particular, with respect to the quantity and reactivity of the tricalcium aluminate ( $C_3A$ ) present in the clinker plays a decisive role in cement production. Mortars and concretes can only be processed with a sufficient workability time with an optimal supply of sulphate.

Sulphate carrier optimisation can be performed by measuring the initial setting time of the cements produced in the laboratory. For this different sulphate quantities in differing ratios of gypsum, anhydrite or hemihydrate are added to the clinker and the initial setting time of the sample is then determined with a penetrometer. Unlike the Vicat method according to DIN EN 196-3, in this case a needle with a diameter of 3 mm is used, which enables a higher resolution of the setting times. In addition, considerably less cement is required for the penetrometer tests.

### **Design of experiments**

Sulphate carrier optimisations are generally expensive due to the high number of necessary tests. The impact of mix ratio of anhydrite to hemihydrate on the processability of the cement for a predefined sulphate content is generally investigated first for a sulphate optimisation. The next step then involves the determination of the impact of the sulphate content for fixed mix ratios of the sulphate carrier. Using the Design of Experiments (DoE) enables the number of necessary tests for sulphate carrier optimisation to be considerably reduced and also allows optimal mixes to be established more quickly. A central composite design (CCD) is created for this purpose using DoE, with which the correlation between the processability of the cement, its sulphate content and the sulphate carrier mix can be calculated.

### Approach

An orthogonal central composite design, which considers the sulphate content in cement and the mix proportion of anhydrite/ hemihydrate, is suitable for sulphate carrier optimisation. Cements consisting of Portland cement clinker, other main constituents (if applicable) and anhydrite (AH) and/or hemihydrate (HH) are then produced according to the statistical design (see points in **Fig. III-6**). The homogenisation of the samples in a ceramic ball mill has proven itself to be an optimal solution in this regard.

The water demand of the cements to be optimised must be determined prior to starting the penetrometer measurements. This takes place according to a method based on DIN EN 196-3, which was esspecially developed for determining the water requirement for small sample quantities. The initial setting time of the cement paste is then determined with the penetrometer and the test results are statistically evaluated. For example, Fig. III-6 shows a surface plot of the initial setting time depending on the sulphate content and the mix proportion of the anhydrite and hemihydrate sulphate carrier. The Fig. indicates that the optimum area for both the supply quantity and the ratios of sulphate carrier in the mixture can be clearly localised after only nine tests. Further tests can be used to investigate the setting time behaviour of the cement paste in this area of composition and to determine the optimal composition of the cement with regard to the sulphate carrier quantity and composition.

This described process also enables the sulphate carrier optimisation of cement with regard to other parameters, such as compressive strength according to DIN EN 196-1 or isothermal hydration heat release.

### Influencing the effectiveness of chromate reducers

Tin(II) sulphate is frequently used for the chromate reduction of cement and cementitious mixtures. However, in practice, it has been found that the content of water-soluble chromate of cements with added tin(II) sulphate will sometimes rise again considerably, after only a few months. The chromate reducing effect, surface changes and phase conversion reactions of various tin(II) sulphate compounds were investigated over a period of nine months in the Research Institute in order to clarify the cause.



### Long-term effectiveness

Mixtures of a cement CEM I 42,5 R with about 14 ppm water-soluble chromate were produced with various tin(II) sulphate compounds for the investigations. The compounds differed with regard to their content of residual moisture and residual sulphuric acid, the particle size and morphology.

All of the investigated chromate reducers showed a reduced effectiveness over the nine months storage period, i.e. the measured contents of water-soluble chromate increased over time. The effectiveness of the coarse-grained tin(II) sulphate compound decreased constantly over the storage time. The fine-grained tin(II) sulphate compound displayed a good reducing efficacy over a period of six months. However, its effectiveness subsequently sunk to a level comparable with the other compounds.

### Surface reactions

The behaviour of two industrially produced tin(II) sulphate compounds were investigated in more detail in order to clarify whether chemical reactions were responsible for the loss of effectiveness. The fine-grained compound had a BET surface of about 1.2 m<sup>2</sup>/g, residual moisture of 0.4 mass % and residual sulphuric acid of 0.3 mass %. The particles were predominantly rounded and flattened and formed agglomerates with diameters of between about 5 and 30 µm (Fig. III-7). The coarse-grained compound displayed a BET surface of about 0.05 m<sup>2</sup>/g and contained less than 0.1 mass % residual moisture and less than 0.1 mass % residual sulphuric acid. The particles were mostly euhedral acicular with lengths of between 20 and 200  $\mu$ m (Fig. III-8).

Mixtures of Portland cement CEM I 42,5 R were produced with a tin(II) sulphate compound in proportions of 80 mass % cement and 20 mass % SnSO4 for the series of investigations. Tin(II) sulphate particles of both mixtures were investigated on a monthly basis with the aid of X-ray diffractometry. Furthermore, the mixtures were characterised with the aid of X-ray photoelectron spectroscopy (XPS) after a storage time of nine months. This method of surface analysis provided information on the elemental composition and the chemical bonding of the elements present. The unusually high fraction of tin(II) sulphate in the mixtures ensured that a sufficient fraction of tin(II) sulphate particles could be observed for the REM investigations and that sufficient cement was also available for possible interactions. In addition,



Fig. III-7: Finegrained tin(II) sulphate



Fig. III-8: **Coarse-grained** tin(II) sulphate



after 7 months of storage in a mixture with cement

face of SnSO<sub>4</sub>

the high tin(II) sulphate fraction was expected to help verify any phase conversions with the aid of X-ray diffractometry.

The investigations showed that tin(II) sulphate in cement is subject to chemical conversion processes. Thin layers of various tin(IV) compounds with low solubility initially form on the surface of the SnSO<sub>4</sub> particles (Fig. III-9). This allows their dis-

solution to be inhibited when processing cement or for testing with regard to the content of water-soluble chromate. Surprisingly, the conversion of the investigated coarsegrained particles took place more quickly than the fine-grained material. The chemical reactions continued over the storage time until the tin(II) sulphate completely converted to tin(IV) compounds.

The investigation results clearly show that tin(II) sulphate is subject to chemical conversion processes in cement. Free lime, moisture and the production-related morphology of the tin(II) sulphate particles influence the speed of the relevant reactions and thereby the chromate reducing effectiveness of tin(II) sulphate. In view of the many variables, a forecast with regard to the effectiveness of a specific chromate reducer is virtually impossible. Determinations of the content of water-soluble chromate are therefore essential. Compensating the expected loss of effectiveness by a corresponding overdose of tin(II) sulphate has established itself in practice. This allows the chromate reduction to be ensured up to the specified expiration date with proper storage.

# Reference material and cements

## Reference material for determining chlorine

The increasing diversity and use of secondary fuels lead to higher requirements on the analytics of these materials. The determination of chlorine is a central parameter, in particular when burning plastics. A reference material to determine the chlorine in secondary fuels was provided based on an initiative by the VDZ Analytical Chemistry working group in cooperation with plastics producers. This material is a polymer that was homogenously dosed in defined quantities by the targeted amount of PVC.

An interlaboratory test was performed in the autumn of 2010 in cooperation with the Gütegemeinschaft Sekundärbrennstoffe und Recyclingholz e.V. (BGS). This involved 43 test laboratories determining the chlorine content and calorific value of the untreated material. The average chlorine content of the reference material was approx. 0.8 mass % and the average calorific value was approx. 39,200 kJ/kg. The material can be purchased from the VDZ.

### Reference material for determining chromate

In the reporting period, the VDZ Analytical Chemistry working group also worked on developing a reference material for determining water-soluble chromate in cements. A non-reduced CEM I cement free of minor additional constituents was selected for this purpose and analysed by the members of the working group. Its storage stability was also investigated. The chromate content of cement is expected to be determined in an interlaboratory test by the cement industry laboratories in 2012 so that this can then be provided as a reference cement for chromate determination.

#### **ASR test cement**

Test cement with a high alkali content is used in order to test the alkali reactivity of aggregates according to Part 3 of the Alkali Guidelines. All the testing laboratories should use the same cement in order to reduce fluctuations between the various laboratories during these determinations. The VDZ provides a uniform ASR test cement with additional information on the cement properties and indicates the additional considerations when using the cement.

# Reactivity of main constituents of cement

In 2011 about 68 % of all cements produced in Germany had several main constituents. In order to successfully continue this trend, a more detailed understanding of the reactions of the cement constituents used in the hardened cement paste matrix is required, in particular for the production of powerful cements with high fractions of additional main constituents apart from clinker. Several research projects were involved in producing and improving the properties of cements with several main constituents in the reporting period.

### Siliceous fly ash as a cement main constituent

The hydration reactions of eight different siliceous fly ashes were thoroughly investigated in a research project supported by the AiF (IGF no. 16206 N), which allowed conclusions to be drawn on their reactivity. The chemical compositions, the density and the granulometric properties of the fly ashes used are listed in **Table III-4**.

### Suspension tests

The suspension of siliceous fly ashes and of fly ash-calcium hydroxide mixtures in various test solutions allowed the corrosion of the ashes to be accelerated and their hydration reactions to be investigated in quick time. More potassium than sodium was contained in the reaction products of the fly ashes during suspension in an alkali test solution consisting of 0.54 mol/l KOH and 0.11 mol/l NaOH, which generally corresponded to the pore solution of a CEM I cement. The aluminium content in the eluate of the fly ash-calcium hydroxide mixture was lower as the sulphate contained in the ash increased. The aluminium was required for the formation of AFt and AFm phases, when sufficient sulphate was available, and was therefore no longer dissolved in the eluate.

### Hydration products

The isolated investigation of reaction products of siliceous fly ashes formed in cementitious systems is practically impossible. Ashes were therefore mixed with various calcium hydroxide contents and hydrated in order to obtain corresponding hydration products of fly ash. This allowed the reaction of siliceous fly ashes to be adjusted. The arising hydration products were investigated using various methods. Ettringite formed when the ash contained sufficient amounts of sulphate. The fly ashes also formed mono and hemi carboaluminate as crystalline reaction products as well as stratlingite to some extent. Increasing the watersolid ratio increased the conversion of the pozzolanic reaction and more calcium hydroxide was used.

The reaction of the siliceous fly ashes in fly ash-containing cements was also investigated. The cements were produced in the laboratory by intensively mixing the relevant ash with a CEM I cement (cf. Table III-4). The formation of various carboaluminates was determined by using X-ray diffraction analysis. The type (mono or hemi carboaluminate) depended on the chemical composition of the fly ash. Fig. III-10 shows the structure of a CEM II/ B-V cement with 30 mass % siliceous fly ash after a hydration period of 28 days, magnified 5000x. The reaction products of the fly ash are clearly visible. The formation of strength-related products from the reaction of the fly ash was most intense between days 7 and 28 of testing. The microstructure of the hydrated samples became looser as the ash content of the cement increased and there was a reduction in the quantity of pozzolanic reacting fly ash particles.

### Conversion determinations and compressive strengths

The conversion of the relevant siliceous fly ashes in cementitious systems was able to be determined by methanol-salicylic acidhydrochloric acid (MSS-) digestion of the hydrated hardened cement paste. The conversion of the ash in hardened cement paste with 30, 50 or 70 mass % siliceous fly ash was between 15 and 27 % after 7 days of hydration and between 21 and 39 % after 28 days. The relevant ash conversion reduced as the ash content in cement increased. This is predominantly due to the reducing pH value of the pore solution and the lack of reaction partners in systems with high ash content and explains the rising porosity of the hardened cement paste with increasing fly ash fractions

8										
Components	Unit	A1	A2	A7	A8	A10	A11	A13	A14	CEM I
Loss on ignition		4.89	2.58	2.28	3.27	2.88	7.12	3.77	4.20	3.02
Silicon(IV) oxide		40.96	39.48	45.07	50.48	51.82	50.17	51.57	48.72	20.07
Aluminium oxide		26.56	22.56	28.31	30.25	24.86	24.12	26.83	28.90	4.34
Iron(III) oxide		9.98	14.27	12.13	6.04	7.30	6.22	6.65	4.66	2.54
Calcium oxide		7.73	11.28	2.14	0.75	5.74	3.31	3.62	7.47	64.02
Sodium oxide		1.48	1.04	1.40	1.13	0.66	1.03	0.85	0.17	0.18
Potassium oxide	01	1.79	2.28	3.25	3.92	1.97	3.74	3.07	0.60	1.15
Phosphorous(V) oxide	mass %	0.94	0.06	0.58	0.44	0.94	1.13	0.58	1.06	0.07
Magnesium oxide		3.82	3.02	2.58	1.92	1.93	1.76	1.65	1.45	1.44
Manganese(III) oxide		0.21	0.21	0.18	0.08	0.09	0.07	0.06	0.06	0.04
Titanium oxide		1.09	0.81	1.14	1.26	1.14	1.07	1.24	1.64	0.19
Sulphate a SO <sub>3</sub>		0.65	2.09	0.94	0.40	0.67	0.22	0.34	0.26	3.66
Free lime		1.27	1.10	0.39	n.v.	0.82	0.14	0.22	0.89	n.v.
Reactive SiO <sub>2</sub>		33.8	33.8	36.5	44.3	39.0	44.1	40.6	34.1	n.a.
Density	g/cm <sup>3</sup>	2.70	2.79	2.64	2.53	2.20	2.36	2.58	2.64	3.12
x' (RRSB function)	$\mu$ m	27.27	32.04	25.46	13.20	32.42	26.01	27.79	36.39	12.41
n (RRSB function)	-	0.77	0.87	0.80	1.10	0.90	0.70	0.80	0.88	0.87

Table III-4: Chemical composition and granulometric parameters of the siliceous fly ashes and the Portland cement used for the production of fly ash-containing cements

n.v. = not verifiable

n.a. = not analysed

The impact of the chemical composition of the fly ash on its strengthening contribution in cement increased as the fly ash content in the cement increased. The content of reactive  $SiO_2$ ,  $Al_2O_3$ ,  $Na_2O$  and  $K_2O$  of the fly ash generally had a positive influence on the compressive strength of cement containing fly ash. In contrast, reactive CaO had a negative impact on compressive strength (cf. **Fig. III-11**).

# Hydration of siliceous fly ashes with mineral additives

The addition of various mineral additives to cement containing fly ash and the mixing of various ashes had an, in part, strong impact on the hydration of these systems. The addition of 5 mass % sodium sulphate had a positive effect on strength for cements with low-sulphate ashes. The addition of 5 mass % of an aluminium-containing substance (e.g. aluminium sulphate or metakaolin) was more effective for cements with calcium-rich ashes than for those with aluminium and silicon-rich ashes. In addition, it was determined that mixing equal parts of calcium-rich ash (A2) with low-calcium ash (A7) had a similar effect with regard to strength as for the addition of additives (cf. Fig. III-12).



Fig. III-10: CEM II/B-V with 30 mass % siliceous fly ash A8 after 28 days of hydration with a w/c value of 0.50; fracture surface magnified  $5\,000x$ 

## Calcined clay as cement main constituent

Calcined clays can be used as pozzolanic cement main constituents in accordance with the requirements of DIN EN 197-1, if they have a minimum reactive silicon dioxide content of 25 mass %. The objective

of the AiF research project (IGF no. 16566) was the production of calcined clays, which are suitable for use as a cement main constituent. The performance of these clays as cement main constituents should also be determined and evaluated.



Fig. III-11: Compressive strength of the CEM II/B-V cements with 30 mass % siliceous fly ash after 91 days depending on the chemical composition of the fly ash



Fig. III-12: Strength development according to DIN EN 196-1 of CEM IV cements with 50 mass % siliceous fly ash A2 with various mineral additives, as well as CEM IV cements with 25 mass % fly ash A2 and 25 mass % fly ash A7

Fifteen different clays from German clay deposits were selected and comprehensively characterised for the research project. The mineralogical composition of the clays is indicated in Table III-5. Low quantities of the clays were tempered under various burning conditions (variation of the burning period and temperature) and then chemically and mineralogically characterised. Larger quantities of clay were tempered after the optimal burning conditions had been determined for each clay. The samples were then ground to equal fineness and CEM II/A-Q cements, each with 20 mass % tempered clay, and CEM IV/B cements, each with 40 mass % tempered clay, were produced in the laboratory. A CEM I cement, which met the requirements of a test cement in accordance with DIN EN 450-1, was used as clinker component.

### **Calcined clay samples**

The phase change of the clay samples during the burning process was traced using X-ray diffraction analysis. For example, **Fig. III-13** shows the phase change of a kaolinitic clay sample. A burning temperature of 1 000 °C and a burning duration of 30 min were determined as the optimal burning conditions for this clay. Under these burning conditions, the clay minerals kaolin and illite/muscovite contained in the sample decomposed, while reactivity-re-

	Clay 1	Clay 2	Clay 3	Clay 4	Clay 5	Clay 6	Clay 7	Clay 8	Clay 9	Clay 10	Clay 11	Clay 12	Clay 13	Clay 14	Clay 15
Quartz	+	Т	Т	Т	+	+	++	+	++	?	+++	++	++	+	+
Microline	?	Т	-	-	-	-	Т	Т	-	-	Т	Т	-	?	?
Calcite	Т	Т	Т	Т	-	+	-	-	-	-	-	-	-	+	-
Chlorite group	Т	?	?	?	+++	++	-	-	-	-	-	-	+	-	-
Kaolinite	++	+	Т	Т	?	?	++	++	+++	++++	++	++	++	+	+
Montmorillonite	++	+++	+++	+++	?	?	+	++	-	-	-	-	-	+	++
Muscovite/Illite	+	++	++	++	+++	++	+	Т	+	+	++	+ 2)	+++	++	++
Goethite	?	-	-	-	-	-	+	-	-		-	-	+	-	++
Ankerite	+	Т	Т	-	-	+ 1)	-	-	-	-	-	-	-	++	-
Siderite	Т	-	-	-	-	-	-	-	+	?	Т	-	+	?	+
Gypsum	Т	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Albite	-	-	-	-	Т	-	-	-	-	-	-	-	-	-	-
Lepidocrocite	-	-	-	-	-	-	-	-	-	-	-	-	+	-	-
Pyrite	Т	-	-	-	-	-	-	-	-	-	-	-	-	Т	-
Temp. in °C	650	600	900	750	850	1000	1 200	1 200	600	1000	1 200	1 200	950	600	950
Duration in min	30	30	30	30	30	30	30	5	30	30	5	5	5	30	5
Reactive SiO <sub>2</sub>	41.9	28.3	52.6	47.3	51.0	35.2	29.4	35.0	38.5	35.4	41.3	32.5	35.2	33.8	34.6
T = Traces		1)	fron-rich a	nkerite											

Table III-5: Mineralogical phases of the clay samples used estimated using X-ray diffraction analysis, as well as information on the determined burning conditions (temperature and burning period) and the related reactive silicon dioxide content, mass %

? = Not verifiable

<sup>1)</sup> Iron-rich ankerite
<sup>2)</sup> Poorly crystallised

ducing high-temperature phases such as mullite and christobalite had not yet formed.

The reactive silicon dioxide content of the calcined clay was strongly dependent on the composition of the respective clay as well as the selected burning conditions. Table III-5 shows the burning conditions for each clay that led to high fractions of reactive components. The corresponding reactive silicon dioxide contents are also provided. With regard to the reactive components, it was generally noticeable that the content of reactive silicon-rich components increased as the burning temperatures increased, while the content of reactive aluminium-rich components reduced. Reactive aluminium-rich components were more likely to form at lower temperatures and reactive silicon-rich components at higher temperatures.

### **Cements containing clay**

CEM II and CEM IV cements containing calcined clays were produced with calcined samples mentioned in Table III-5, which contained about 28 to 51 mass % reactive silicon dioxide. The cements were investigated with regard to their performance based on DIN EN 196. As expected, the water demand of the cements increased as the fraction of clay increased. The compressive strengths of the CEM II cements were de-



Fig. III-13: X-ray diffraction patterns of a kaolinitic clay tempered under various burning conditions (burning conditions right in the Fig.: Temperature in °C – burning duration in minutes)

termined on mini-prisms, 15 mm x 15 mm xx 60 mm in size, with a w/c value of 0.5 pursuant to the standard, while the CEM IV cements had a w/c value of 0.60. The results are displayed in **Fig. III-14**. The compressive strengths of the CEM II cements after 2 days were between 24 and 29 N/mm<sup>2</sup> and the standard strengths between 48 and 66 N/mm<sup>2</sup>. Most of the cements could therefore be allocated to strength





class 52,5 N. The compressive strengths of CEM IV cements with a w/c value of 0.60 were between 9 and 13 N/mm<sup>2</sup> after 2 days and between 24 and 49 N/mm<sup>2</sup> after 28 days.

With regard to the strength development of the cements containing clay, higher reactive silicon dioxide contents did not automatically lead to higher compressive strengths. Whereas the original clay minerals present in the clay had a clear impact on the strength development of the cements. The strength of the tempered products increased as follows: Muscovite/Illite < Montmorillonite < Kaolinite.

# Ternary cements with fly ash and blastfurnace slag as main components

The production and use of cements with a clinker fraction under 65 mass % is becoming increasingly common due to the efforts of the cement industry to reduce  $CO_2$  emissions per ton of cement. However, to date, only a small number of practical experiences have been gained with cements with lower clinker fractions in Germany, apart from blastfurnace cements. The Research Institute of the Cement Industry, together with the FEhS – Institut für Baustoff-Forschung e.V., carried out an AiF research project (IGF no. 16148 N) in which a large range of possible cement compositions in the ternary system of clinker, blastfurnace

slag and siliceous fly ashes were investigated with regard to their cement properties and the durability of the concretes produced with these cements. The investigated combinations ranged from CEM II cements through to CEM IV and CEM V cements and even non-standardised cements. The preparation of the test design and the evaluation of the results were performed with the aid of statistical methods.

### **Raw materials**

Two different Portland cements (Z) from strength class 42,5 R, which fulfilled the requirements according to DIN EN 450-1, were used to produce cements containing blastfurnace slag and fly ash. Two blastfurnace slags (S) with differing activity indices (AI) were also used. Two different grades of fineness (4200 cm<sup>2</sup>/g and 5500 cm<sup>2</sup>/g according to blaine) of blastfurnace slag were used. Two types of siliceous fly ashes (V) from German coal-fired power stations, which had different chemical compositions, were also used. The chemical composition and the granulometric parameters of the raw materials are provided in Table III-6.

### **Parameter study**

The Design of Experiments (DoE) was used to prepare a test matrix with 108 cements with 15 different compositions (cf. Fig. III-**15**) for which the 28-day compressive strengths as well as the quantity of released hydration heat after 2 and 7 days were determined. The results were statistically evaluated to produce a model with the highest possible regression for each parameter, which only contained significant influencing parameters. The results of the determination of the 28-day compressive strength are displayed in Fig. III-16. The cement compositions, standardised according to DIN EN 197-1, are highlighted in grey in order to better classify the cement compositions. The Fig. indicates that it was possible to produce cements with a 28-day compressive strength over 42.5 N/mm<sup>2</sup> for a wide range of investigated cement compositions. The quality of the blastfurnace slag had a considerable impact in this regard. The use of a particularly reactive blastfurnace slag (left diagram in Fig. III-16) enabled the use of up to 40 mass % of siliceous fly ash in the cement.

The lower the Portland cement clinker content in the cement, the higher the importance of the reactivity of the other main constituents. In the event of unfavourable combinations (low clinker and blastfurnace slag reactivity), it was not always possible to achieve a 28-day compressive strength

Table III-6: Chemical composition and granulometric parameters of the raw materials used

Components	Unit	Z 1	Z 2	HS 1 <sup>1)</sup>	HS 2 <sup>1)</sup>	FA 1	FA 3
IR in HCl/Na <sub>2</sub> CO <sub>3</sub>		0.63	0.41	0.06	0.22	a.b.	a.b.
Loss on ignition at 950 °C		2.90	2.30	1.10	0.40	2.39	4.57
TOC	mass %	a.b.	a.b.	a.b.	a.b.	1.57	4.68
CO <sub>2</sub>		2.25	1.42	0.32	< 0.20	0.06	0.05
Water		0.65	0.84	0.86	< 0.20	0.31	< 0.10
Silicon(IV) oxide		20.48	20.06	32.5	39.1	48.19	54.58
Aluminium oxide		3.99	4.38	14.0	11.8	23.22	26.15
Titanium oxide		0.21	0.20	0.81	0.47	0.94	1.31
Phosphorous(V) oxide		0.13	0.08	0.04	0.02	0.03	0.80
Iron(III) oxide		2.56	2.47	0.66	0.52	12.14	4.95
Manganese(III) oxide		0.06	0.04	0.32	1.80	0.13	0.07
Magnesium oxide	mass %	0.81	1.37	9.93	9.03	2.02	1.00
Calcium oxide	mass 70	64.28	64.73	39.8	35.8	5.14	2.48
Sulphate as SO <sub>3</sub>		2.89	3.45	0.055	0.084	0.90	0.21
Potassium oxide		0.59	1.17	0.57	1.11	2.30	1.12
Potassium oxide		0.20	0.20	0.50	0.36	0.96	0.22
Sodium equivalent		0.59	0.97	0.87	1.08	2.47	0.95
Glass content		a.b.	a.b.	100.0	98.6	73.5	64.2
Reactive silicon dioxide		a.b.	a.b.	a.b.	a.b.	36.4	41.3
Particle density	g/cm <sup>3</sup>	3.142	3.116	2.917	2.923	2.675	2.543
Spec. surface acc. to Blaine	cm <sup>2</sup> /g	3 5 4 3	4620	4230	4260	3010	4970
x' (RRSB function)	μm	20.86	12.41	15.17	15.69	33.13	23.32
n (RRSB function)		0.85	0.87	0.79	0.73	1.00	0.84

n.a. = Not available <sup>1)</sup> Activity index after 28 d: HS 1 = 104; HS 2 = 88



Fig. III-16: Attainable 28-day compressive strengths of cements with clinker component Z 2 and blastfurnace slag HS 1 (left) and HS 2 (right)

cicic investiga	tions, data in	mass 70				
Cement	Z 1	Z 2	HS 1	HS 2	FA 1	FA 3
SVA 1	25	-	5	-	-	70
SVA 2	31	-	-	17	52	-
SVA 3	-	20	-	45	-	35
SVA 4	30	-	-	-	-	70
SVA 5	-	36	-	12	52	-
SVA 6	31	-	52	-	17	-
SVA 7	56	-	27	-	17	-
SVA-8	70	-	-	-	30	-
Concrete 1	-	20	80	-	-	-
Concrete 2	-	60	-	-	40	-
Concrete 3	-	30	35	-	35	-
Concrete 4	-	30	35	-	35	-
Concrete 5	-	56	12	-	32	-
Concrete 6	-	56	36	-	12	-
Concrete 7	-	31	52	-	17	-
Concrete 8	-	40	45	-	15	-

Table III-7: Composition of the cements selected to investigate sulphate resistance and for concrete investigations, data in mass %

of at least 42.5 N/mm<sup>2</sup> in the investigations performed during the research project.

It must be taken into account that the investigated cements were produced by mixing of the three components Portland cement, blastfurnace slag meal and siliceous fly ash. Strength optimisation aligned to the individual raw materials by adjusting the meal fineness or by sulphate optimisation was not performed. It must therefore be assumed that cements with less than 40 mass % Portland cement clinker and with a mortar compressive strength of more than 42.5 N/mm<sup>2</sup> after 28 days can be produced under practical conditions.

Further investigations suggest that marketable cements can be produced in the investigated composition ranges with regard to the early strength development and the additional requirements of DIN EN 197-1.

Eight cements from the test program were investigated with regard to their sulphate resistance according to the SVA method. The composition of these cements is listed in **Table III-7**. The expansions of the mortar prisms were below the limit value of 0.500 mm/m. These cements therefore displayed a high sulphate resistance.

### **Concrete investigations**

Based on the results of the cement investigations, eight cements were selected and two different concretes were produced using each of the cements in order to perform concrete tests. The compositions of the cements for the concrete investigations are listed in Table III-7. Concrete type 1 corresponded to the provisions of the German Institute for Building Technology for approval tests for binders to be approved for use in concrete in exposure class XF3  $(z = 300 \text{ kg/m}^3; \text{ w/c} = 0.60)$ . Concrete type 2 was composed according to the minimum concrete composition requirements of DIN 1045-2 for concretes in exposure class XF4  $(z = 320 \text{ kg/m}^3; \text{ w/c} = 0.50; \text{LP} = 4.5 \text{ vol}.$ %). The fresh concrete properties of the investigated concretes were within the usual range for both concrete compositions produced. With the exception of both of the investigated CEM V/B cements (20 mass % Z; 45 mass % S; 35 mass % V) all cements in type 1 concretes resulted in 28day compressive strengths which allowed the targeted realisation of concrete strength class C25/30.

With regard to frost resistance, the weathering damage of the concretes determined based on the cube test method was similar to those of concretes with cements approved for exposure class XF3 according to DIN 1045-2. All of the concretes tested according to the CDF method displayed scaling values of over 1.5 kg/m<sup>2</sup>. This was characterised by a severe initial scaling during the first freeze-thaw-cycles, which is primarily due to the unfavourable preliminary storage period and conditions of the test specimens (20 °C / 65 % rel. h.) for cements with longer hardening period.

#### **Ecological considerations**

The CO<sub>2</sub> emissions for the possible combinations of Portland cement clinker, blastfurnace slag and siliceous fly ash could be estimated based on the boundary conditions selected for Design of Experiments. The following input variables were selected: for blastfurnace slag 0.1 t CO<sub>2</sub>/t blastfurnace slag, for Portland cement 0.89 t CO<sub>2</sub>/t cement and for siliceous fly ash 0.05 t CO<sub>2</sub>/t of fly ash. Fig. III-17 displays the calculated CO<sub>2</sub> savings potential for the example of ternary cements with Z 1 as the clinker component, HS 2 as the blastfurnace slag component and both of the investigated fly ashes. A standard compressive strength of more than 42.5 N/mm<sup>2</sup> was modelled for cements consisting of the above-mentioned components to the left of the white dotted line, while a standard compressive strength of more than 52.5 N/mm<sup>2</sup> was modelled for cements left of the blue dotted line. The composition of standardised cements is represented in grey and serves as an orientation. The calculation established that cements with standard compressive strengths over 42.5 N/mm<sup>2</sup> and over 52.5 N/mm<sup>2</sup> could be produced with up to 77 % and 55 % lower CO2 emissions respectively compared to Portland cement. In particular, the non-standardised area between the CEM III and CEM V cements was extremely promising, both in regard to the achievable compressive strengths as well as the potential CO<sub>2</sub> savings. However, the area between the CEM IV and CEM V/A cements is not covered by the standard provisions. But, the production of cements in strength class 42,5 is also possible within this composition range.

# Sulphate resistance at magnesium exposure

Unexpected damage was determined on some originally sulphate-resistant concrete and mortar test specimens during the laboratory and field investigations when these were exposed to magnesium as well as sulphate in aggressive water. The damage occurred even though the magnesium content was clearly below the limit value of 300 mg/l for exposure class XA1. Test specimens based on Portland and Portland limestone cement in combination with fly ash from hard coal as concrete addition were affected.

The material requirements and boundary conditions under which a sulphate attack of 1 500 mg sulphate/l and magnesium of up to 300 mg/l may result in damage to mortars and concretes, if these have been produced with cement and fly ash from hard coal pursuant to the fly ash regulation according to DIN 1045-2 have been investigated in a research project (IGF no. 16710 N).

Five cements were tested (CEM I, CEM II/ A-LL, CEM II/B-S, CEM II/B-M (S-LL), CEM III/A) in combination with two fly ashes from hard coal as well as a CEM III/ B-SR and a CEM I-SR for reference. However the majority of the tests were performed with Portland and Portland limestone cement. Initial damage in the form of structure-deteriorating thaumasite formation occurred after about 6 months for test specimens based on Portland limestone cement that were stored at a lower temperature (8 °C) and that were exposed to a magnesium concentration of 300 mg/l. The test specimens based on pure Portland cement showed comparable behaviour after about 12 months. An insufficient structure density at the beginning of the sulphate attack was decisive with regard to the occurrence of the damage. Despite the rapid formation of a thin brucite layer close to the surface, sulphate was still able to penetrate the structure to form secondary ettringite and thaumasite in cases of the normal, short preliminary storage time of 14 days during SVA testing. All the tested cements remained undamaged in cases of a longer preliminary storage period of the test specimens (90 days) or when stored at 20 °C. Both of the reference cements CEM I-SR and CEM III/B-SR did not show any weaknesses under any of the test conditions, which indicates that the presence of magnesium ( $\leq 300 \text{ mg/l}$ ) does not pose any additional attack potential for SR cements. An additional, more detailed report on this research project is provided in Chapter V in the sulphate resistance section.



Fig. III-17: Calculated  $CO_2$  savings potential depending on the cement composition and the modelled standard compressive strengths 42.5 and 52.5 N/mm<sup>2</sup>

# Nano-optimised binding agents with high acid resistance

Experience with ultra-high performance concretes has revealed that particle optimisation with fine particles can considerably improve the structural density, strength and durability of concretes. In mid-2009, a joint research project titled "Cold-curing ceramics by nano-technological structure optimisation" was commenced on this basis, supported by the Federal Ministry of Education and Research (BMBF). Besides the Research Institute of the Cement Industry, nine additional partners are also involved in the project. They represent the entire value chain, from producers of individual raw materials over formulators and producers of building products, through to consumers.

### **Objective: High acid resistance**

The new binder formulations should harden at temperatures less than 100 °C without expensive autoclave treatment and should enable the production of chemically and mechanically highly resistant concrete components and coating mortar. The focus is on applications for which concrete according to DIN EN 206-1/DIN 1045-2 has not previously been able to be used, or only with additional expensive protective measures (e.g. exposure classes XA3 and XM3).

The Research Institute of the Cement Industry predominantly concerned with the structure optimisation of an ultra-high performance concrete, whose composition (M3Q) is indicated in Table III-8. On the one hand, the structure density must be optimised by minimising the packing density and the porosity. On the other, a partial replacement of Portland cement with combinations of blastfurnace slag and fly ash, or fine blastfurnace slag and fine fly ash, is expected to increase acid resistance. The required model calculations on the packing density and structure optimisation were performed by a project partner, the University of Kassel. The Fraunhofer Institute for Silicate Research had the task of developing silica with defined particle sizes of about 100 to 800 nm for an extensive structural density, which can be used as redispersible microparticles.

### **Optimised concrete compositions**

A specifically purchased high-performance mixer enabled the production of homogenous, reproducible binder mixtures and concretes. A total of about 30 different compositions with Portland cement fractions between 10 and 34 vol. % were produced in the Research Institute and investigated

Components/Parameters	Unit	Reference M3Q	Optimisation A	Optimisation B	Optimisation C	Optimisation D	Optimisation E
CEM I	Vol. %	34	14	14	14	14	10
Blastfurnace slag 1/2	Vol. %	-	3/10	2.3/7.5	2.4/8	8/-	8/-
Fine blastfurnace slag	Vol. %	-	7	5.3	5.6	3	5
Fly ash 2	Vol. %	-	-	-	-	-	5
Silica	Vol. %	10	10	12	12	14	13
Quartz meal	Vol. %	10	10	9	8	9	1
Quartz sand	Vol. %	46	46	50	50	52	58
Packing density, calc.	Vol. %	81.4	82.4	84.0	85.1	85.7	86.1
7-day compressive strength	N/mm <sup>2</sup>	136	127	121	122	122	98
28-day compressive strength	N/mm <sup>2</sup>	167	159	145	146	141	127
Gel porosity, $\leq 0.01 \mu$ m	Vol. %	3.3	3.3	3.4	3.3	4.0	5.0
Capillary porosity $> 0.01-100 \ \mu m$	Vol. %	1.7	0.8	0.9	1.3	1.4	1.6
Acid resistance	-	0	++	++	+	+	++

Table III-8: Selected concrete compositions together with their compressive strengths, porosities and acid resistance

Water binder value = 0.193; superplasticizer (PCE): 1.2 mass % of binder

(Binder: Mass of CEM I, blastfurnace slag, fine blastfurnace slag, fly ash and silica)



Fig. III-18: Particle size distribution of the blastfurnace slags, fly ashes and Portland cement used in the concrete compositions

with regard to their strength and porosity. In this case the Portland cement fraction was predominantly substituted with blastfurnace slag and fine blastfurnace slag in order to achieve the highest possible acid resistance at pH1.

Table III-8 shows a selection of concrete compositions, the correspondingly achieved compressive strengths, porosities and an estimate of the relevant acid resistance. The selection includes cement compositions for which relatively high packing densities, compressive strengths and acid resistances were achieved. For example, for concrete pursuant to optimisation A, when substituting about 60 % of the cement volume with blastfurnace slag or fine blastfurnace slag compared to the reference mixture M3Q, the capillary porosity was halved to 0.8 vol. % and the acid resistance increased significantly. However, as indicated in Table III-8, the calculated packing densities did not correlate with the obtained porosities and compressive strengths. The highest packing density was calculated for optimisation E. However, the compressive strengths obtained in the age of 7 and 28 days were clearly under those of the reference composition, while the porosities considerably

exceeded those of the reference composition. This was presumably due to the lowest Portland cement fraction of 10 vol. % of all of the investigated compositions. The use of blastfurnace slag was more favourable than the use of fly ash for the targeted highest possible compressive strength. One reason for this may be the differing particle size distributions, which are represented in Fig. III-18. The two fly ashes were clearly and the air classified fine fly ash slightly coarser than the Portland cement component. The blastfurnace slags barely differed from each other and differed only slightly to the Portland cement. They were therefore very well suited for substitution. The fine blastfurnace slag was the finest component by some distance and was therefore particularly well suited for packing density optimisation.

Selected samples were investigated by the University of Kassel project partner for their acid resistance according to the German sewerage construction guideline 2001. Based on the positive results, individual compositions were used by project partners to produce concrete pipes with an internal diameter of 20 cm and a length of about 1 m. Test specimens of these concrete pipes are currently also being tested for their acid resistance. Furthermore, additional investigations on the fresh concrete and durability properties (incl. sulphate resistance, frost resistance) are in progress in the Research Institute until Autumn 2012.
#### Impact of additives on compressive strength and carbonation propensity of blastfurnace cement

The impact of additives on the strength development and the carbonation behaviour of hardened cement paste, mortar and concretes with blastfurnace cements (CEM III/A) were investigated in a Federal Ministry of Education and Research project. In particular, the impact of different additives such as metakaolin, calcium hydroxide and silica fume was investigated. (See also Chapter V, "Carbonation of blastfurnace cement concretes").

#### Impact of different additives

The basic investigations were performed with two blastfurnace slags (HS 1 and HS 2). According to the chemical composition in Table III-9, it can be assumed that blastfurnace slag HS 1, with a higher Al<sub>2</sub>O<sub>3</sub> content and lower SiO<sub>2</sub> content, will provide a higher strengthening contribution than blastfurnace slag HS 2. The blastfurnace slags were ground to a fineness of approx. 3800 cm<sup>2</sup>/g according to Blaine. A white cement clinker (KA) and a Portland cement clinker (KB), both with a fineness of approx. 4000 cm<sup>2</sup>/g, were selected as cement clinker (see Table III-9). The low-iron white cement clinker was selected in order to better investigate amorphous silicate hydrogels and any arising amorphous alumosilicates using NMR spectroscopy. The aluminium-containing additive metakaolin (A) was produced by tempering kaolin for two hours at 700 °C. Silica fume (S) and calcium hydroxide (C) were also used as additives.

The investigated blastfurnace cements (HOZ 1 to HOZ 4) contained 35 mass % Portland cement clinker (KA or KB) and 65 mass % blastfurnace slag (HS 1 or HS 2). A mixture of gypsum and anhydrite at a ratio of 1:1 was used as setting regulator. The setting regulator content was set at 3.5 mass % SO<sub>3</sub> for all the cements, with regard to the fraction of main constituents. The blastfurnace cements always contained 5 mass % of an additive (metakaolin (A), silica fume (S) and calcium hydroxide (C)). The reference cements consisted of the respective clinker and blastfurnace slag and contained 5 mass % limestone (N) instead of the additive.

The compressive strength of the blastfurnace cements produced in the laboratory was determined on standard mortar prisms pursuant to DIN EN 196-1 at the age of 2, 7, 28 and 91 days. The carbonation depths

Komponente HS<sub>1</sub> HS<sub>2</sub> KA KB Ν А SiO<sub>2</sub> 31.98 38.36 23.25 21.46 2.59 51.54  $Al_2O_3$ 16.61 9.13 4.99 5.33 0.55 43.94 TiO<sub>2</sub> 0.95 0.97 0.15 0.28 0.03 1.41  $P_2O_5$ 0.01 0.01 0.04 0.24 0.10 0.11 0.15 3.04 0.20 0.85 Fe<sub>2</sub>O<sub>3</sub> 0.24 1.76 0.02 0.11 0.06 0.01  $Mn_2O_3$ 0.41 1.10 CaO 36.29 36.56 67.34 67.47 53.01 0.02 MgO 10.58 8.29 0.57 1.25 0.45 0.07 SO<sub>3</sub> 0.04 0.01 0.47 0.21 0.02 0.09 S<sup>2-</sup> 1.07 1.05 K<sub>2</sub>O 1.37 0.27 0.41 1.25 0.12 0.18

0.12

0.11

Table III-9: Chemical composition of the raw materials used: HS = Blastfurnace slag; KA = White cement clinker; KB = Portland cement clinker; N = Limestone; A = Metakaolin; data in mass %

were also determined on standard mortar prisms under standard conditions (20  $^{\circ}$ C / 65% rel. h.) at the age of 28, 42, 56, 84, 119, 208 and 393 days pursuant to Issue 422 of the DAfStb.

0.38

Na<sub>2</sub>O

0.41

**Fig. III-19** to **Fig. III-22** display the standard mortar compressive strengths and the carbonation depths of the investigated blast-furnace cements. The blastfurnace cements without limestone (N) displayed almost the same compressive strengths as those with 5 mass % limestone (N) at the same age and are therefore not represented.

#### **Compressive strength**

As shown in Figures III-19 and III-20, the blastfurnace cements with blastfurnace slag HS 2 with the lower aluminate and higher silicon content (HOZ 2 and 4) generally displayed lower compressive strengths than the blastfurnace cements with blastfurnace slag HS 1 with the higher aluminate and lower silicon content (HOZ 1 and 3), regardless of the clinker (KA or KB).

As indicated in Fig. III-19, the addition of the aluminium-containing additive metakaolin (A), in particular for the low-performance blastfurnace cement HOZ 2, led to an increase of the 2-day compressive strength of about 50 % and by about 20 % for the high-performance blastfurnace cement HOZ 1. The compressive strength was also higher at the age of 7 days. The addition of 5 mass % calcium hydroxide (C) had no significant impact on the compressive strength of blastfurnace cements HOZ 1 and HOZ 2.

0.01

0.06

The addition of 5 mass % silica fume (S) effected an increase of the 2-day compressive strength of around 20 % and a slightly higher compressive strength at the age of 28 (HOZ 2) and 91 days (HOZ 1 and 2).

As shown in Fig. III-20, the addition of the aluminium-containing additive metakaolin (A), in particular for the high-performance cement HOZ 3, effected an increase in the compressive strength at the age of 7 to 91 days. The compressive strength only increased slightly at the age of 7 days for the low-performance blastfurnace cement HOZ 4.

The addition of 5 mass % calcium hydroxide (C) had no significant impact on the compressive strength of blastfurnace cements HOZ 3 and HOZ 4, regardless of the blastfurnace slag.

The addition of 5 mass % silica fume (S) effected a slight increase of the 91-day compressive strength of blastfurnace cement HOZ 3 and an increase of the 28 and 91-day compressive strength of the blastfurnace cement HOZ 4.



Fig. III-19: Standard mortar compressive strengths pursuant to DIN EN 196-1 of the blastfurnace cements from clinker KA with blastfurnace slag HS 1 and HS 2 and with 5 mass % additive (N = Limestone, A = Metakaolin, C = Calcium hydroxide, S = Silica fume)



Fig. III-20: Standard mortar compressive strengths pursuant to DIN EN 196-1 of the blastfurnace cements from clinker KB with blastfurnace slag HS 1 and HS 2 and with 5 mass % additive (N = Limestone, A = Metakaolin, C = Calcium hydroxide, S = Silica fume)

#### Carbonation

Apart from the generally higher compressive strength, the blastfurnace cements with blastfurnace slag HS 1 (HOZ 1 and HOZ 3) also displayed a considerably higher carbonation resistance compared to the blastfurnace cements with blastfurnace slag HS 2 (HOZ 2 and 4) (see Fig.s III-21 and III-22).

As indicated in Fig. III-21, the addition of 5 mass % metakaolin (A) led to a slight increase in carbonation resistance up to 56 days for the blastfurnace cement HOZ 1 and up to 119 days for blastfurnace cement HOZ 2.

The addition of 5 mass % calcium hydroxide (C) effected an increase in the carbonation resistance of blastfurnace cement HOZ 1 up to 208 days and up to 393 days for blastfurnace cement HOZ 2. The addition of 5 mass % silica fume (S) most effectively increased the carbonation resistance of blastfurnace cement HOZ 2. In contrast, no significant differences were detected in the carbonation resistance of blastfurnace cement HOZ 1.

Fig. III-22 indicates that the additives metakaolin (A), calcium hydroxide (C) and silica fume (S) always tendentially increased the carbonation resistance of blastfurnace cement HOZ 3. Depending on the storage period, the addition of 5 mass % metakaolin (A) had no significant impact on the carbonation behaviour of blastfurnace cement HOZ 4. Whereas a slight increased carbonation resistance of samples produced with HOZ 4 was detected on adding calcium hydroxide (C) and silica fume (S).



Fig. III-21: Carbonation depths of the blastfurnace cements from clinker KA with blastfurnace slag HS 1 and HS 2 and with 5 mass % additive (N = Limestone, A = Metakaolin, C = Calcium hydroxide, S = Silica fume) when stored under standard conditions





# IV

### **Quality surveillance and quality assurance of cement**



#### VDZ' s quality surveillance organisation

The testing, inspection and certification of cement and cement-type binders are part of the traditional core competencies of the VDZ. The association has been contributing to the fulfilment of the protection objectives of the Construction Products Directive and their national implementation as well as the Federal State Building Codes for many decades. The related activities are executed by the testing, inspection and certification body (PÜZ body) in the quality assurance and analytics department of the Research Institute of the Cement Industry. The results of the third party inspection are discussed twice a year in the technical committee of the VDZ supervisory association.

Binders, whose conformity with the requirements of a harmonised European standard has been proven, are identified with the CE sign. They may then be freely traded in all of the states of the European Economic Area. These days, almost all the binders in Germany have the CE sign. This relates, in particular, to all cements according to EN 197-1, including those with the additional property of low hydration heat LH and all masonry cements according to EN 413-1. Cements with high sulphate resistance and a low effective alkali content also meet the requirements of common cements and are currently covered by national standards, DIN 1164-10 in Germany. As cements with high sulphate resistance will be regulated in the harmonised European standard EN 197-1 in the future, DIN 1164-10 will only deal with cements with low effective alkali content from 2013. Hydraulic road binders are currently regulated in DIN 18506 in Germany. A European standard series EN 13282 is also in progress for these binders.

#### Approval and accreditation

The testing, inspection and certification body in the Research Institute of the Cement Industry has been active in the legislated area for many years. It is notified according to the German Construction Products Law (BauPG), which implements the EU Construction Products Directive, and administered by the European Commission as notified body no. 0840 until the final inception of the Construction Products Regulation. In addition, the testing, inspection and certification body is also recognised nationally according to the applicable Federal State Building Codes (LBO).

The recognition of the testing, inspection and certification body by the German InTable IV-1: Approval areas of the testing, inspection and certification body for construction products

ducts			
Construction products	Technical regulation(s)	Confo attestati	ormity on level
1		BPG	LBO
Binders			
Common cement	EN 197-1	1+	
Cement with special properties	EN 197-1	1+	
	EN 14216	1+	
	DIN 1164-10, -11, -12		ÜZ
Calcium aluminate cement	EN 14647	1+	
Masonry cement	EN 413-1	1+	
Hydraulic road binder	DIN 18506		(ÜZ) <sup>1)</sup>
Building lime	EN 459-1	2	
Other cement-type binders	Approval 2)		ÜΖ
(incl. sprayed concrete cements)			
Concrete additions			
Pigments	EN 12878	2+	
Fly ash	EN 450-1	1+	
Silica fume	EN 13263-1	1+	
Ground granulated blastfurnace slag	EN 15167-1	1+	
Natural pozzolana (trass)	DIN 51043		ÜZ
Other concrete additions	Approval <sup>2)</sup>		ÜΖ
Concrete admixtures			
	EN 934-2, -3, -4	2+	
	DIN V 18998		ÜHP
	Approval <sup>2)</sup>		ÜΖ
Aggregates			
	EN 12620	2+	
	EN 13055-1	2+	
	EN 13139	2+	
Masonry mortar			
	EN 998-2	2+	
Grout			
	EN 447		ÜZ
Concrete according to properties	EN 206-1/		
Concrete according to composition	DIN 1045-2		ÜZ
	rmity certificate from approved co rmity declaration by the manufact		

ÜHP: Conformity declaration by the manufacturer after the construction product has been tested by a approved testing laboratory

 $^{1)}\,$  Not relevant in building authority terms, attestation level conforms to  $\ddot{U}Z$ 

<sup>2)</sup> If the production process, the composition or the properties deviate substantially from the standard

stitute for Building Technology (DIBt) as the responsible building supervisory authority (Table IV-1) extends, in particular, to cements and cement-type binders. Furthermore, the recognition also applies for concrete additions and admixtures, aggregates and cementitious mixtures (e.g. masonry mortar). It relates to both standardised products as well as those permitted by the building inspectorate.

The new Construction Products Regulation (CPR) will finally enter into force on 01.07.2013 and replace the current European Construction Products Directive. Bodies that wish to operate according to the Construction Products Regulation (CPR) with regard to the evaluation and inspection of performance consistency must apply for relevant notification with the national recognition authority. This also applies for all bodies that currently operate according to the Construction Products Directive.

In the future, the accreditation of the bodies will be a requirement for their notification, at least in the harmonised area. Product certification bodies and certification bodies for factory production control must be accredited according to EN 45011 and testing laboratories according to EN ISO / IEC 17025. This new regulation affects 234 notified bodies in Germany, which operate in the harmonised testing and certification of construction products area or corresponding factory production control.

Binder	Standard / Regulation	Scope	Type of certification	Certification body	Inspection body	Number of binders	Number of works
	EN 197-1	EU					
	DIN 1164	Germany		PÜZ body <sup>1)</sup>	PÜZ body1)	577 <sup>2)</sup>	58
	Approval	Germany	Statutory			577	50
	TL Technical-StB (rein- forced concrete)	Germany		-	PÜZ body1)	51	30
	BRL 2601, NEN 3550	The Netherlands		bmc	PÜZ body1)	123	26
Cement	TRA 600, PTV 603 NBN B 12	Belgium	Under	PÜZ body1)	PÜZ body <sup>1)</sup>	50	18
	NF regulation	France	private law	AFNOR	PÜZ body1)	44	15
	DS/INF 135	Denmark		Dancert	PÜZ body1)	10	7
Maganwi	EN 413	Germany	Statutory	PÜZ body1)	PÜZ body1)	15	12
Masonry cement	BRL 2601	The Netherlands	Under private law	bmc	PÜZ body <sup>1)</sup>	5	4
Hydraulic road binder	DIN 18506	Germany	Statutory	$P \ddot{U} Z \ body^{1)}$	PÜZ body <sup>1)</sup>	17	17

Table IV-2: Overview of the cements and hydraulic binders certified and inspected by the testing, inspection and certification body in 2011

<sup>1)</sup> [Translator comment] PÜZ body = Testing, inspection and certification body

<sup>2)</sup> These figures include 105 multiple certificates for identical cements and 31 cements approved by the building authorities.



spected by the third party testing, inspection and certification body



Fig. IV-2: Average number of inspected binders per work for the works inspected by the testing, inspection and certification body

The testing, inspection and certification body, including the VDZ laboratories have been accredited since 2002. A re-accreditation and accreditation extension was initiated in 2011. The relevant audits by the German Accreditation Body DAkkS were successful and a renewed accreditation was announced in 2012. The key requirement for the future notification of the testing, inspection and certification body according to the Construction Products Regulation has therefore been established.

#### Third party inspection of cement according to the statutory regulations

**Table IV-2** provides an overview of the cements and hydraulic binders certified and inspected by the testing, inspection and certification body in 2011. 609 binders and 58 works were certified and inspected according to the statutory provisions, this included 577 cements, of which 9 cements were from 5 foreign works. Multiple certificates for identical cements were issued for 105 of the 577 cements, i.e. both EC conformity certificates according to EN 197-1 as well as conformity certificates according to DIN 1164-10.

The number of investigated binders remained almost unchanged compared to 2008 (**Fig. IV-1**). However, the average number of investigated binders per work has increased over the past 30 years and is now at about 8.6 binders per work (**Fig. IV-2**).

Furthermore, 51 cements approved for use for concrete paving were investigated in 2011. The testing, inspection and certification body also investigated 15 plastering and masonry binders according to EN 413-1 as well as 17 hydraulic road binders according to DIN 18506.

Table IV-3 summarises the number of certificates (without multiple certificates for identical cements) and the relevant domestic dispatching quantities in 2011 compared to 2008 (value in brackets) for the domestic cements inspected by the testing, inspection and certification body. The cements were generally assigned to the main cement types CEM I, CEM II, CEM III, CEM IV and CEM V and to strength classes 32,5, 42,5 and 52,5. The table indicates that the number of cements in strength class 32,5 has reduced, while the number in strength class 52,5 has increased. The reason for this is that, in the past few years, a series of cements in classes 32,5 R and 42,5 R were reassigned to the next higher strength class 42,5 N and 52,5 N.

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Table IV of Admissi of domestic control in appendix sy the costing, inspection and certainention souly in 2017 (2006)																	
Cement			Number of cements					Share of cement dispatch (domestic) in mass %									
		3	2.5	4	2.5	5	2.5	Т	otal	3	2.5	4	2.5	5	2.5	Т	otal
Portland cement	CEM I	28	(36)	78	(78)	80	(61)	186	(175)	5.6	(5.6)	16.6	(16.6)	8.0	(8.0)	30.2	(30.2)
Portland composite cement	CEM II	56	(64)	82	(71)	33	(32)	171	(167)	24.3	(24.3)	20.0	(20.0)	4.8	(4.8)	49.1	(49.1)
Blastfurnace cement	CEM III	49	(56)	46	(44)	6	(8)	101	(108)	7.0	(7.0)	13.4	(13.4)	0.3	(0.3)	20.7	(20.7)
Pozzolanic cement	CEM IV	3	(3)	-	(-)	-	(-)	3	(3)	0.0	(0.0)	-	(-)	-	(-)	0.0	(0.0)
Composite cement	CEM V	-	(-)	-	(-)	1	(1)	1	(1)	-	(-)	-	(-)	0.0	(0.0)	0.0	(0.0)
Total		136	(159)	206	(193)	120	(102)	462	(454)	36.9	(36.9)	50.0	50.0	13.1	(13.1)	100.0	(100.0)
Cements with high eastrength (R)	arly	78	(95)	84	(103)	61	(54)	223	(252)	29.5	(29.5)	26.0	(26.0)	9.0	(9.0)	64.5	(64.5)
Cements with normal strength (N/L)	l early	58	(64)	122	(90)	59	(48)	239	(202)	7.4	(7.4)	24.0	(24.0)	4.1	(4.1)	35.5	(35.5)
Cements with special ties (LH, HS, NA)	l proper-	46	(46)	51	(48)	13	(7)	110	(101)				No	o data			

Table IV-3: Number of domestic cements inspected by the testing, inspection and certification body in 2011 (2008)





The fall in the dispatching quantities of Portland cements, already observed in previous years, has continued and the fraction of blastfurnace cements in domestic dispatching has increased. **Fig. IV-3** illustrates the changes in the domestic dispatching of various cements. The table displays the fraction of cement types and strength classes dispatched domestically in 2011 as well as 2000 (by way of comparison). The fraction of cements in strength class 32,5 has decreased to 26.1 %. At the same time, the fraction of cements in the higher strength classes has risen accordingly.

A similar shift can be seen in the cement types. The dispatching quantity fraction of Portland cements has reduced considerably as part of the increased efforts to reduce  $CO_2$  emissions. The fraction of Port-

land cements has almost halved since 2000 and now lies at 31.6%. At the same time, the fraction of CEM II cements has increased from 23.6% to 45.7% in absolute terms. The dispatching quantity fraction of CEM III cements has also increased.

### Third party inspection of cements according to voluntary regulations

Bilateral agreements on the mutual recognition of testing, inspection and certification activities have existed between the testing, inspection and certification body and the corresponding Belgian, Danish, French, Dutch and Russian bodies for many years. This relates to third party inspections according to national legislation that exceed the requirements of EN 197. The testing, inspection and certification body performs the required supplementary tests and inspections for German producers in coordination with the foreign bodies. This reduces the additional expense for the cement producer by a considerable amount.

In 2011 the testing, inspection and certification body inspected 123 cements and 5 masonry cements from 26 works according to the Dutch evaluation criteria (BVL 2601) (cf. Table IV-2). The testing, inspection and certification body also certified and inspected 50 cements from 18 works according to Belgian regulations, which entitled the works to use the Belgian BENOR label. 44 cements and 15 production plants were tested and inspected according to a French regulation in order to receive the NF label. In 2011, 10 cements from 7 works were inspected according to Danish regulations in order to receive the Dancert certificate according to DS/INF 135.

#### Other construction products

The testing, inspection and certification of cements and cement-type binders remains the focus of the testing, inspection and certification body's activities. However, their competency continued to expand over previous years and now also includes numerous construction products.

For example, the factory production control of various pigment producers has been certified and inspected since the building inspectorate's introduction of the pigment standard EN 12878 in 2006. In 2006, this affected the production of 65 different pigments.

The testing, inspection and certification of ground granulated blast furnace slag according to EN 15167-1 started in 2008. The

testing, inspection and certification body currently inspects three ground granulated blast furnace slags.

#### **Comparative tests**

The European standard 197-2 for the conformity evaluation of cement requires that the testing bodies assigned to perform the inspection tests participate in regular comparative tests. The obligation to regularly participate in comparative tests also arose following the accreditation of the test laboratories of the Research Institute of the Cement Industry according to EN ISO/IEC 17025. The testing, inspection and certification body has been regularly participating in various interlaboratory tests for many years. In particular, the standard tests for cement are compared several times a year at both a national and international level.

For example, a Dutch body organises weekly comparative tests with a reference cement that is evaluated on a quarterly basis. The results are discussed at annual meetings of representatives of the participating third party inspection bodies. Furthermore, the results of the weekly reference cement tests are documented in a quality control chart in order to be able to rapidly identify and respond to any fluctuations.

In addition the Research Institute of the Cement Industry participates in the annual cement comparative tests of the Association Technique de l'Industrie des Liants Hydrauliques (ATILH), in which about 180 testing laboratories from 37 countries participate.

In addition to these international interlaboratory tests, comparative tests are also performed on cements and other building materials, such as fly ash and concrete admixtures, at a national level.

#### **Test laboratory**

Around 3 700 binder samples are tested annually in the laboratories of the Research Institute of the Cement Industry in connection with the third party testing and associated contract and comparative tests. This relates to about 44000 tests for an average of twelve properties to be tested. This high sample throughput requires efficient processes in the laboratories. On the other hand, a consistently high level of testing and high testing quality must also be ensured. This is achieved by a high level of standardisation of the processes and constant training. The competency of the testing laboratories is constantly verified by comparative tests and accreditation.

System	Conformity attestation	Tasks of the notified body	Binder
1+	Certification by the	Third party inspection with testing spot samples	Cement <sup>1)</sup> PM binders
1	certification body	Third party inspection without testing spot samples	-
2+	Declaration of	Initial inspection and continuous surveillance	Road binder, building lime
3	conformity by manufacturer	Initial testing	-
4	munulacturer	_	_

Table IV-4: Systems for conformity attestation according to the Construction Products Directive

<sup>1)</sup> Common cement, cements with special properties, special binders

#### Quality assurance

Common cements that have been issued the CE label have been able to be circulated on the European internal market without restriction since April 2001. These cements are inspected pursuant to the European harmonised standard EN 197-2 "Conformity Evaluation". In addition, the CEN report CEN/CR 14245 contains guidelines for the application of EN 197-2. The European sector group 02 of the Notified Bodies has also prepared various proposition papers with additional information. The CEN report, published as DIN technical report 197 in the German version, and the position papers enable a uniform application of the inspection standard by the various bodies in Europe. These experiences have been extremely positive over the past few years.

#### Proof of conformity according to the EU Construction Products Directive

The conformity verification process for the various building materials are specified by the European standardisation organisation CEN in associated harmonised standards. Four systems of conformity certification are defined in the Construction Products Directive (**Table IV-4**). For all these systems the producer is responsible for operating an internal production control. The difference between the systems is based on the degree of integration with an independent external body in the conformity verification.

The recognised body inspects either the factory production control (system 2+) or performs an initial test of the products (system 3). System 4 does not provide for the integration of a recognised body. Regular third party inspection tests only take place in the event of product certification accord-

ing to system 1+. This is only required for a few building materials, for example, for common cements, cements with special properties and special binders, as they are particularly important for stability. System 2+ is provided for hydraulic road binders, for which the factory production control is inspected by a notified body.

In contrast to many other related European directives, the Construction Products Directive does not contain any direct product requirements. Rather, European harmonised product standards and European technical permits apply in this regard.

The relevant standards specify the required producer verification including the tests to be performed together with the testing frequencies and processes. The extent of the tests to be performed for the factory production controls has increased for many building materials following the introduction of harmonised standards.

The conformity of cement is evaluated according to inspection standard EN 197-2. The standard has proven itself in practice and is therefore also the template for corresponding determinations for concrete additions such as fly ash, silica fume and blastfurnace slag.

#### **Construction Products Regulation**

The EU Construction Products Directive 89/106/EEC was published in 1988 as one of 26 directives according to the so-called "New Approach". The goal was to dismantle trade barriers in the EU. In May 2008, the European Commission submitted the first proposal for revising this directive. Barely three years later, on 04.04.2011, the Construction Products Regulation (BauP-VO) was published as the successor regulation for the Construction Products Directive. Parts of the regulation have already been in force since 24.04.2011. The full regulation enters into force on 01.07.2013 and replaces the Construction Products Directive, which will remain applicable until then.

The Construction Products Regulation describes the duties of all the economic operators involved in the supply and distribution chain, i.e. producers, representatives and importers. For example, in the future, they will be responsible for the preparation of a declaration of performance as a description of the assured properties and as a requirement for the CE label. Furthermore, the Construction Products Regulation redefines the requirements of the notified bodies. It also contains regulations on the European technical evaluation process and market inspection. Some terms will also change. For example, the current "Conformity evaluation" term will be replaced by "assessment and verification of constancy of performance".

Another important innovation in the Construction Products Regulation is the extension of the basic requirements of structures with regard to the "sustainable use of natural resources". It is not yet clear how this new basic requirement will be specified in the standards and regulations.

### Restructuring of the European accreditation system

The European regulation (EC) no. 765/2008 on the requirements for accreditation and market inspection was released in August 2008. The regulation became effective on 01.01.2010 and necessitated the realignment of the German accreditation system.

Germany has many certification bodies and laboratories that provide various services. In the past there were five private accreditation bodies for evaluating the competence and qualifications of these bodies. They had different areas of expertise and activities, such as the accreditation of laboratories, testing and certification bodies for various products and certification bodies for management systems. There were also nine federal and four state bodies in the legislated area (recognition authorities).

As a result of the European regulation, a single German accreditation body had to be established by 01.01.2010. An accreditation law was therefore enacted in Germany, which provided for an accreditation organisation that was equally supported by the federal government, the states and industry. The Deutsche Akkreditierungsstelle GmbH, DAkkS for short, was authorised

in the form of a pledge by the public authorities and is responsible for all accreditations within the scope of the 26 directives of the New Approach in Germany.

#### Market inspection

The above-mentioned European regulation on the provisions for accreditation and market inspection obliges the EU member states to participate in a new and uniform market inspection organisation. The focus is on the introduction of national market inspection programs. In Germany, the responsibility for the implementation of the market inspection lies with the federal state authorities and the German Institute for Building Technology (DIBt). In the future, these may perform both scheduled as well as random sample tests. In general, this initially investigates whether construction products meet the formal requirements (administrative verification with regard to identification, etc.). However, physical and/or chemical product tests may also take place.

### Cooperation between the notified bodies

Europe has several hundred notified bodies that originate from areas with different traditions and experiences. It is therefore important that the standards and regulations are designed and applied in a harmonised manner. The Construction Products Directive and the Construction Products Regulation prescribe the regular participation of notified bodies in an exchange of experiences as a key requirement for the notification.

In accordance with the provisions of the EU commission, the notified bodies organise this cooperation amongst themselves. Both horizontal as well as sectoral European committees exist. As there are a large number of notified bodies operating in Germany, the activities are also reflected at a national level.

As has been the case in previous reporting periods, the testing, inspection and certification body once again regularly participated in the exchange of experiences, both within the relevant European as well as the national committees. This enabled the body to make significant contributions to the position papers for cement, fly ash, silica fume and blastfurnace slag, etc.

### Certification of management systems

Some companies in the cement and building materials industry operate factory production control management systems over and above what is required by law. In the past years there has been a clear trend towards integrated management systems that cover the specific requirements with regard to quality (EN ISO 9001), the environment (EN ISO 14001), energy (EN 16001 and EN ISO 50001) as well as occupational health and safety protection (OHSAS 18001) (Fig. IV-4). Product and system certification can be jointly evaluated, even if they differ as regards content. The product certifier operates in the legislated area and controls the fulfilment of the formal standard provisions. Management systems have the strong character of a management tool. The system certifier operates under private law and audits the system selected independently by the producer on a random sample basis and in dialogue with the producer.

The Research Institute of the Cement Industry has operated a certification body for management systems (FIZ-Zert) since 1996. This was accredited for the certification of quality management systems in 1998. The accreditation according to EN ISO/IEC 17021 has been constantly expanded over the past years and now also includes the certification of environmental management systems, energy management systems and occupational health and safety management systems. For FIZ-Zert customers, this provides synergies for the joint certification of various management systems, factory production controls and the produced products.

 $CO_2$  emissions trading is extremely important for the companies in the cement industry. All cement works with clinker production have had to verify their  $CO_2$  emissions pursuant to the greenhouse gas emissions trading law (TEHG) since 2004. FIZ-Zert has also verified the  $CO_2$  emissions of cement works, as well as lime works to some extent, since then. Several Research Institute employees are publically appointed as experts in their relevant fields in this regard.

#### Standardisation

Uniform and binding regulations are important to be able to ensure the quality of cement as a building material and hence the safety and durability of structures. Efforts to define minimum standards and specify uniform test processes have been around for over 130 years.

The first cement standard was completed in 1878 and published in the "Ministerial paper for internal administration in the Royal Prussian states" on 15.01.1879. It was certainly one of the world's first stand-





ards for industrial products and it had the charm of being only four pages long. In addition, it not only contained the product requirements but also the description of the relevant test processes. These days we obviously smile at some of the verbalisations. The statement "60 kg was found to be a suitable weight for the uniform introduction of 1 bag as this weight can be transported with ease" certainly no longer applies from the perspective of modern occupational health and safety protection. However, many of the regulations specified at the time remain valid. For example, the strength test is still performed "with 3 parts by weight of common sand to 1 part by weight of cement after a 28 day hardening period". Uniform apparatus and standard forms were recommended to produce the test specimens, "in order to ensure the complete consistency of the tests". A modern standard could not express this any better.

### Revision of EN 197-1 and DIN 1164-10

The European Standardisation Committee CEN / TC 51 "Cement and building lime" continued the tradition of early cement standardisation and introduced the first harmonised European standard for a construction product with EN 197-1 "Composition, specifications and conformity criteria for common cement". The standard has been expanded several times since its introduction in 2000. The A1 amendment (2004) regulated LH cements with low heat of hydration. Regulations on the use of fly ash as a main constituent of cement were modified in the A3 amendment (2007). The proposed amendment prA2 (2006) regulated SR cements with high sulphate resistance, but did not become effective.

In addition, the standard EN 197-4 "Composition, specifications and conformity criteria for low early strength blastfurnace cements" was published in 2004. The proposed amendment 197-4/prA1 (2006) with regulations on CEM III-LH/SR did not become effective.

All extensions and EN 197-4 should have been implemented in the revision of EN 197-1 performed in previous years. However, the compromise for cements with high sulphate resistance (so-called SR cements - "sulphate resisting common cements") reached throughout Europe was not able to reflect all of the requirements of the EU member states. Many countries therefore insisted on maintaining their relevant national regulations. However, this contradicts the provisions of the European Commission. As the new 197-1 represents almost 90% of the SR cements traded in the EU, after lengthy negotiations, the Commission ultimately agreed to both the amendment of EN 197-1 and the continuance of the currently applicable national SR regulations.

Together with the 27 common cements, EN 197-1 now also regulates 7 SR cements: Portland cements with 3 different  $C_3A$  contents, blastfurnace cements with at least 66 mass % blastfurnace slag and CEM IV cements. Nationally approved cements that are not considered are listed in Annex A of the standard. They may not be identified as SR but may continue to be used.

Apart from the SR cements, blastfurnace cements with low early strength, so-called L cements (previously regulated in EN 197-4), were also included in the standard. It did not include any significant technical changes. The regulations for the various cement types have now been harmonised throughout Europe, with the exception of the NA cements (low alkali content).

The requirements for cement additives were also revised during the revision in order to satisfy the requirements for the drinking water area. The cements produced in Germany had already fulfilled these criteria in the past.

The new version of EN 197-1 was published in September 2011 in the Official Journal of the European Union while the German version DIN EN 197-1 was published in November 2011. The old version can continue to be applied within the coexistence period of 21 months, until the end of June 2013, however the new DIN EN 197-1 will apply exclusively after this period.

As SR cements will be regulated in EN 197-1 in the future, and contrary national standards will have to be repealed, this also necessitates a revision of DIN 1164-10 "Cement with special properties – part 10: Compositions, specifications and attestation of conformity of common cement with special characteristics". The new DIN 1164-10 should then only contain regulations on NA cements (with low active alkali content) and no longer include HS cements.

The draft of the standard was published with the new title "Cement with special properties – part 10: Composition, specifications and attestation of conformity of common cements with low active alkali content" (publication date 27.02.2012). The completion of the standard is planned for 2013.

#### **Revision of EN 197-2**

At the end of 2010 the responsible European Standardisation Committee CEN/TC 51 decided to revise the then 10-year-old EN 197-2. As experiences with this stand-

ard are extremely positive, essentially only necessary clarifications and a small number of larger changes will be made. These include:

- Instructions with regard to measuring uncertainty when evaluating test results
- The process in the event of non-conformity of the factory production control
- The requirements for dispatching centres
- Numerical criteria for the evaluation process of alumina cement according to EN 14547
- A reference to the connection between EN 197-2 and the annexes ZA of the European product standards
- An image in which the cement certification process in a new work, or the certification of a new type of cement in an existing work by a third party, is described

The guidelines for the application of the standard are expected to be revised parallel to the revision of EN 197-2. In Germany this affects the DIN technical report 197.

#### Hydraulic road binders

Hydraulic road binders have previously been regulated in DIN 18506 in Germany. CEN/ TC 51/WG 14 has been working on three related draft standards for several years. EN 13282 part 1 is expected to regulate rapid hardening hydraulic road binders, while part 2 regulates normal hardening hydraulic road binders. Part 3 contains conformity evaluation regulations.

The rapid hardening hydraulic road binders generally correspond to the base and road binders according to DIN 18506. However, a more varied composition with various components is possible for normal hardening hydraulic road binders. These binders may also contain considerably higher fractions of burnt lime (CaO). As these mixtures cannot necessarily be characterised with the usual test methods, the standard provides a slaking procedure for the lime component prior to actual testing.

#### **Test procedures**

The test standards are also revised and updated at regular intervals in parallel with the product standards. **Table IV-5** provides an overview of the current state of the EN 196 series of test methods. The performance-test methods that will be developed together with the Standardisation Committee CEN/TC 104 "Concrete and associated products" are not included in this representation.

DIN EN 196 Part	Content	Valid version	Corresponding ISO standards	
1	Strength	2005	ISO 679	
2	Chemical analysis	2005	ISO 29581-1	
3	Setting, soundness	2009	ISO 9597	
(4) 1)	Composition	2007	-	
5	Pozzolanicity	2011	ISO 863	
6	Fineness	2010	-	
7	Sampling	2008	-	
8,9	Heat of hydration	2010	ISO/DIS 29582-1/-2	
10	Water-soluble chromate	2006	-	

<sup>1)</sup> Published as CEN report CEN/TR 196-4



Fig. IV-5: Possible composition of CEM X

The test standards to determine the setting times and the soundness according to EN 196-3, to determine the pozzolanicity of pozzolanic cements according to EN 196-5, to determine the fineness according to EN 196-6 and to determine the heat of hydration according to EN 196-8 and EN 196-9 have been developed since 2009.

#### **Other binders**

A series of standards and draft standards have been developed for special cements

and special binders in the past years. Based on these developments, binders that could previously only be used either regionally or for special areas of application may now be used. Examples include cements with extremely low hydration heat, which may be used for mass concrete and alumina cements that may be used for special applications, e.g. as repair mortar. Other standardised binders are masonry cements sulphate slag cements and hydraulic binders for non-load bearing applications.

Standard no.	Cement / Binder	Type of cer	ment / binder	Strength class	Additional	Status
Standard IIO.	Cement / Dilidei	Number	Number Designation		classes	Status
EN 197-1	Common cements	27 (34 in new version)	CEM I CEM II CEM III CEM IV	32,5 N/R 42,5 N/R 52,5 N/R	_	2000, new ver- sion published in 2011 but not yet introduced under construction law
A1	Common cements with low heat of hydration		CEM V		LH ( $\leq 270 \text{ J/g}$ )	2004
prA2	Sulphate resisting common cement		CEM I CEM III/B and /C CEM IV		SR 0, SR 3, SR 5 SR S SR P	2008, did not ente into force
A3	Fly ash as cement constituent					2007
EN 197-4	Low early strength blastfurnace cement	3	CEM III	32,5 L 42,5 L 52,5 L	LH (≤ 270 J/g)	2004
prA1	Sulphate resisting blastfurnace cement					2008, did not ente into force
Open	Cement with increased quantities of blastfurnace slag and limestone or fly ash		CEM X			Standardisation process introduced in 2012
EN 14216	Cements with very low heat of hydration	6	VLH III/B and /C VLH IV VLH V	22.5	VLH (≤ 220 J/g)	2004, revision intro duced in 2012
EN 14647	Calcium aluminate cement	1	CAC	40	-	2005
EN 15743	Supersulfated cement	1	CSS	30 40 50	-	2010
prEN 13282-1 prEN 13282-2	Hydraulic road binder	2 <sup>1)</sup>	HRB	N 1 E 2 N 2 E 3 N 3 E 4 N 4	RS <sup>2)</sup>	CEN enquiry initi ated in 2012
EN 413-1	Masonry cement	1	МС	5 12.5 22.5	X (without AE agents)	2011
EN 15368	Hydraulic binders for non-structural applications	1	НВ	1.5 3.0	-	2008
A1	Hydraulic binders for non-structural applications	1	HB	1.5 3.0	-	2010 (Annex ZA was expanded)

#### Table IV-6: Existing and planned European product standards for cements and other hydraulic binders

<sup>1)</sup> Declaration of composition within given limits
<sup>2)</sup> RS = rapid setting
Contained in new EN 197-1

**Table IV-6** provides a summary of the current state of existing and planned product standards for cements and other hydraulic binders.

#### CEM X

In light of the great challenges faced by the cement industry with regard to the reduction of  $CO_2$  emissions in cement production, in the past few years the focus of the

standardisation activities has shifted to new cements with reduced clinker content. A corresponding standardisation project is focusing on ternary cements with the main constituents clinker, limestone and blastfurnace slag or natural pozzolana or siliceous fly ash as the third main constituent. The fraction of the main constituents besides clinker exceed the current limits of EN 197-1 (**Fig. IV-5**). As the field of application of these cements has not yet been determined, they have been referred to as CEM X in the current standardisation process. The European task force CEN/TC 51/ WG 6 will submit proposals for the standard composition limits, the designation of the cements and the standard itself (e.g. EN 197-1 or 197-5) in the near future based on the results of laboratory investigations compiled in previous years.

## **Concrete raw materials and technology, concrete construction technology**



B15n between Schierling and Neufahrn: Concrete surfacing of the first 22 km construction section

### Cements with several main constituents

### Carbonation of blastfurnace cement concretes

In laboratory tests, blastfurnace cement concretes displayed higher carbonation depths compared to Portland cement concretes, even if investigations on reinforced concrete and prestressed concrete structures, produced with concretes of different strength classes and various compositions, have to date generally not revealed any considerable impact of the cement type on the carbonation behaviour for structures exposed to weathering outdoors. The properties of blastfurnace cements and the characteristic durability features of the concretes produced as a result were therefore included in service life calculations. Updated probabilistic calculations of the carbonation progress in concretes with cements rich in blastfurnace slag display a considerably higher carbonation depth and therefore a potentially earlier depassivation of the reinforcing steel, resulting in the conditions for corrosive damage. Fig. V-1 shows an example of the development of the reliability index of a reinforced concrete with common concrete covering for a concrete with CEM I cement (Portland cement) and a concrete with CEM III/B cement (blastfurnace cement). The reliability index is a measure of the probability that exposure of the reinforced concrete is still passivated after the observation period.

This displays the unfavourable behaviour for a concrete produced with a CEM III/B compared to a concrete produced with a CEM I in the probabilistic service life calculation. These concretes still meet the durability requirements in common applications covered by standard DIN 1045-2, but may not be used in demanding structures as a result. This may lead to a weaker overall acceptance of cements containing blastfurance slag.

Earlier investigations in the Research Institute of the Cement Industry have shown that the formation of silicate hydrogels is already possible in the process of hydration in blastfurnace cements. These silicate hydrogels may result in the formation of porous silicates in the further development of the hydration, just as the formation of silicate hydrogel in the carbonation of calcium silicate hydrates in blastfurnace hardened cement paste. These porous silicates may encourage the intrusion of carbon dioxide into the blastfurnace hardened cement paste and deeper carbonation. The objective of a research project supported by the Federal Ministry of Education and Research (BMBF) as part of the tendering for "Nano-technology in the building trade - NanoTecture" was to impact the hydration of cements containing blastfurnace slag by the targeted application of secondary cement constituents/additives, e.g. in the form of reactive aluminium compounds, in order to affect the structure of hardened cement paste, mortar and concrete in the nano range. This impact aims to supply various reactive "external" additives and to enable the hydrating cement to, for example, form a sufficient amount of alumosilicates to reduce the formation of silicate hydrogels and to contribute to a more stable and dense structure. The research project recorded the impacts of the use of the above-mentioned additives on the concrete structure as well as on the strength and durability-related properties, such as the carbonation behaviour of the concrete. The causes and boundary conditions of the carbonation behaviour of blastfurnace cements and the carbonation processes in hardened cement paste structures will continue to be researched. Granulometric influences of the cements and their main constituents, as well as the impacts of the chemical-mineralogical blastfurnace slag properties, are to be observed in order to obtain an overall optimised concrete structure.

Investigations on the carbonation behaviour of blastfurnace concretes were performed based on the underlying experiments regarding the performance of the blastfurnace cements (cf. Chapter III). The CEM III/A and CEM III/B cements used were produced in the laboratory with a clinker-blastfurnace slag mass ratio of 50:50 and 20:80. In order to test the impacts of various additives, cements without additive and cements with 5 mass % additive were prepared by separate grinding and subsequent mixing. Aluminate (A) and limestone (N) were used as additives, while calcium hydroxide (C) was also used in tests. The majority of the tests were performed using clinker C, which corresponded to clinker KB in Chapter III with regard to its origin. Blastfurnace slags SI and SII had different compositions; higher performance was expected for blastfurnace slag SI than blastfurnace slag SII due to its higher aluminium oxide content. Blastfurnace slag SII had the same origin as blastfurnace slag HS1 in Chapter III. An overview of the main constituents and additives used is shown in Table V-1.



Fig. V-1: Reliability index for the passivation of the reinforcement in concrete with regard to an attack resulting from carbonation, depending on the exposure period for exposure class XC4 (typical external components) for nominal concrete cover of 40 m and a curing period of 3 days (calculations of the Research Institute of the Cement Industry)

Designat	ion	Fineness in cm <sup>2</sup> /g
	Clinker compo	nents
C5	CEM I 52,5 R	5510
C4	CEM I 42,5 R	3050
E5	CEM I 52,5 R	5 500
	Blastfurnace s	lags
SI 40	-	Approx. 4000
SII 40	-	Approx. 4000
SI 50	-	Approx. 5000
	Additives	
А	Aluminate	Condition at works
Ν	Limestone	Approx. 6700
С	Calcium hydroxide	Condition at works

Table V-1: Overview of the raw materials of blastfurnace cements

Concretes with the blastfurnace cements were produced and tested. The composition of the mixture is aligned towards the composition limit values and the concrete properties according to DIN technical report 100 "Concrete". This resulted in a concrete composition with a water-cement ratio w/c = 0.65 and a cement content c =  $260 \text{ kg/m}^3$ . Aggregates (Rhine sand and Rhine gravel from the inventories of the

Research Institute of the Cement Industry) with particle size composition A16/B16 according to DIN 1045-2, Annex L were used for the concrete production. The determination of the carbonation depth was carried out on concrete bars with dimensions of 100 mm x 100 mm x 500 mm. The 7-day preliminary storage (7 dVL) test specimens were stored in the humidity chamber for 1 day, underwater at  $(20 \pm 2)$  °C for 6 days (preliminary storage) and then at a temperature of  $(20 \pm 2)$  °C and a relative humidity of  $(65 \pm 5)$  % (main storage). The 28-day preliminary storage (28 dVL) test specimens were stored in the humidity chamber for 1 day, underwater at  $(20 \pm 2)$  °C for 27 days (preliminary storage) and then at a temperature of  $(20 \pm 2)$  °C and a relative humidity of  $(65 \pm 5)$  % (main storage). The carbonation depths were generally determined after 42, 91, 180 and 364 days.

Carbonation of CEM III/A concretes CEM III/A concretes that were produced based on cements with clinker C in combination with blastfurnace slag SI and SII were investigated. Fig. V-2 and V-3 show the development of the carbonation depth of the concretes in relation to the test age.

No significant differences of the carbonation depths, depending on the type of the additive used, were determined after 364 days on concretes that were preliminarily stored for 28 days.

Certain differences in carbonation depths were determined when using cements with blastfurnace slag SI when the concretes were preliminarily stored for 7 days. An approx. 1 mm lower carbonation depth was determined after 364 days when using additive A compared to the use of additive N. The compressive strengths of these concretes were between 37 and 40 N/mm<sup>2</sup>. No significant differences in the carbonation depths were determined when using the cements with blastfurnace slag SII. The compressive strengths of these concretes were between 37 and 39 N/mm<sup>2</sup>.

The duration of preliminary storage had a considerably higher impact on the test result after 364 days. Differences of up to 3 mm were determined after 364 days, depending on the preliminary storage period, when using cements with blastfurnace slag SI. However, when blastfurnace slag SII was used, the differences in carbonation depths reduced to about 1 mm.

Furthermore, the combination of the blastfurnace slag used and the corresponding fineness of the clinker had certain effects



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Fig. V-3: Carbonation of CEM III/A concretes  $(c = 260 \text{ kg/m}^3,$ w/c = 0.65) for a preliminary storage of 7 and 28 days using clinker C5 and blastfurnace slag SII 40 in the cement

Fig. V-2:

cement

28d V 150 200 250 300 350 400 Test age in days 10 Cement with 5 % limestone additive q O Cement with 5 % aluminate additive Cement with 5 % limestone additive 8 Cement with 5 % aluminate additive 7 7d VL 6 5

7d VL

ō



on the level of carbonation depth after 364 days. With preliminary storage of 28 days, the concretes based on blastfurnace slag SI (combined with the coarser clinker C4) achieved lower carbonation depths than when using blastfurnace slag SII (combined with finer clinker C5).

CEM III/A cements with blastfurnace slag SI and additive A were produced with separate and joint grinding in the tests. The

fineness of both cements was about 5,550 cm<sup>2</sup>/g. Their 28-day compressive strengths were about 70 N/mm<sup>2</sup>. The carbonation depth of the concrete produced with the separately ground cement was 6 mm after 364 days. The concrete based on the jointly ground cement had a carbonation depth of about 8 mm. The 28-day concrete compressive strengths were 49 N/mm<sup>2</sup> (separate) and 41 N/mm<sup>2</sup> (joint).



Fig. V-4: Carbonation of CEM III/B concretes (c = 260 kg/m<sup>3</sup>, w/c = 0.65) for a preliminary storage of 7 and 28 days using clinker C5 and blastfurnace slag SI 40 in the cement



Fig. V-5: Carbonation of CEM III/B concretes (c = 260 kg/m<sup>3</sup>, w/c = 0.65) for a preliminary storage of 7 and 28 days using clinker C5 and blastfurnace slag SII 50 in the cement

*Carbonation of CEM III/B concretes* Fig. V-4 and V-5 show the progress of the carbonation of the CEM III/B concretes, produced with cements containing clinker C in combination with blastfurnace slag SI and SII, in relation to the test age.

No significant effects on the carbonation depth of the concretes were determined depending on the type of additives used in the cement after 364 days. The carbonation depths were approx. 2 to 3 mm lower for concrete with a preliminary storage period of 28 days than for concretes with 7-day preliminary storage periods.

Carbonation depths were 2 to 3 mm higher when using the cements with blastfurnace slag SII in the concrete after 364 days than for concretes based on blastfurnace slag SI, although the blastfurnace slag SII was approx. 1,000 cm<sup>2</sup>/g finer than blastfurnace slag SI.

The concretes show compressive strengths between 30 and 32 N/mm<sup>2</sup> (cements with SI) and between 28 and 29 N/mm<sup>2</sup> (cements with SII) after preliminary storage of 7 days.

In addition to the previously presented scope of tests, investigations with CEM III/B cements and additive C were also carried out. At approx. 33 N/mm<sup>2</sup> (with SI) and 31 N/mm<sup>2</sup> (with SII), the concrete compressive strengths were slightly higher than for comparable concretes with additives A and N. The preliminary storage duration of the concrete had a lower impact on the carbonation depth after 364 days. Carbonation depths for concretes with 28 days of preliminary storage were 1 mm lower than for concretes with 7 days of preliminary storage. Compared to concretes with additives A and N, significant differences of approx. 1 to 2.5 mm were only determined when the cement based on blastfurnace slag SII and additive C was used. However, no significant differences were determined, depending on the type of additives used, for cements with blastfurnace slag SI.

Another addition was provided by the investigations with CEM III/B cement based on a clinker with a different origin and quality (clinker E). In particular, clinker E has a higher lime standard and a higher free lime content than clinker C. For cements produced based on clinker E, blastfurnace slag SI 40 and additives A and N, the compressive strengths of the concretes were approx. 36 and 34 N/mm<sup>2</sup> respectively. A carbonation depth 1 mm higher than comparable concretes with clinker C was recorded for concretes with clinker E after 364 days. Concretes with clinker E also did not show any clear differences depending on the type of additive used.

In summary, it can be determined that the observed effects fell short of expectations. However, the investigations of the carbonation resistance of mortar and concretes using optimised blastfurnace cements with 50, 60 and 80 mass % blastfurnace slag did show some positive effects. But the effects are generally not applicable to all cement compositions and clinker-blastfurnace slag combinations. Various additives - also depending on the cement composition - displayed different effects to the carbonation behaviour. A certain reduction of the carbonation sensitivity of blastfurnace cement concretes was observed - depending on the type and the fraction of constituents used and the test conditions (e.g. preliminary storage period). The calculated impact of the observed maximum differences in the carbonation depths on the development of the reliability index of a reinforced concrete component with common concrete covering must be reviewed.

#### Cements with higher limestone contents – strength development and durability Introduction

The use of cements with several main constituents has a long and successful tradition. Thus, the question regarding new types of cement and their application options arises. With regard to the, in part, limited availability of other main cement constituents, the focus then switches to the technical performance of cements with higher limestone contents.

The connection between the clinker content related to the compressive strength and the concrete compressive strength displayed in Fig. V-6 resulted from an evaluation of literature results in the Research Institute of the Cement Industry as well as internal investigation results. The specific clinker content, in this case related to the concrete compressive strength, reduces as the compressive strength increases. In the represented cases, with regard to the compressive strength, the clinker will be more effectively used when the compressive strength is higher. The reasons for this relationship are known: Reduction in the effective water-cement ratio, optimisation of the granulometry of the fines and the use of effective concrete admixtures.

### Potentials of limestone-containing cements

If, for example, the compressive strength in the range of  $40 \pm 5 \text{ N/mm}^2$  (see figure V-6) is analysed with regard to the composition of the main constituents, combinations with relatively low clinker and extremely high limestone contents can be found.

Limestone, as the main raw material of Portland cement clinker is present at every cement work location. Therefore, transport costs and emissions related to transport are omitted when limestone is used as a main cement constituent. However, as limestone is an inert material, a considerable increase of its content in cement is currently not possible due to insufficient knowledge and normatively defined boundary conditions. In addition, the restriction of the issue to the "compressive strength (in the laboratory)" aspect is not expedient. The uniformity of the concrete raw materials, the robustness of the concrete in construction and, primarily, the durability of the concrete are essential parameters. The following example clarifies this: In a test series carried out in the Research Institute of the Cement Industry, the particle size and the constituent distributions, in particular also

Fig. V-6: Relationship between the clinker content related to the concrete compressive strength and the concrete compressive strength; highlighted area: Concretes with a 28-day compressive strength of 40  $\pm$ 5 N/mm<sup>2</sup>







for cements containing limestone, were optimised in a targeted manner. **Fig. V-7** displays a test series with CEM II/B-LL cements (30 % limestone). All four cements were produced from the same raw materials in the same cement work. The mode of operation of the grinding plant for the joint grinding of the main constituents was deliberately changed. A comparison, in particular, of trials 3 and 4, shows that an identical strength development is not necessarily associated with comparable durability parameters – in this case, scaling in the cube test (frost resistance).



Fig. V-8: Strength development of cements with constant paste volume (variation of the w/c ratios)



Fig. V-9: Strength development of cements with constant paste volume (variation of the limestone quality)

#### New research project

A research project titled "Reduction of the environmental impact of concrete construction with new cements and concretes made therefrom" commenced, supported by the Deutsche Bundesstiftung Umwelt. This project is being carried out by the cooperation partners Spenner Zement GmbH, the Technische Universität Darmstadt and VDZ gGmbH. The aim of the research project is to produce and test cements, in a laboratory and cement work, with limestone contents beyond the maximum contents described in DIN EN 197-1. Limestone contents between 50 and 70 mass % will primarily be used. The impact of the clinker reduction in the cement on the strength development and the durability of concrete shall be investigated. The impacts of this substitution should be counteracted by optimising the particle size and constituents distribution and a potential adjustment of the concrete technology.

#### State of the research project

**Fig. V-8** shows the initial results of the strength development. All mortars had a constant paste content and were produced using a targeted superplastiziser dosage with constant spread. The mortar with a cement with 50 mass % limestone LL1 and a water-cement ratio of w/c = 0.4 displays a strength development similar to a standard mortar with CEM II/B-LL 32,5 R. A further reduction of the water-cement ratio to w/c = 0.3 resulted in a strength development similar to a standard mortar with CEM I 52,5 R.

Fig. V-9 displays the strength development of cements with 50 mass % limestone of different quality and particle size distribution (see Table V-2) and a water-cement ratio of w/c = 0.3. This mortar was also produced with a constant paste content and constant spread. Limestone LL3 and LL3-2 originate from the same quarry but have been ground using different methods. The cement with limestone LL3-2 has similar compressive strengths compared to the cements with limestone LL1 and LL2, and thus considerably higher strengths than the cement with LL3. These statements also apply to water-cement ratios of w/c = 0.4and w/c = 0.5. The strength development when using higher limestone contents outside the maximum contents specified in DIN EN 197-1 depends less on the chemical composition of the limestone and more on the particle size and constituent distribution of the main cement constituents. An example for constituent distribution dependent on particle size is displayed in Fig. V-10. The same clinker components were used for the two cements. The Y-axis represents the fraction of the main cement constituents clinker and limestone of cements with 50 mass % limestone LL3 and LL3-2 depending on the particle size. The average volume fraction of the components with regard to the overall cement are displayed by the straight lines at 46 % by volume clinker and 54 % by volume limestone. Up to a particle size of about 30  $\mu$ m, the clinker fraction of the cement with LL3-2 was clearly above the 46 % by volume contained in the overall system, while the clinker in cement LL3 was near the average value in this particle size range. In particular, the cement with LL3-2 exhibited distinctly higher clinker fractions up to about 70 % by volume up to 10  $\mu$ m, which is significant for the early strength development. The linking of the hydration products in the particle size ranges of up to 10  $\mu$ m and up to 30  $\mu$ m is considerably less affected by inert particles when using limestone LL3-2. This leads to considerably higher strength at all test dates for apart from that equal starting conditions. Coordinating the particle size distribution of all the main constituents in the cement work is therefore vital.

#### Further action

It has been shown that a targeted optimisation of the particle size and constituent distribution of cements with high limestone contents results in improved strength development. However, both the strength development and the durability of concretes is important for the use of cements. Corresponding concretes with factory-produced cements are produced in the next work step. The durability is tested in the same way as the mortar compressive strength. Concretes with reference cements and common compositions are compared with selected new limestone cements. The impacts of a reduction in the water-cement ratio with the simultaneous optimisation of the paste content and a potential optimisation of the grading curve of concrete for durability will be investigated. The frost resistance will be tested using the CIF method, as well as the chloride migration resistance pursuant to the BAW code of practice "Chloride penetration resistance" and the carbonation resistance of concretes with a maximum particle size of 8 and 16 mm.

#### Practical assessment

A test with one of the factory produced cements in a concrete plant is planned to conclude the research project. The robustness of concretes with these types of CEM X-LL cements, optimal mixing times, pumpability, compaction behaviour and, potentially, the fair-faced concrete quality will be analysed in this regard.

Finally, the results of the research project will then be evaluated on the basis of Life Cycle Assessments.

#### Cement and admixtures

Some 90 % of the concretes produced in Germany contain concrete admixtures. In 2009 the admixture use in Germany amounted to about 7 kg/t cement. Overall, more than 550 concrete admixtures, which are classified in 15 different functional groups, are currently available in Germany. Approximately 85 %, plasticizers (BV) and superplasticizers (FM) form the largest fraction of the concrete admixtures used.

The influence of concrete admixtures on the hydration of cement as well as on the fresh and hardened concrete properties is generally determined empirically. Scientifically-based knowledge is lacking with regard to the precise operating mechanisms of some of the concrete admixtures or they are the subject of controversial discussions. This applies, in particular, for superplasticizers based on polycarboxylate ether, for shrinkage reducing admixtures and for air entraining admixtures. These are the subject of extensive investigations at the Research Institute of the Cement Industry.

#### Superplasticisers

Synthetic organic polymers with carboxylic acid groups such as polycarboxylate ether (PCE) represent advancement in the

#### Table V-2: Analysis of the limestone qualities

	Limestone LL1	Limestone LL2	Limestone LL3	Limestone LL3-2
CaCO <sub>3</sub> content in %	97.8	88.1	79.6	78.0
TOC in %	0.02	0.05	0.09	0.11
Methylene blue value in g/100g	0.03	0.53	0.63	0.40
Blaine fineness in cm <sup>2</sup> /g	4205	4190	7960	4830
Slope n	0.80	0.90	0.70	0.66
Position parameter d' in $\mu$ m	20.1	18.9	10.7	23.9



Fig. V-10: Particle size-dependent constituent distribution of cements with limestone LL3 and limestone LL3-2

field of effective substances of superplasticizers. Some 60 % of the superplasticizers used are already based on PCE - and rising. PCE consist of main chain molecules, such as polyacrylic acid, and side chain molecules, e.g. polyethylene oxide, which are bound to the main chain. Via their negatively charged main chain, the PCE adsorb on the positively charged surfaces of the cement, its initial hydration products and other fine solid particles. The dispersing effect is largely attributed to the steric repulsion of the side chains. Variation of the charge and the lengths ratios of the main chain to the side chain allow different properties, such as a strong initial plastification effect and/or an extended workability time of the fresh concrete.

In addition to parameters such as, for example, the exact point when the superplasticizer is added, the mixing time and the temperature of the fresh concrete, also the cement may influence the effect of superplasticizers. Practical experience has shown that in unfavourable circumstances for cements with different main constituents the same type and quantity of superplasticizer may lead to a rapid loss of consistency, to segregation, to intense bleeding and to delayed strength development of concrete. While knowledge of the effects that traditional superplasticizers have on Portland cement exists, research is needed on the interactions between Portland-composite and blastfurnace cements and superplasticizers based on polycarboxylate ether.

Supported financially by the AiF, in a research project (IGF project no.: 15876 N) at the Research Institute of the Cement Industry influences of the cement main constituents clinker, blastfurnace slag and limestone on the adsorption of superplas-



#### Pore solution and zeta-potential

Investigations revealed that, with increasing substitution of the clinker and sulphate agent components with blastfurnace slag or limestone in the cement, the ionic strength and the sodium, potassium and sulphate ion concentrations in the pore solution decreased virtually linearly due to the dilution effect. Conversely, the calcium ion concentration increased. Changes in the ionic strength and the composition of the pore solution influenced, for example, the effective amount of charge of the superplasticizers depending on the nature and molecular structure of the effective substances. Compared to the paste with Portland cement, the zeta-potential, as a measure for the surface charge of the particles, did not change significantly when substituting the clinker and sulphate agent components of up to 35 mass % with blastfurnace slag or limestone. For higher fractions of blastfurnace slag in the cement the zetapotential of the cement paste was influenced considerably. A change in the zeta-potential of the cement paste in combination with a change in the effective amount of the superplasticizer charge may influence the adsorption behaviour and the plasticizing effect of superplasticizers.

#### Adsorption and plasticizing effect

Pastes produced with cements containing granulated blastfurnace slag or limestone could be plasticized more effectively with smaller quantities of PCE than the reference paste produced with Portland cement (Fig. V-11). Fig. V-12 shows that the quantity of PCE needed for maximum plasticizing of a particular cement paste (saturation point dosage) fell with increasing substitution of the clinker in the cement. The effective substances adsorbed primarily on the clinker component or on the initial hydration products. Clayey components within the limestone component of Portland-limestone cements may increase the saturation point dosage depending on the molecular structure of the PCE used.

#### Duration of plastification

**Fig. V-13** shows the flow table spread of concrete in relation to the PCE and cement used plotted against the time after adding water. In each case the amount of PCE added was 90 % of the saturation point dosage. Both PCE exhibited marked specific effects when combined with Portland cement (CEM I). Because of its low effective amount of charge and the high sulphate ion concentration in the pore solution (see table in Fig. V-13) PCE11 was adsorbed only slowly on the clinker and the initial hydration products and was available for a

ticizers were investigated. The investigations were carried out using cements with the same Portland cement clinker and sulphate agent components and varied proportions of different blastfurnace slags or limestones. In combination with rheological measurements, based on the composition of the pore solution and the zeta-potential it was determined whether conclusions regarding the plasticizing effect of superplasticizers with different effective substances and molecular structures could be drawn. The objective was to determine substance parameters responsible for scheduled interactions between cements and superplasticizers in order, for example, to reduce discolorations in fair-faced concrete surfaces as a result of sedimentation. correspondingly long time for maintaining the consistency. Because of its greater effective amount of charge PCE22 was adsorbed substantially faster and to a greater extent than PCE11. As a result the concrete exhibited marked stiffening.

The specific effects of both PCE had virtually disappeared when they were used in combination with cement containing the same clinker and 80 mass % granulated blastfurnace slag (CEM III/B). PCE11 was adsorbed more strongly because of the interaction with the pore solution, which, with this cement, had a substantially lower concentration of sulphate ions and higher calcium ion concentration. Therefore, the concrete showed a higher spread loss. On the other hand, the improved maintenance of consistency when using the CEM III/B in combination with PCE22 could be attributed less to interactions between the pore solution and the PCE22; it is more a result of the reduction in the proportion of the clinker in the cement. This essentially reduced the reactive surface area so that less PCE22 was adsorbed and was available longer for providing the plasticizing action.

The type and the quantity of superplasticizer always have to be adjusted to concrete technology parameters, such as the reactivity of the cement, the water-cement ratio, the mixing time, the temperature and the time until the concrete is placed. The objective is to determine the optimal plastification and duration of plastification without sedimentation. An overdose of the superplasticizer with regard to the saturation point dosage results in distinct sedimentation and leads to a significant delay of the hydration of the cement as well as the strength development of the concrete. Therefore, the quantity of superplasticizer added must always be lower as the respective saturation point dosage in order to, for example, prevent the formation of discolorations in fair-faced concrete surfaces as a result of sedimentation.

### Shrinkage-reducing admixtures (SRA)

A subsequent research project (IGF no. 15681 N), funded by the AiF, was carried out, based on the knowledge gained from the research project, on the working mechanisms of shrinkage-reducing admixtures in hardened cement paste and mortar (cf. VDZ Activity Report 2007-2009). This project investigated the impact of SRA on shrinkage, the mechanical properties and the durability of concrete. Two commercially available shrinkage-reducers based

Fig. V-14: Overall shrinkage deformation after 364 days of concrete with w/c = 0.50 and with Portland cement CEM I depending on the cement paste content: reference without SRA and with shrinkage-reducer SRA1 and SRA2; storage conditions L2



on glycol (SRA1) and glycol ether (SRA2) were used.

### Impact of SRA on the properties of fresh concrete

The shrinkage-reducers used had no significant impact on the consistency and the air content of fresh concrete with Portland cement CEM I, Portland composite cement CEM II/B-M (S-LL) and blastfurnace cement CEM III/A with cement contents between 270 and 420 kg/m<sup>3</sup> and water-cement ratios of w/c = 0.42 and 0.50.

Impact of SRA on concrete shrinkage The investigations on unrestrained (free) total shrinkage of concrete with CEM I, CEM II/B-M (S-LL) and CEM III/A with cement contents between 270 and 420 kg/  $m^3$  and water-cement ratios of w/c = 0.42 and 0.50 under different storage/drying conditions showed that the shrinkage-reducing effect of the shrinkage-reducers decreased over time, regardless of the shrinkage-reducer, the cement type, the cement content and the water-cement ratio. The shrinkage-reducing effect of shrinkage-reducer SRA2 was always larger than that of shrinkage-reducer SRA1. Shrinkage-reducer SRA1 reduced the overall shrinkage of concrete with Portland cement CEM I by about 11 % to about 21 % for storage conditions L1 (1 day in mould, then climate 20/65) and L2 (1 day in mould, 6 days in water, then climate 20/65) at the age of one year. For concretes for which the investigations were performed over a threeyear period, the effect of the shrinkage-reducers continued to decrease in the climate 20/65. With a cement content of 320 kg/m<sup>3</sup> and under storage conditions L2, the effect of shrinkage-reducer SRA1was neutralised after a three-year storage period in the 20/65 climate. Shrinkage-reducer SRA2 reduced the free total shrinkage by about 39 % after a year. However, the effect was largely independent of the cement type, the cement content, the water-cement ratio and the storage condition.

The comparison of the total shrinkage deformation of the concretes with and without SRA after 364 days and the relevant cement paste/hardened cement paste content showed that the concretes with SRA exhibited considerably lower shrinkages compared to reference samples with the same cement paste content. The correlation lines displayed in Fig. V-14 (e.g. for concrete with Portland cement and w/c = 0.50) can be applied to review how high the cement paste/hardened cement paste content can be with concretes with shrinkage-reducers in order to exhibit a comparable total shrinkage deformation to the reference. This showed that the cement paste content in concrete without SRA could be increased by a factor of up to 1.7 (SRA2, CEM I, w/c = 0.50, L2) using linear extrapolation. In light of this, it can be assumed that concretes with SRA with considerably higher cement paste/hardened cement paste content exhibit the same shrinkage as concretes with less cement paste without SRA, whose workability is considerably restricted due to the lower cement paste content.

### Impact of SRA on the mechanical properties of concretes

A series of publications has shown that the compressive strength of concretes may be reduced by SRA. These findings were widely confirmed in this research project. Based on these results, a reduction of the concrete compressive strength of up to 20 % must be expected when shrinkage-reducers are used in practice.



Fig. V-15: Carbonation depth of fine concrete with w/c = 0.50 after 364 days in storage at climate 20/65, preliminary storage of 7 and 28 days in water

The investigations on the impact of SRA on the flexural strength showed no systematic impact of the various shrinkage-reducers. In summary, it can be determined that a reduction of the flexural strength by up to 20 % should also be expected when using shrinkage-reducers in practice.

The static modulus of elasticity was only slightly influenced by the shrinkage-reducers compared to the concrete compressive strength and the flexural strength. The maximum reduction of the static modulus of elasticity was about 4 % after 28 days.

### Impact of SRA on the durability of concretes

The carbonation depths of fine concretes with shrinkage-reducers were larger than those of the relevant reference samples without shrinkage reducers after a one-year storage period in the climate 20/65, regardless of the cement type and the preliminary storage period (Fig. V-15). However, barely any consequences are expected in practice. The concrete resistance towards penetrating chlorides was increased by the shrinkage-reducers by up to 20 %. This is due to a finer pore system of concretes with shrinkage-reducers. The investigations on the impact of shrinkage-reducers on the frost resistance of concrete showed that the scaling in the CIF test were negligible overall. The concretes with CEM I and CEM III/A and the applied shrinkage-reducers complied with the criterion specified by the Federal Waterways Engineering and Research Institute (BAW) for evaluating the frost resistance of concrete based on the relative dynamic modulus of elasticity (>75 % after 28 freeze-thaw cycles). The concrete with CEM II/B-M (S-LL) and shrinkage-reducer SRA2 did not comply with the criterion. This shows that the extent of the internal damage (relative dynamic modulus of elasticity) depends on the combination of cement and shrinkage-reducer. However, what is still unclear, is the extent to which the reduction of the relative dynamic modulus of elasticity in the laboratory test can be used as a benchmark for the expected damage in exposure class XF3-even when using shrinkage-reducing admixtures. The investigations on the saturation state of the concretes showed that the concretes with shrinkage-reducers always showed a lower capillary water uptake than the reference concretes prior to the freeze-thaw stress. In contrast, the fraction that was recorded during the first 28 freeze-thaw cycles was larger for the concretes with SRA than for the corresponding reference. The theoretical critical degree of saturation of 91 % according to Fagerlund was partially exceeded without any significant internal damage.

#### Air entraining admixtures

Air entraining admixtures (AEA) are expected to generate a large number of equally distributed air pores with a diameter of  $\leq 300 \ \mu$ m in fresh concrete. In hardened concrete, the pores serve as expansion space to reduce the pressure that arises when the pore fluid freezes. They also reduce the capillary water absorption. In tandem, the two operating mechanisms ensure a high freeze-thaw resistance of the concrete.

Soaps from natural resins (wood resin) and synthetic surfactants are used as base materials for AEAs. During mixing, a part of the AEA molecules dissolved in the pore solution stabilises the air bubbles that enter the concrete by mixing. Other molecules attach to cement particles. This allows air bubbles to attach to cement particles in order to improve the stability of the air void system. Another part of the molecules is precipitated by salt formation in the pore solution. New air voids are constantly stabilised during the mixing process until no more dissolved AEA is present in the pore solution. Different mixing times are required until the AEA is completely activated depending on the type of active agent and the added quantity of AEA.

### Research in the Research Institute of the Cement Industry

In practice, some concrete pavement showed a much higher air content in the hardened concrete when using AEAs based on a synthetic active agent. Investigation in the Research Institute of the Cement Industry with commercially available AEAs showed that a considerable increase of the air content may occur when there is an overdose of the AEA due to a mixing time that has been shortened in order to comply with the targeted air content. In this case the fresh concrete contains a sufficient quantity of the AEA, that is inadequately activated. Additional air bubbles are stabilised during a subsequent input of mixing energy in the fresh concrete, e.g. during placement by the distribution screw, and the air content increases. Similar effects have been noted for ready-mixed concrete, where the air content can increase between the mixing plant and the construction site, especially with rotating drums. As the composition of commercially available AEAs was not known, the impact of the active agent on the air void formation was not initially able to be determined. As a result, four pure active agents (natural active agent: Vinsol resin; synthetic surfactants: Alkyl sulphate, alkyl sulphonate, alkyl polyglycol ether sulphate) were also used in the Research Institute of the Cement Industry in order to investigate the air void formation of a fine concrete with 4 mm maximum particle size depending on the mixing time and the added quantity (Fig. V-16). Initially a preliminary test determined the addition quantity of the active agent in order to obtain an air content of about 5 % by volume in fresh concrete after a mixing time of two minutes (see bar in Fig. V-16). This added quantity was designated the single added amount.



Fig. V-16: Air content of fresh concrete (fine concrete with maximum particle size 4 mm) depending on the mixing time and the quantity of active agent added

For the vinsol resin active agent, considerably higher quantities had to be added in order to adjust the air content than for the synthetic surfactants. The development of the air content was then determined depending on the mixing time (30 seconds and 1, 2, 4, 7, 10 and 15 minutes) with single and elevated (double and triple) dosages. Almost identical behaviour was displayed regardless of the active agent when a single quantity was added. The targeted air content of about 5 % by volume was achieved after a mixing time of about one minute and did not change significantly thereafter. Varying behaviour, depending on the active agent, was observed when elevated quantities were added. With regard to the admixture with the natural active agent, the air content of the fresh concrete increased only slightly from about 5 to 8 % by volume when elevated quantities were added and mixing times were increased. The air void formation concluded after mixing times of about one minute. With regard to the synthetic active agents, the air content increased to about 15 % by volume when triple the amount was added (alkyl sulphate and alkyl sulphonate) and to more than 30 % by volume for the active agent alkyl polyglycol ether sulphate. Considerably longer mixing times were also re-

Fig. V-17: Additional tests as part of initial testing with normal and double the input quantity of the AE agent and extended mixing period. Objective: Predict the risk of the subsequent increase of the air content due to an overdose and reduced mixing period

Second mix with 10 double addition level of AE agent Rise in air content Air content in % by volume 5 Initial test: Addition level AEA selected for mixing time of 2 min. and fresh concrete temperature approx, 20°C 0 0.5 2 6 Concrete mixing time in minutes

quired until the entire active agent was activated and a constant air content reached. The behaviour was dependent on the active agent as the synthetic surfactants had a better solubility, while the major fraction of the natural active agents in the pore solution precipitated in a non-specific fashion. A subsequent activation potential is therefore only expected for synthetic surfactants.

Proposals for an extended initial testing were derived from the test results in the Research Institute of the Cement Industry. The initial testing will determine the quantity of the AEA to be added in order to achieve the required air content. The determined AEA quantity must be doubled and the air content of the mixtures with both of the added quantities must be determined for a short mixing time (30 seconds) and after an extended mixing time (six minutes) in order to review the subsequent activation potential (**Fig. V-17**). If there is a considerable increase in the air content when double the amount is added and the mixing time is extended, this means that there is the risk of increased air content in practice.

#### Transferability into practice

The previous investigations and recommendations are based on tests with laboratory mixers (volumes of about 0.1 m<sup>3</sup>). However, the air void formation is also influenced by the mixer type, mix size, fill quantity and mixing intensity. This means that the results of the laboratory tests cannot be directly transferred, for example, to the mixing plant of a ready-mix cement works (volumes around 2 m<sup>3</sup>). Precondition for the production of an air-entrained concrete according to the requirement is knowledge of the air void formation relating to the mixing time in practice. A new research project by the Research Institute of the Cement Industry will investigate whether the results of laboratory tests can be transferred to the mixing volumes generally used in practice. The mixing time-dependent air void formation in fresh and hardened concrete in the laboratory and in a mixing plant will be determined in this regard. The impact of the time at which the AEA is added and the post-activation potential during transport in truck mixers will also be determined. The investigation is expected to provide fundamental knowledge of the interaction mechanisms of AEAs during production in a mixing plant. Knowledge of the connections protects against incorrect applications that may, for example, result in reduced strength due to elevated air content or a lack of freeze-thaw resistance due to insufficient air void structures.

#### Alkali-silica reaction

#### **Revision of the Alkali Guidelines**

The German Committee for Structural Concrete (DAfStb) published two amendments to the Alkali Guidelines (issue 2007) in 2010 and 2011. In 2011 a start was made to revise the Guidelines according to the structures of the European building material standards and to make them easier to read. The amendments were integrated. The 2010 amendment sheet suspended the requirements and measures for concrete road pavements (moisture class WS). It also specified the requirements of aggregates with flint outside the extraction area according to Part 2 of the Guidelines. Following ASR damage to structures in central Germany, the second amendment also specified new requirements for gravel from these regions.

#### Moisture class WS

Moisture class WS components include concrete road pavements in load classes Bk100 to Bk 1,8 according to RStO (Directive for standardising the paving of road pavement). The determination of requirements for concrete road pavements was originally within the Federal Ministry of Transport, Building and Urban Development's (BMVBS) area of responsibility, which specified requirements by General Circulars on Road Construction (ARS). The requirements and measures for humidity class WS were removed from the Alkali Guidelines and are described by the TL Beton-StB and the General Circular on Road Construction No. 04/2013 (see WS basic and confirmation tests section).

#### Additional specifications on flint

The Alkali Guidelines have to be applied nation-wide for all aggregates according to DIN EN 12620 in connection with DIN 1045-2. This created the uncertainty of how aggregates containing flint that are extracted outside of Part 2 of the Alkali Guidelines (parts of northern Germany) would be classified in an alkali reactivity class. The amendment sheet provides specified criteria that, in many cases, enable a simple classification of aggregates with flint fractions outside of the extraction area of Part 2 of the Guidelines.

#### Gravel from central Germany

Damage occurred to concrete constructions produced with gravel from central Germany, which experts verified were predominantly the result of damaging ASRs. Subsequent investigations with various testing methods and the evaluation of petrographic investigations determined that the aggregates may have been alkali-reactive. In order to prevent further damage, the German Committee for Structural Concrete (DAfStb) specified that these aggregates would be included in Part 3 of the Guidelines and subsequently categorised.

#### New structure of the Guidelines

The first regulation to prevent ASR damage on concrete constructions was set by the German Committee for Structural Concrete with the "Provisional Alkali Guidelines" in 1974. Since then the Alkali Guidelines have been extended by additional regions and rock types. In 2011 and 2012 the Committee for Structural Concrete restructured the Guidelines according to the European standards and integrated the two amendments. The revised Guidelines now clearly regulate the classification of all aggregates, according to DIN EN 12620 in connection with DIN 1045-2, into an alkali reactivity class. The classification of the aggregates, the preventative measures and the test methods are covered in separate chapters. The test methods are described in annexes. The "Classification" chapter is structured so that it must first be determined whether an aggregate meets all the requirements for classification in the alkali reactivity class E I. If this is not fulfilled, then the aggregate has to be classified through further tests. The revision is largely complete, so it is expected that the revised Guidelines will be ready to be published at the end of 2013.

### Specifications for concrete road pavements

The TL Beton-StB 07 and the General Circular on Road Construction (ARS) no. 04/2013 issued by the Federal Ministry of Transport, Building and Urban Development specify requirements in order to prevent damage to concrete road pavements as a result of alkali-silica reactions (ASR). According to the General Circular on Road Construction no. 04/2013 an ASR expert is necessary to confirm that no damage with the coarse aggregate or concrete is expected as a result of an ASR if used in the moisture class WS. The ASR damage potential of the concrete is investigated by means of an ASR performance test. The suitability of a coarse aggregate can be confirmed by WS basic test.

Once the suitability of an aggregate or concrete mix has been verified, only a WS confirmation test is required for any future constructions. The WS confirmation test should prove that the aggregate or the concrete constituents have not changed significantly. The Research Institute of the Cement Industry together with the Bauhaus-Universität Weimar developed the WS basic and WS confirmation test concept for the Research Association for Roads and Traffic (FGSV) task force 8.2.3. The Federal Ministry of Transport, Building and Urban Development introduced the concept with the General Circular on Road Construction no. 04/2013.

#### WS basic test

The WS basic test includes the testing of the alkali reactivity of the relevant fractions of an aggregate with accelerated mortar bar tests (reference or alternative methods) according to Part 3 of the Alkali Guidelines stipulated by the German Committee for Structural Concrete (DAfStb) (**Fig. V-18**). In order to take natural fluctuations into consideration, this is performed for three samples that are taken at intervals of at least four weeks. The fractions of the relevant sample for which the highest expansion occurred in the accelerated mortar bar tests are used for further investigations. These fractions are then mineralogically and petrographically characterised and tested in a WS concrete test.

The concept distinguishes between a WS basic test for concrete with a maximum particle size of 8 mm (top layer concrete (0/8) pursuant to TL Beton-StB 07) and for concrete with a maximum particle size larger than 8 mm (top layer concrete (D >8) and bottom layer concrete pursuant to TL Beton-StB 07), as at least 420 kg/m<sup>3</sup> of cement is used in the top layer concrete (0/8) and only a maximum of 360 kg/m<sup>3</sup> of cement is used in the top layer concrete (D > 8) and bottom layer concrete. This distinction is required as a damaging ASR in the top layer concrete (0/8) is generally more likely than in the top layer concrete (D > 8) or bottom layer concrete. This was demonstrated by comparative investigations with "washed concrete 0/8" (cement content  $c = 430 \text{ kg/m}^3$ ), maximum aggregate size 8 mm) and "standard concrete 0/16" (cement content c = 350 kg/ m<sup>3</sup>, maximum aggregate size 16 mm) in a research project carried out by the Research Institute of the Cement Industry.

If a 2/8 fraction passes the WS basic test in a concrete composition for top layer concrete (0/8), the expert must determine whether the results can also be transferred to other fractions (e.g. 8/16 and 16/22). If the results cannot be transferred, then a second WS concrete test must be performed for a concrete composition for "top layer concrete (D > 8) and bottom layer concrete" in order to confirm the suitability of the delivered fraction.

#### WS confirmation test

If the fractions of an aggregate plant pass the WS basic test then, at a later date, fractions from the same plant can be subjected to a short assessment in a WS confirmation test and used for the construction of corresponding concrete road pavements if the fractions are sufficiently equal. The current samples undergo an accelerated mortar bar test and are mineralogically and petrographically investigated in order to determine the compliance. The suitability can either be confirmed regularly by third-party inspection or as a one-off prior to casting the concrete in a construction project.



Fig. V-18: Flowchart of the WS basic test and WS confirmation test

### Experience with performance testing

The objective of the IGF project 16569 N, that will run until 2013, is to be able to recommend specifications for a practical evaluation of concretes for the moisture classes WF and WA. To do this, concretes will be prepared according to the regulations of the preventative measures of the Alkali Guidelines of the German Committee for Structural Concrete (DAfStb) (**Table V-3**) and tested under varying conditions in ASR performance tests. The tests should provide information on whether concrete with a specific aggregate and specific cement can be used for a certain moisture class so that there is no risk that the concrete will be damaged by an ASR during the planned service life. The preliminary storage until testing and the sodium chloride concentration (NaCl) were varied in the tests. The results achieved up to Mid-2012 can be summarised as follows depending on the moisture class:

60 °C concrete prism test with external alkali supply (moisture class WA) The concretes in moisture class WA were tested in the "60 °C concrete prism test with external alkali supply". The alkali supply took place via a 3 % and 10 % sodium chloride solution. The expansion limit value of 0.50 mm/m after ten alternating storage cycles was used to evaluate

Alkali reactivity	Cement content	I	Preventative measures	for the moisture class			
class	in kg/m <sup>3</sup>	WO	WF	WA			
E I, E I-O, E I-OF, E I-S	No specifi- cation		None	None			
E II-O	≤ 330			Low-alkali cement			
E II-O, E II-OF	> 330		Low-alkali cement				
E III-O, E III-OF	> 330		Low-alkali cement	Aggregate replacement			
	≤ 300	None		None			
E III-S	≤ 350		None	Performance test <sup>1)</sup> or Low-alkali cement			
	> 350		Performance test <sup>1)</sup> or Low-alkali cement	Performance test <sup>1)</sup> or aggregate replacement			

Table V-3: Preventative measures according to the Alkali Guidelines of the German Committee for Structural Concrete (DAfStb)

1) Only by assessment until further notice



Fig. V-19: Expansion of different concretes with different coarse aggregates in the 60  $^\circ$ C concrete prism test with external alkali supply by a 3 % (left) and 10 % (right) NaCl solution



Fig. V-20: Expansion of different concretes with different cements in the 60 °C concrete prism test with external alkali supply by a 3 % (left) and 10 % (right) NaCl solution

the results. This is also used to evaluate concretes in moisture class WS (see section "VDZ/FIB performance testing composition"). Fig. V-19 shows the expansion of two concretes with Rhine gravel E I and crushed rhyolite E I-S that were produced with a CEM I 42,5 R with a high alkali content. Pursuant to the Alkali Guidelines, no preventative measures are required for aggregates in alkali reactivity classes E I and E I-S. According to these Guidelines no ASR damage will occur with these aggregates, even if the alkali content of the cement has an Na2O-equivalent value of 1.20 mass %. Both concretes passed the test when a 3 % NaCl solution was used (Fig. V-19, left). However, the test with a 10 % NaCl solution was too severe as the expansion of the concrete with Rhine gravel E I was above the limit value and this concrete would have been assessed as unsuitable

Fig. V-20 shows the expansions of concretes with crushed greywacke (reactivity class E III-S) that may only be used with low-alkali cements for a cement content of 350 kg/m<sup>3</sup> pursuant to the Alkali Guidelines. The Portland cement CEM I that was used had a Na2O-equivalent of 0.62 mass % and was therefore on the low-alkali cement limit. The CEM III/A (laboratory cement) fulfilled the requirement for an low-alkali cement with a Na<sub>2</sub>O-equivalent of 0.95 mass %. Both concretes passed the test with a 3 % NaCl solution. The expansions were considerably higher with a 10 % NaCl solution and above the limit value. In this case the concretes would be assessed as unsuitable and excluded from use, even though they may be used according to the Alkali Guidelines. The test with a 10 % NaCl solution would therefore not represent the alkali non-reactivity according to the Alkali Guidelines. The results of concrete tests with a 3 % sodium chloride solution are presented in the following based on the above results.

The test method does not unreasonably exclude concretes that have been well-proven in practice, but it identifies reactive concretes. **Fig. V-21** provides individual examples that show that the expansion of concretes with a reactive E III-S aggregate and 370 kg/m<sup>3</sup> CEM I 32,5 R (Na<sub>2</sub>O-equi. = 0.89 mass %) and 430 kg/m<sup>3</sup> CEM I 42,5 N (Na<sub>2</sub>O-equi. = 0.62 mass %) were clearly above the assessment criterion. Both concretes should not be permitted pursuant to the Alkali Guidelines. The reactive E III-S aggregate should be replaced with a non-reactive aggregate (E I, E I-S, E I-O, E I-OF). When a low-alkali cement

(Na<sub>2</sub>O-equi. = 0.56 mass %) was used for concrete with 370 kg/m<sup>3</sup> cement, then the concrete passed the test with the reactive E III-S aggregate. In individual cases the test may be passed while using a low-alkali cement. However, this does not apply in general. The concrete with 430 kg/m<sup>3</sup> cement would still have failed the test with a low-alkali cement (Fig. V-21, left).

No measures have to be applied to concrete with a reactive E III-S aggregate and 300 kg/m<sup>3</sup> cement and the alkali content is not restricted. **Fig. V-22** shows that the test method provided conservative evaluations of new solutions that had not been used in practice. It can be assumed that this concrete would clearly fail the test with a higher cement content of 350 kg/m<sup>3</sup>. In this case the test method would correctly represent the Alkali Guidelines, as a lowalkali cement would need to be used.

The expansion in the 60 °C concrete prism test with external alkali supply ceased near the limit value when a laboratory cement CEM II/B-V with 31 mass % fly ash was used instead of a low-alkali cement (Fig. V-22, right). If the CEM II/B-V contained only 21 mass % fly ash then the test clearly failed.

#### 60 °C concrete prism test without external alkali supply (moisture class WF)

The concretes in moisture class WF were tested with the "60 °C concrete prism test without external alkali supply". The test method corresponded to the 60 °C concrete prism test according to the Alkali Guidelines. In some cases concrete prisms were additionally stored in the stainless steel container, used for the 60 °C concrete prism test, for 27 days after demoulding at 20 °C and a relative humidity of 100 %. For these prisms the 60 °C testing started after 28 days. The zero measurement at 20 °C was taken prior to storage. The tests were evaluated as having passed if the expansions were  $\leq 0.20$  mm/m 140 days after the initial storage at 60 °C. This limit value was determined based on AFNOR P 18-456. For concretes with Portland-fly-ash-cement, the expansion was also compared with the limit value of 0.30 mm/m after 52 weeks based on AFNOR P 18-456.

Concrete with non-reactive aggregates in alkali reactivity classes E I and E I-S passed the 60 °C concrete prism test, even when the cement content was 400 kg/m<sup>3</sup> and had a cement Na<sub>2</sub>O equi. of 1.20 mass % (**Fig. V-23**, left). In both cases the test method was in accordance with the Alkali



Fig. V-21: Expansion of different concretes with crushed greywacke (E III-S) in the 60  $^\circ C$  concrete prism test with external alkali supply by a 3 % sodium chloride solution



Fig. V-22: Expansion of a concrete with crushed greywacke (E III-S) in the 60 °C concrete prism test with external alkali supply by a 3 % sodium chloride solution

Guidelines. However, the Alkali Guidelines do not specify any requirements regarding the alkali content of the cement and the cement content for the alkali reactivity classes E I and E I-S.

Fig. V-23, right, shows the expansion of concretes that were produced with reactive crushed greywacke E III-S, a cement content of 370 kg/m<sup>3</sup> and in combination

with various cements. In this case, the Alkali Guidelines stipulate that a low-alkali cement must be used. By means of this test method it was possible to distinguish easily between concretes with various cements and alkali contents. In the presented material combination and concrete composition low-alkali cement is not necessarily to be used.



Fig. V-23: Expansion of different concretes in the 60 °C concrete prism test without alkali supply; left: Concrete with aggregates in alkali reactivity classes E I and E I-S; right: Concretes with crushed greywacke (E III-S) and various Portland cements



Fig. V-24: Expansion of different concretes with crushed greywacke (E III-S) in the 60 °C concrete prism test without alkali supply; left: Concrete with CEM III/A and various preliminary storage periods at 20 °C and 100 % relative humidity; right: Concrete with 350 kg/m<sup>3</sup> CEM I 42,5 R and high Na<sub>2</sub>O-equivalent



Fig. V-25: Expansion of concretes with different water-cement ratios in the 60  $^\circ$ C concrete prism test without alkali supply

Concrete with laboratory cement containing blastfurnace slag, which met the requirements for a low-alkali cement according to DIN 1164-10, also passed the test and was evaluated according to the Alkali Guidelines (Fig. V-24, left). When cements containing blastfurnace slag were used, the concrete initially displayed shrinkage deformations within the first 28 days when it was stored in the 60 °C-reactor above water. If expansion resulting from an ASR were to occur within the first 28 days, no distinction could be made between the shrinkage and the ASR expansion. If the concrete was allowed to hydrate in preliminary storage of 28 days at 20 °C and 100 % relative humidity, this significantly reduced the shrinkage deformation when the concrete was tested after 28 days at 60 °C. The 28-day-preliminary-storage of

concretes with cements containing blastfurnace slag and fly ash is therefore also recommended for this reason.

No measures are required pursuant to the Alkali Guidelines for a reactive E III-S aggregate and 350 kg/m<sup>3</sup> cement. Fig. V-24, right, shows the expansion of a concrete with an unfavourable composition that is above the limit value. This result can be used as evidence that the test method would provide a conservative evaluation of new solutions that have not been established in practice.

#### Impact of concrete microstructure on ASR in case of an external alkali supply

In IGF project 15248 N, the Research Institute of the Cement Industry and the Federal Institute for Materials Research and Testing (BAM) investigated the impact of microstructure of concrete on the course of a damaging ASR. The starting point for the IGF project was the finding that, unlike the concrete road pavements that were constructed using slipform pavers after the 1980s, concrete road paving from the 1960s did not display any ASR damage with partially similar concrete compositions. The objective of the IGF project was to clarify whether a targeted influencing of the concrete microstructure could reduce or prevent ASR damage.

The results show that the water-cement ratio does not systematically influence the development of ASR damage. There are two contrasting trends. On the one hand, the concretes with low water-cement ratios of 0.35 and 0.45, without an external alkali supply, expanded earlier and more quickly than those with a water-cement ratio of 0.55 in laboratory tests (Fig. V-25). They also showed the highest maximum expansions, whereby they occurred for water-cement ratios of 0.45 or 0.35 depending on the aggregate (Fig. V-26). Prism expansions and crack formation on 30 cm cubes occurred later for a water-cement ratio of 0.55 than for water-cement ratios of 0.45 and 0.35 (no Fig.). On the other hand, the maximum crack widths on the 30 cm cube in the 40 °C fog chamber (Fig. V-26) and the expansion of the prisms in the 60 °C concrete prism test with alkali supply (Fig. V-27) were lowest for the low watercement ratio. This indicates that lower watercement ratios, i.e. dense concretes, do not necessarily increase the severity of a damaging ASR in road pavements.

The 30 cm cube and the 60 °C concrete prism test with external alkali supply were



Fig. V-26: Expansion of concrete prisms (7.5 cm x 7.5 cm x 28 cm) after 140 days in the 60 °C concrete prism test (60 °C), of concrete prisms (10 cm x 10 cm x 50 cm) after 9 months in fog chamber storage (40 °C) and maximum crack widths in 30 cm cubes after 9 months in fog chamber storage (40 °C) for various aggregates



Fig. V-27: Expansion of concretes with various water-cement ratios in the 60 °C concrete prism test with alkali supply by 10 % NaCl solution

better able to take the conditions of concrete road pavements into account in practice because the large and compact cube is protected against the alkali leaching in a different manner compared to the prismatic test specimens and the impact of deicing agents is simulated in the 60 °C concrete prism test with alkali supply. The previously mentioned test illustrated that the penetration of the de-icing agent, and therefore the expansion, is reduced at lower watercement ratios (Fig. V-27).

The fact that some road pavements from the 1960s do not display any macroscopic ASR damage may be explained by hard shoulders to a certain extent. Microscopic investigations on thin sections showed that an ASR had taken place to some extent but that this did not lead to macroscopic damage due to the lack of high dynamic strain caused by traffic.

#### Impact of air voids

Artificial air voids did not impact the expansion process of concretes with dense alkali-reactive aggregates either in the 40 °C fog chamber, nor in the 60 °C concrete prism test with or without external alkali supply (Fig. V-28).

#### Impact of superplasticizer

The application of superplasticizer may increase the expansion of concrete if it introduces additional alkalis into the concrete (no Fig.). However, the impact of the superplasticizer alkalis should be low as the maximum dose of superplasticizer is rarely used.

The expansion development for concretes with superplasticizer was delayed for road pavement concretes that were investigated in the 60 °C concrete prism test with external alkali supply (**Fig. V-29**). The quantity of alkalis that were introduced by the superplasticizer was low for these concretes as small doses of a highly plasticising superplasticizer based on PCE were used.

#### Impact of density

The results in the 60 °C concrete prism test without alkali supply show that the expansions increase as the density of the concrete increases. A reverse trend is displayed for an external alkali supply. The sodium and chloride ions in the test solution were able to penetrate the less dense concrete and increase the severity and speed up a damaging ASR (no Fig.).

#### Conclusions

The investigations lead to the conclusion that an increasing microstructure density of the concrete does not necessarily lead to an increased ASR. A change to the structural properties of concrete investigated in the project was not able to prevent a damaging ASR. It was not possible to prevent a damaging ASR by the selection of a certain water-cement ratio, by setting the use of superplasticizer aside and/or a soft consistency, or by using air-entraining agents when reactive aggregates were used.



Fig. V-28: Expansion of concrete prisms with and without air-entraining agents (AE) in the 60 °C concrete prism test with alkali supply by 10 % NaCl solution



Fig. V-29: Expansion of concrete prisms with and without superplasticizer (SP) in the 60 °C concrete prism test with alkali supply by 10 % NaCl solution



Fig. V-30: Expansion of various concretes for moisture class WS after 8 cycles of the cyclic climate storage with 0.6 mol sodium chloride solution (limit value 0.5 mm/m) and expansion after 10 cycles in the 60 °C concrete prism test with alkali supply by 10 % sodium chloride solution (limit value 0.5 mm/m).



Fig. V-31: Expansion of various concretes for moisture class WS after 8 cycles of the cyclic climate storage with 0.6 mol sodium chloride solution (limit value 0.5 mm/m) and expansion after 10 cycles in the 60 °C concrete prism test with alkali supply by 3 % sodium chloride solution (limit value 0.3 mm/m).

Furthermore, the investigations confirm that the progression of a damaging ASR depends on the resistance of the concrete against the externally penetrating alkalis. Sufficient non-reactive aggregates must therefore always be used based on the external alkali supply for road pavements in order to prevent ASR damage.

### VDZ/FIB performance testing comparison

ASR performance tests allow the alkali reactivity of concretes to be evaluated. The testing enables a conclusion to be drawn on whether there is the risk that an ASR will damage the concrete depending on the exposure (moisture class). Concrete for moisture classes WA and WS and for airfields are tested with an external alkali supply in order to simulate the impact of deicing agents. The 60 °C concrete prism test with and without external alkali supply and the cyclic climate storage are used as performance test methods in Germany.

### *Comparison of the performance test methods*

In previous years, comparative investigations on performance test methods were performed on a total of 18 concretes in the Research Institute of the Cement Industry (60 °C concrete prism test without and with external alkali supply) and at the Bauhaus-Universität Weimar (cyclic climate storage). The concretes were composed of the following:

- w/c = 0.42, c = 370 kg/m<sup>3</sup>, AE agent content: 4.5 ± 0.5 % by volume or
- w/c = 0.42, c = 430 kg/m<sup>3</sup>, AE agent content:  $\geq$  5.5 % by volume

Different aggregates and Portland cements (Na<sub>2</sub>O-equivalent between 0.56 and 0.89 mass %) were used. The suitability of the concretes for moisture class WS were investigated with the 60 °C concrete prism test with a 10 % sodium chloride solution and with the cyclic climate storage with a 0.6 mol sodium chloride solution. The expansions at the evaluation date in both methods are compared for 18 concretes in Fig. V-30. Six results derived from the FE project 89.214/2008/AP "ASR in concrete pavement construction", which was commissioned by the Federal Highway Research Institute (BASt). Comparable results were achieved with both methods for 17 concretes; the tests only provided a different evaluation for one concrete (white point).

Fig. V-31 shows the comparison of the results between the 60 °C concrete prism test with alkali supply and the cyclic climate storage, when the 60 °C concrete prism test was performed with a 3 % sodium chloride solution and 0.3 mm/m was set as the limit value. The general correlation remained unchanged. Four of 16 concretes were evaluated differently. A link between the results of the 60 °C concrete prism test with a 3 % sodium chloride solution and 0.3 mm/m limit value to drill core investigations of damaged and intact road pavement concretes from practice has been established. The adaptation of the testing and the evaluation criteria may improve the transferability to conditions in practice.

#### ASR in concrete pavement construction

The Federal Highway Research Institute commissioned investigations in order to clarify whether the tests according to Part 3 of the Alkali Guidelines are suitable as proof that coarse aggregates in moisture class WS (concrete road pavements) are sufficiently safe with regard to the prevention of a damaging ASR. Various coarse aggregates were investigated with all test methods according to Part 3 of the Alkali Guidelines and in a pessimally composed road pavement concrete (top layer concrete 0/8 with 430 kg/m3 CEM I 42,5 N,  $Na_2O$ -equivalent of cement = 0.80 mass %) with the 60 °C concrete prism test with external alkali supply.

The results in **Table V-4** show that three aggregates passed the 60 °C concrete prism test with alkali supply, and are therefore suitable for moisture class WS as there is no risk of a damaging ASR. The aggregates were also suitable when one of the following conditions was fulfilled:

- All tests according to Part 3 of the Alkali Guidelines were passed.
- The accelerated mortar bar test (alternative method) according to Part 3 of the Alkali Guidelines was passed.
- The 60 °C concrete prism test according to Part 3 of the Alkali Guidelines was passed.

Experience with the ASR performance tests for testing and evaluating the alkali-reactivity of concretes in moisture classes WF and WA is currently being collected (cf. section "Experience with performance test methods").

#### External alkali supply

De-icing salts can penetrate the surfaces of building concretes and partially transform the mineral phase composition in the hardened cement paste. The resulting change in the chemical composition of the pore solution may increase the severity of a damaging ASR. The chemical and mineralogical effects of de-icing agents were investigated on hardened cement paste, mortar and on road pavement concretes in IGF project 15977 N.

#### De-icing salt content in 20-year old concrete road pavements

The starting point of the investigations was the determination of the de-icing agent distribution, their chemical bonding and the reaction products present in up to 20 years old road pavements. Increased chloride content to a depth of approx. 50 mm was detected in uncracked concrete, while sodium had only accumulated up to a depth of approx. 20 mm. A part of the chloride was incorporated in aluminate hydration products, while a fraction remained in the pore solution similar to the sodium. Using an empirical calculation for the water-saturated pore volume of the concrete, the salt content in the pore solution in the area near to the surface was estimated at about 3 mass % NaCl. In the area of insufficiently sealed joints and in cracks, the vertical penetration was overlaid with a lateral dispersion with a comparable penetration depth (Fig. V-32). Joint and crack edges were most severely affected by the deicing agent, however, without any further accumulation of the salt concentration. So a considerable proportion of the concrete volume of the road pavement can therefore be reached by the de-icing agents with a corresponding crack frequency. A significant impact of the traffic load (traffic lane or hard shoulder) or the surface texture (broom finish, sheet or washed concrete) on the penetration depths in the uncracked concrete was not observed.

A detailed observation of the mineralogical changes of hydration products or the pore solutions was not possible due to the domination of the aggregate content in the concrete samples. Therefore hardened cement pastes of various cements were stressed with the de-icing contents determined in the concrete road pavements. Characteristic conversion reactions were observed depending on the primary hydrate phase composition, the de-icing agent concentration and the storage temperature and storage duration (Fig. V-33). Of particular mineralogical interest were solid solutions between Friedel's salt and hydroxide-containing calcium aluminate hydrates, which led to small but reproducible shifts in the crystal lattice parameters and therefore the peak positions in the x-ray diffractograms.

Table V-4: Expansions at the time of evaluation for various coarse aggregates in tests according to Part 3 of the Alkali Guidelines and in a pessimally composed road paving concrete (top layer concrete 0/8) in a 60 °C concrete prism test with external alkali supply (ASR performance test)

	Expansion at the time of evaluation in mm/m											
Aggregate	I	ASR performance test										
	AMBT <sup>7)</sup>	70 °C mortar bar test <sup>1)</sup>	Fog chamber storage (40 °C)	60 °C concrete test	60 °C concrete prism test with alkali supply (10 % NaCl)							
Fraction	5/8		5/1	16	5/8							
Andesite I	0.34	0.53	0.32	0.08	0.13							
Rhyolite I	0.70	0.89	0.38	0.15	0.22							
Gabbro	0.06	0.73	0.40	0.24	0.28							
Rhyolite II	1.38	2.05	0.42 4)	0.45	0.40 5)							
Andesite II	1.40	2.30	0.43 4)	0.36	0.53							
Granodiori- te II	0.79	1.74	0.64 6)	0.89	0.57							
Limit value	≤ 1.0	≤ 1.5	$\leq 0.6^{2}$	≤ 0.30 <sup>3</sup> )	≤ 0.50							
1) Data from the Bau	houe Universit	ät Weimer	4) Crack width $> 0.2$	mm after 365 d								

Data from the Bauhaus-Universität Weimar

2) Additional maximum crack width < 0.2 mm

3) Preliminary limit value

Test passed

Test failed

<sup>4)</sup> Crack width  $\geq 0.2$  mm after 365 d

5) Limit value not exceeded, but more severe expansion increase after 8 cycles, questionable

6) Crack width 0.05 mm

7) AMBT: Accelerated mortar bar test



Fig. V-32: Depth profiles of the water-soluble ion content of a pavement concrete drilled across a joint



Fig. V-33: X-ray diffractograms of hardened cement paste (28-day hydrated CEM I, w/c = 0.50; stored in various test solutions for an additional 28 days at 20 °C)



### Chloride incorporation increases the pH value

The incorporation of chloride in the hydrate phases released OH-ions, which resulted in a slight increase of the pH value of the pore solution. At higher storage temperatures, the thermal instability of ettringite influenced the ion balance, by releasing sulphate ions, and therefore also the pH value. These effects were largely independent on the Na<sub>2</sub>O-equivalence of the cement used.

Mortar tests with alkali-reactive aggregates were carried out to investigate the extent to which the de-icing salt effects in the hardened cement pastes also had an impact on a damaging ASR. When the mortar with alkali-reactive aggregates was exposed to de-icing salt, it fundamentally displayed higher expansion values than for water storage. Additional differentiations, e.g. according to the extent of the phase changes in the hardened cement pastes or the storage impacts, were not able to be determined from the results of the expansion measurements.

### Measures for medium reactive aggregates

The alkali reactivity class E II-S for dense aggregates that exhibit a moderate alkali reactivity is not currently defined in Germany. With the exception of gravels from parts of northern Germany (Part 2), Part 3 of the Alkali Guidelines only distinguish between aggregates that are alkali reactive or non-reactivity - determined by testing - (alkali reactivity classes E I-S and E III-S). In IGF project 17248, the Research Institute of the Cement Industry and the Brandenburg University of Technology Cottbus (BTU) investigated whether it is possible to define an alkali reactivity class E II-S and the relevant preventative measures to avoid a damaging ASR.

#### Need for further research

The German Committee for Structural Concrete's Alkali Guidelines require certain measures to be taken for alkali reactive aggregates in alkali reactivity classes E II-O, E II-OF, E III-O, E III-OF and E III-S depending on the structure's environmental conditions (moisture class) and the cement content. The current measures include exchanging the aggregate or the use of low-alkali cements according to DIN 1164-10.

By way of example, Fig. V-34 displays the range of the expansions of coarse aggregates in the 60 °C concrete prism test according to the Alkali Guidelines. A limit value of 0.30 mm/m after 140 days is currently assumed as the limit value in order to distinguish between alkali reactive and non-reactive aggregates. For the alkali reactive aggregates, the range of expansions from 0.30 to 2.00 mm/m is extremely large. The concrete measures that must be applied to these aggregates pursuant to the Alkali Guidelines are the same for all aggregates - for both greywacke I as well as greywacke II. Pursuant to the Alkali Guidelines, greywacke II should not be used in a concrete in moisture class WA (moist + external alkali supply) if the cement content is higher than 350 kg/m<sup>3</sup>. However, a concrete with this greywacke and a cement content of 370 kg/m3 passed an ASR performance test with an external alkali supply with a 3 % sodium chloride solution (NaCl). The ASR performance test shows that no damaging ASR is expected for this concrete in moisture class WA (Fig. V-35). Greywacke II would therefore be an aggregate that could be categorised into a future alkali reactivity class E II-S.

In contrast, the concrete with greywacke I failed the ASR performance test. In this case, an exchange of the aggregate, as specified in the Alkali Guidelines, is justified.

If it were possible to define an alkali reactivity class E II-S and the corresponding measures, this would improve the competitiveness of concrete construction. Small and medium-sized companies that often only have regional sources for manufacturing concrete raw materials and concrete could use their material resources in a wider range without impairing the durability of the structures manufactured as a result.

#### Sulphate resistance

#### Sulphate resistance with magnesium exposure

Between 2007 and 2010 a special research project by the German Committee for Structural Concrete (DAfStb) entitled "Detailed investigations on the sulphate resistance of concrete" was carried out together with the Research Institute of the Cement Industry (FIZ), the Centre for Building Materials (cbm) at the TU Munich and the F.A. Finger-Institut für Baustoffe (FIB) at the Universität Weimar. As reported in the Activity Report 2007-2009, unexpected damage was detected during exposure tests at the FIB on supposedly sulphate-resistant concrete test specimens. Test specimens based on Portland limestone cement in combination with fly ash from bituminous coal were affected. However, the FIZ exposure tests performed in parallel to the above tests in sulphate-containing lake water and synthetic soils did not display this behaviour. Magnesium was established as the only suspect that could cause this conflicting behaviour, as this was also present in the attacking water of the FIB tests. This assumption was confirmed by subsequent laboratory tests at all three research centres. When the attacking water contained both sulphate and magnesium (< 300 mg/l), this caused significant expansions within just a few months on both test specimens based on mixtures of Portland cement and fly ash from bituminous coal as well as of Portland limestone cement and fly ash from bituminous coal (Fig. V-36). The analyses of the cements and fly ash from bituminous coal (SFA) used are displayed in Table V-5. The damage generally reduced considerably when the content of fly ash from bituminous coal was increased from 20 to 30 mass % (Fig. V-37). The currently specified minimum fly ash content must be increased from 20 to 30 mass % when DIN 1045-2:2008-08, section 5.2.5.2.2, 7th subsection, 3rd bullet applies. All investigations (laboratory and exposure tests) showed that an increase in the fly ash content in the cement and fly ash mixture by this amount significantly improved the sulphate resistance of concretes that reach the high sulphate resistance (SR) property of up to 1500 mg sulphate/l by adding fly ash. This regulation is a preventative measure with regard to sulphate attacks, regardless of whether low amounts of magnesium are present or not. The advantage of this regulation is that it is easy to deal with and it means that additional determinations for new exposure classes with (currently unknown) limit values in the area of lower magnesium concentrations in DIN 1045-2



Fig. V-36: Relative expansion of mortar flat prisms of Portland cement and Portland limestone cement-fly ash mixtures with various test solution compositions, German Committee for Structural Concrete research project (1500 mg sulphate/l, 0-160 mg magnesium/l)

Table V-5: Properties of the cements and fly ashes from bituminous coal used

		CEM I 32,5 R	CEM II/A-LL 3,5 R	SFA A	CEM I 32,5 R	CEM II/A-LL 32,5 R	SFA X	SFA Y
spec. surface acc. to Blaine	cm²/g	2755	4240	3420	2995	3 580	3010	4080
$CO_2$	%	1.39	6.99	0.21	1.75	3.27	0.46	0.44
Water	%	0.56	1.00	0.31	0.55	0.66	0.31	0.10
SiO <sub>2</sub>	%	21.63	17.78	56.58	20.20	20.09	48.19	47.45
$Al_2O_3$	%	4.72	4.68	27.27	5.44	5.31	23.22	27.93
TiO <sub>2</sub>	%	0.26	0.23	1.07	0.27	0.31	0.94	1.21
$P_2O_5$	%	0.22	0.19	0.20	0.11	0.10	0.03	0.7
Fe <sub>2</sub> O <sub>3</sub>	%	1.53	2.56	4.88	2.46	2.56	12.14	9.56
$Mn_2O_3$	%	0.04	0.10	0.04	0.06	0.06	0.13	0.05
MgO	%	0.91	1.28	1.40	1.58	1.53	2.02	1.02
CaO	%	66.34	62.11	0.92	63.66	61.72	5.14	1.45
SO <sub>3</sub>	%	1.99	2.58	0.13	2.92	3.30	0.90	0.27
K <sub>2</sub> O	%	0.80	0.55	4.54	0.76	0.90	2.3	2.86
Na <sub>2</sub> O	%	0.22	0.10	0.89	0.19	0.18	0.96	1.08
C <sub>3</sub> S	%	69.8	-	-	65.9	-	-	-
$C_2S$	%	10.3	-	-	8.5	-	-	-
C <sub>3</sub> A	%	10.0	-	-	10.3	-	-	-
$C_4AF$	%	4.7	-	-	7.5	-	-	-

are unnecessary. This regulation will be incorporated into the new issue of DIN 1045-2 in connection with the revision of EN 206 (source: German Committee for Structural Concrete).



Fig. V-37: Mortar flat prisms based on Portland cement with 20 mass % fly ash from bituminous coal (top) and 30 mass % fly ash from bituminous coal (bottom) after about 10 months storage at 8 °C in sodium sulphate solutions (S1500) with 160 mg magnesium, 14 days preliminary storage, German Committee for Structural Concrete research project



Fig. V-38: Relative expansions of mortar flat prisms with a cement-fly ash mixture with dif-

ferent test solution compositions, preliminary storage periods and storage temperatures, AiF research project

#### AiF research project

The material requirements and boundary conditions under which this type of sulphate attack (with 1500 mg sulphate/l and  $\leq$  300 mg magnesium/l) can lead to damage to mortars and concretes, if these are manufactured with cement and fly ash from bituminous coal pursuant to the fly ash regulation according to DIN 1045-2, have been investigated in more detail in the FIZ in an AiF research project (IGF no. 16710 N) since the end of 2010.The investigations are being carried out with five cements (CEM II/A-LL, CEM II/B-S, CEM II/B-M (S-LL), CEM III/A, CEM I) and two fly ashes from bituminous coal as well as a reference with a CEM III/B-SR and a CEM I-SR. The focus of the investigations is on the use of Portland and Portland limestone cement. The analyses of the cements and the fly ashes from bituminous coal used are also indicated in Table V-5.

#### **Thaumasite formation**

Severe expansion and initial damage in the form of structure softening thaumasite formation occurred after six months, in a similar fashion to the tests from the German Committee for Structural Concrete project (see Fig. V-36). Test specimens based on Portland limestone cement that were stored at lower temperatures (8 °C) were affected first, as well as those that had a magnesium concentration of 300 mg/l. This was followed by correspondingly stored test specimens based on Portland cement after twelve months. At lower magnesium concentrations, in this case 160 mg/l, the test specimens did not display significant expansions or identifiable damage even after twelve months (Fig. V-38). In the German Committee for Structural Concrete tests, damage occurred for 40 and 80 mg magnesium/l. It seems that the material composition of the cements and the fly ash based on bituminous coal has a considerable impact on the sulphate resistance in the flat prism performance test. Additional tests showed that the preliminary storage period and the storage temperature also had a decisive impact on the test results. For shorter preliminary storage periods (2 days instead of 14), high expansions and initial structure damage occurred after only a few months, even for test solutions with 160 mg magnesium/l. The test specimens did not exhibit any significant expansions for longer preliminary storage periods (90 days instead of 14). Fig. V-39 and Fig. V-40 display mortar test specimens after twelve months of storage in test solution.

#### **Pozzolanic reaction**

It seems likely that an insufficiently dense structure in the relevant mortar test specimens was decisive for the occurrence of high expansions and resulting damage. This is influenced by several aspects. Key parameters are the slow pozzolanic reaction of the fly ash in combination with short preliminary storage periods ( $\leq$  14 days), so that the fly ash fraction was not able to contribute significant amounts of hydration products for the structure density.
Although the test specimens were only stored in test solutions with practical, i.e. low, sulphate and magnesium solutions after the preliminary storage period, this still resulted in expansions and structure changes, however, only at 8 °C storage and not at 20 °C storage. This behaviour can be explained with the following reaction sequence: The presence of magnesium in the test solution resulted in the formation of a surface brucite layer (magnesium hydroxide). This withdrew the calcium hydroxide from the microstructure, which was lacking for the pozzolanic stimulation of the fly ash. However, the brucite layer was not sufficient in order to prevent sulphate ions from penetrating into the microstructure underneath. The 20 °C storage therefore resulted in the formation of common hydration products as well as additional ettringite from both the reaction with cement constituents as well as with fly ash. Overall, this resulted in the structure increasing in density more rapidly. The common hydration products progressed more slowly at 8 °C storage. The penetrating sulphate was able to form ettringite as well as thaumasite. This resulted in more severe expansions and loosening of the surface structure. Mixtures with 30 mass % fly ash from bituminous coal displayed a consistently higher sulphate resistance than the mixtures with 20 mass % fly ash from bituminous coal. This is probably caused by the higher physical structure density, since fly ash was applied for the water-cement ratio with k = 0.4. The brucite layer was also less distinct in this sample than for other samples.

## SR cements without problems

Although the Portland and Portland limestone cements barely differed in the two test programs, there were significant differences in the sulphate resistance of the flat prisms. This may be due to differences in the properties of the fly ashes that were used. A corresponding evaluation and additional investigations remain outstanding. The investigation results of the other cements (CEM II/B-S, CEM II/B-M (S-LL) and CEM III/A) always in combination with 20 mass % fly ash from bituminous coal did not display any indications of reduced sulphate resistance even after twelve months. The two reference cements CEM I-SR and CEM III/B-SR also showed no indications in any of the test conditions that the presence of such low magnesium concentrations presented an additional attack potential and that this could reduce the sulphate resistance.



Fig. V-39: Mortar flat prisms based on Portland limestone cement with 20% fly ash from bituminous coal, 14 days preliminary storage, 12 months storage at 8 °C in sodium sulphate solution (S1500) without magnesium (top prism), with 160 mg magnesium (central prism) and 300 mg magnesium (bottom prism), AiF research project



Fig. V-40: Mortar flat prisms based on Portland cement with 20% fly ash from bituminous coal, 12 months storage at 8 °C in sodium sulphate solution (S1500) with 160 mg magnesium after 2 days of preliminary storage (top prism), 14 days of preliminary storage (central prism) and 90 days of preliminary storage (bottom prism), AiF research project

# Freeze-thaw resistance with or without de-icing salt

## **General information**

In many cases the CDF test according to DIN CEN/TS 12390-9 is applied if concrete, which is exposed to de-icing salts and freeze-thaw-cycles with high water saturation (= exposure class XF4), has to be subjected to a freeze-thaw laboratory test in addition to the descriptive requirements of the concrete standard DIN 1045-2. A considerably lower water saturation and associated lower stressing in the event of freeze-thaw-cycles can be assumed for components (exposure class XF2). In this case, the application of the CDF test would represent an inappropriately high stress. The cbm (TU Munich) and the University Duisburg-Essen were asked to jointly develop a suitable laboratory test process for exposure class XF2 on behalf of the Federal Highway Research Institute (Bundesanstalt für Straßenwesen/BASt). Significant changes to the process proposed by the institutions mentioned include raising the minimum temperature from -20 °C to -10 °C and the reduction of the number of freeze-thaw-cycles from 28 to 14.

Table V-6: Composition of the investigated concretes

Concrete	Cement designation	Composition
B1	CEM II/B-LL 32,5 R-AZ	$- c = 320 \text{ kg/m}^3$
B2	CEM II/B-M (S-LL) 32,5 R-AZ	- w/c = 0.50 - FM based on PCE
B3	CEM II/B-M (S-LL) 52,5 N-AZ	<ul> <li>Aggregate</li> </ul>
B4	CEM II/B-M (S-LL) 32,5 R-AZ	Grading curve range A16/B16 (Rhine sand 0/2
В5	CEM II/B-M (S-LL) 42,5 N-AZ	Quartz sand 1/2
B6	CEM II/B-M (S-LL) 42,5 N-AZ	Rhine gravel 2/8
B7	CEM II/B-M (S-LL) 32,5 R-AZ	Rhine gravel 8/16)
B8-1	CEM I 32,5 R	
B8-2	CEM I 42,5 R	
B9	CEM III/A 42,5 N (LH-NA)	



**Investigations by the Research Institute of the Cement Industry** Initial experience with the CDF test XF2 was gathered in the Research Institute of the Cement Industry in 2010. Two CEM I, a CEM III/A, a CEM II/B-LL and six CEM II/B-M (S-LL) were used in a test series with new XF2 concretes according to DIN 1045-2 Tab. F2.1 without artificially entrained air pores (**Table V-6**). The amount of scaling exhibited by the concretes after 14 freeze-thaw-cycles was between 0.65 and 4.5 kg/m<sup>2</sup> (**Fig. V-41**). The standard deviation was up to 20 % of the average within a test specimen series

Due to the extremely large scope of the scaling amounts of standard XF2 concretes, a decision was made to perform an interlaboratory test together with six testing laboratories from the group of VDZ member companies.

(five plates).

## A CEM II/B-S (B1), a CEM II/A-LL (B2),

a CEM I (B3) and a CEM III/A (B4) cement were used in each case. Although all the participating laboratories were extremely experienced in performing tests using the CDF test, the scaling amounts determined differed considerably in some of the tests. The values for B1 concrete were between about 1.1 and 2.6 kg/m<sup>2</sup>, for B2 concrete between about 0.16 and 2.3 kg/m<sup>2</sup>, for B3 concrete between about 0.49 and 0.86 kg/ m<sup>2</sup> and for B4 concrete between about 1.4 and  $2.4 \text{ kg/m}^2$  (Fig. V-42). There were also significant differences in the scaling amounts within some test series (five CDF plates). In this case the standard deviation of the scaling was between about 8.5 and 60 % of the average value.

The experiences gained corresponded to findings of other institutions and were brought to the attention of the Federal Highway Institute (BASt). The significance of the CDF test XF2 remains to be seen. According to the current findings of the Research Institute of the Cement Industry and other centres, a practical evaluation of concretes composed according to the descriptive rules for exposure class XF2 cannot be expected in all cases.

## Freeze-thaw resistance of aggregates in concrete

In the context of the IGF project no. 15213 N, the Research Institute of the Cement Industry and the Federal Institute for Materials Research and Testing (BAM) investigated the influence of aggregate on the freeze-thaw with and without de-icing salt resistance of concrete in freeze-thaw laboratory tests.

The reason for the project was the assessment of the freeze-thaw with and without de-icing salt resistance of aggregates could lead to a different classification with laboratory tests on the aggregates and in concrete depending on the test method and limit values applied. So far, no form of testing of the freeze and freeze-thaw with de-icing salt resistance on the aggregates could rule out the fact that the aggregate may behave differently in this test compared to the subsequent behaviour in a structure when it is embedded in concrete.

Concretes with a similar concrete composition, in which the aggregates were varied, were used to estimate and evaluate the freeze behaviour of concrete depending on the aggregates used. Although the properties of the investigated aggregates differed in part, no clear correlation could be established between the fresh and hardened concrete properties and the aggregates.

The frost resistance of the concretes was tested using test methods and test surfaces by applying freeze-thaw with and without de-icing salt strains.

The investigations performed showed that the approval criteria in the aggregate testing in the freeze-thaw with and without de-icing salt tests did not always correlate with the results of the aggregates testing in the concrete. Some of the investigated aggregates were classified as unsuitable for use in concrete based on the classification of an aggregate in a freeze-thaw with or without de-icing salt resistance category with a standard freeze or freeze-thaw with de-icing salt test. However, the aggregates did not always behave accordingly in the concrete test. A general correlation between the hardened concrete values and the struc-





ture characteristics and moisture content could not be derived. The compressive strength, flexural strength and tensile splitting strength, carbonation depth, air pore characteristics, water absorption and mercury porosimetry were investigated, among others. **Fig. V-43** and **V-44** provide an example of the hardened concrete test and the freeze-thaw test on concrete with various aggregates. **Table V-7** displays the results of the freeze-thaw tests on concretes with various aggregates and the evaluation based on the relevant test methods for the currently assigned approval criteria.

An approval criterion for concretes for the construction of hydraulic engineering structures includes 1000 g/m<sup>2</sup> as the maximum permitted scaling on cast test surfaces after 28 freeze-thaw-cycles in the CIF test. The reduction of the relative dynamic modulus of elasticity is also an important approval criterion. These criteria relate to the cast test surfaces. The investigations showed that an impact on the test surface (cast and sawn surfaces) could not be determined in the CIF test. The testing of the concretes depending on the aggregates for pure freeze stresses with the reference test (slab test) also showed no differentiation.

The concretes investigated in the CDF test showed that the concrete scaling may depend on the aggregate. Aggregates with high FTS values according to DIN EN 1397-1 displayed high amounts of scaling of the concretes manufactured after 28 freeze-thaw-cycles in the aggregates testing. These results were confirmed with the reference test methods (slab test). With regard to the freeze-thaw with de-icing salt resistance, it was shown that, despite comparable water absorption, the sawn test surfaces had considerably higher surface damage than the cast test surfaces.

It was also determined that concretes that were manufactured with unsuitable aggregates pursuant to the aggregate freeze-thaw testing displayed an improved behaviour in the freeze-thaw laboratory test by reducing the water-cement ratio and providing additional expansion space by using air entraining agents.

The non-destructive investigations using the  $\mu$  x-ray 3D-CT enabled the internal microstructure status in concrete to be visualised, including the visualisation of the internal crack formation in the event of low amounts of freeze damage. A correlation between the findings of the  $\mu$  x-ray 3D-CT and the ultrasonic measurements was also established. The influence of preliminary damage of aggregates on the damage progression could also be represented for certain concretes. For example, it was determined that for concretes with gravel as coarse particles, damage was frequently detected in the ITZ (Interfacial Transition Zone) and that for concretes with crushed stone the damage emanated from

the aggregate and continued into the matrix. The use of  $\mu$  x-ray 3D-CT opened new possibilities for analysing freeze-thaw-induced damage processes in concretes.

In conclusion, the research project expanded the current knowledge of testing aggregates with regard to their freeze-thaw with and without de-icing salt resistance in concrete. Exposure tests on concretes that were investigated in the laboratory as part of this project are part of a further IGF research project. The results of the exposure tests will enable the significance of laboratory tests to be better evaluated in the future.

## Special applications

Ultra high performance concrete – Correct measurement of the autogenous shrinkage cracking propensity Starting situation

Ultra high performance concretes contain considerably less water than would be required for the complete hydration of their reactive components. Depending on the composition, the relative humidity in the pore void can significantly reduce at a very early stage of strength development. This type of internal drying is connected with autogenous shrinkage, which can lead to cracks in the event of expansion impairment (restraint stress). Cracks may impair the durability, density and the aesthetic impact of components manufactured from ultra high performance concrete. It is therefore of fundamental importance that autogenous shrinkage, the restraint stresses and the related risk of crack formation are reduced to the greatest possible extent.

To date, there is no uniform method for the experimental quantification of the autogenous shrinkage cracking propensity. The restraint stress and tensile strength ratio is usually determined. It is assumed that the cracking propensity is lower at lower ratios. However, the determination of both parameter methods is already extremely difficult.

The two predominant parameter methods for measuring restraint stresses are the fixing of prismatic test specimens and the ring test. The ring test involves a steel ring with internal strain gauges that prevent the concrete ring from contracting. The compression of the steel ring allows the tension in the concrete to be calculated (**Fig. V-45**).

Certain experimental problems that arise in the fixing method are prevented in the ring test. The relatively simple structure





Fig. V-43: Investigating similar XF3 concretes with variable aggregates with sawn test surfaces



		Results of the freeze-thaw testing of the aggregates (AiF				So	caling in g/m <sup>2</sup>	Rel. dyn. modules of elasticity in %				
			gregates and AiF			C		CEM I 32,5 R				
		13212		13214)		Cement	Cement content: 320 kg/m <sup>3</sup>					
s	u					Water/	cement ratio: (	),50		Water/cement ratio: 0,50		
gate	viatio				No ar	tif. AP	Air conte	ent: ≥ 4.5 % b	y volume	No artif. AP		
Aggregates	Abbreviation				Exposure	class: XF3	Exj	posure class: X	KF4	Exposure	class: XF3	
A	Al					,	Fest method			Test method		
		FTC	FTC	MS	CF/	CIF	CI	OF	Reference	CF/CIF		
		value	value	value	Cast surface	Sawn surface	Cast surface	Sawn surface	Slab	Cast surface	Sawn surface	
		i	n mass %	, 2	28 FTC	28 FTC	28 FTC	28 FTC	56 FTC	28 FTC	28 FTC	
	K26	0.3	3.5	1.8	130 98		326	362	116	93	98	
Gravel	K4	0.3	2.4	7.1	n.a.	169	n.a.	522	193	n.a.	98	
Gra	K5	0.5	13.2	12.8	n.a.	228	579	829	989	n.a.	94	
	K9	0.7	30.6	37.6	93	75	1030	1121	1076	99	96	
tone	N11	0.6	1.2	4.6	n.a.	75	n.a.	134	87	n.a.	94	
Crushed stone	N19	1.0	29.1	9.7	150	108	692	1781	1846	77	72	
Crus	N22	2.7	18.1	11.5	n.a.	95	n.a.	1316	400	n.a.	72	
Approval criteria fu				al criteri	a fulfilled		FTC: DI	IN EN 1367-1	; FTS: DIN EN	N 1367-1 annex	В	
Approval criteria				al criteri	a not fulfilled		MS: DIN EN 1367-2 n.a. not available					

Table V-7: Results of the freeze-thaw-tests depending on the aggregate and evaluation based on approval criteria

XF3: High water saturation without de-icing agent

Criterion for aggregates according to DIN 1045-2: F2 according to DIN EN 12620; FTC value ≤ 2 mass %

Criteria for concrete CF/CIF: Scaling (formed surface)  $\leq 1,000 \text{ g/m}^2$  in accordance with 28 FTC according to BAW; rel. dyn. modulus of elasticity (formed surface):  $\geq 75 \%$  according to BAW and 80 % according to RILEM TC 176

XF4: High water saturation with de-icing agent

Criterion for aggregates according to DIN 1045-2: MS18 according to DIN EN 12620; MS value < 18 mass % and alternative FTS value < 8 mass %

Criteria for concrete CDF and reference: Scaling: CDF and cast surfaces:  $\leq 1500 \text{ g/m}^2$  in accordance with 28 FTC according to BAW; Reference:  $\leq 1,000 \text{ g/m}^2$  according to 56 FTC Swedish Standard SS137244 or  $\leq 500 \text{ g/m}^2$  in accordance with 56 FTC according to DIN 1045/2 Annex U

also allows for a large number of tests to be performed, which is a great benefit from a methodological point of view. The disadvantage is that it is a passive test method. Expansions and stresses cannot be controlled, so conventional creep and relaxation tests are not possible. However, an additional stress component can be created, e.g. by drying the concrete. This allows the severe impact of viscoelastic deformation components on the restraint stresses to be investigated, especially at a young age. Restraint stress and cracking propensity also depend on the progression of the hardening temperature – however, in a manner that was previously barely understood. In principal, the tensile strength as resistivity can also be determined on fixed prisms. However, testing the tensile splitting strength and the flexural strength is considerably easier. In particular, at this very young age it is currently unclear how the results of this testing can be converted into centric tensile strengths.

#### Investigations in the Research Institute of the Cement Industry

The investigations were performed on unreinforced ultra-large performance concretes with a maximum particle size of 0.5 mm and at an approximately constant concrete temperature of 20 °C. A Portland cement CEM I 52,5 R-HS/NA was used. Apart from the reference concrete (composition see Table V-8), variants with super-absorbent polymers (SAP), a shrinkage-reducing admixture (SRA) and a high fraction of blastfurnace slag meal (HSM) were investigated.

Initially, the cone shrinkage test method was used to measure the free autogenous shrinkage. The start of the resistant stresses in parallel ring tests was used as the initial starting point (time zero). The autogenous shrinkage reduced particularly dramatically compared to the reference cement (24 h: 0.7 mm/m) for the super-absorbent polymers (0.25 mm/m) and the shrinkagereducing admixture (0.35 mm/m).

The restraint stresses were determined using the ring test. A very large part of the stresses expected pursuant to Hooke's law were relieved by creeping and relaxation. The relaxation characterised at a very early stage was the key reason behind the fact that no crack formation was detected even in the event of high autogenous shrinkage.

The tensile splitting strength was tested in order to determine the resistance against crack formation. The results were converted into centric tensile strengths using a non-linear function depending on age. The applicability of the conversion function was confirmed by the ring tests in which the concrete was severely dried to fracture.

The reference concrete displayed a high cracking propensity of up to 0.7. The cracking propensity was more than halved by the super-absorbent polymers and the shrinkage-reducing admixture. The maximum value for concrete with a high fraction of blastfurnace slag meal was about 0.5. Despite the strong influence of viscoelastic deformations there was a roughly linear correlation between the autogenous shrinkage and the maximum autogenous shrinkage cracking propensity (Fig. V-46).

However, the dependence on the temperature of these investigations performed at 20 °C does not allow an ultimate evaluation of the cracking propensity under typical construction conditions.



#### Table V-8: Composition of reference concrete 1A

Cement c (CEM I 52,5 R-HS/NA)	800 kg/m <sup>3</sup>
Water w	168 kg/m <sup>3</sup>
w/c	0.230
Silica fume s	130 kg/m <sup>3</sup>
w/(c+s)	0.198
Super-plasticiser	24 kg/m <sup>3</sup>
Quartz sand (0.125-0.5 mm)	1019 kg/m <sup>3</sup>
Quartz meal (0-0.125 mm)	220 kg/m <sup>3</sup>



In order to provide an empirical model of the autogenous shrinkage cracking propensity as a function of temperature and load level in the future, an analytical stress solution for a non-isothermal ring test and a new approach to investigating the residual carrying capacity and relaxation capacity using non-passive ring tests were proposed. In this case an additional stress component is created either by additional drying shrinkage or by the targeted heating of concrete and steel rings.

cracking

The research project based on these results was able to proceed due to subsidies from priority program 1182 "Sustainable construction with ultra high performance concrete" from the German Research Foundation (project duration from October 2005 to September 2011).

## Adhesion of textile-reinforced concrete - Development of cement-based adhesives

The functional properties of TiO<sub>2</sub>-modified textile-reinforced concretes were investigated in the Research Institute of the Cement Industry as part of a joint research project under the direction of the Institute of Building Materials Research of the RWTH Aachen University (ibac). The impact of ultra-fine TiO2 particles on the decomposition of pollutants (NO<sub>x</sub>) and the self-cleaning effect under UV light is currently being researched at the RWTH Aachen itself. The objective of the subproject in the Research Institute of the Cement Industry is to investigate cement-based adhesives with which TiO2-modified, superhydrophilic façade elements can be securely adhered.

Table V-9: Composition of adhesives S and V modified with classified fine blastfurnace slag and
fine fly ash

Raw material in kg/m <sup>3</sup> and water/cement value	Adhesive S	Adhesive V
CEM I 52,5 N	467.5	467.5
Fly ash (coarse)	280.5	280.5
Fly ash (fine)	-	187.0
Blastfurnace slag (fine)	187.0	-
Water	345.0	345.0
Quartz sand	765.0	765.0
Dispersion powder	51.0	51.0
Cellulose methyl ether	5.0	5.0
w/c	0.74	0.74

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Fig. V-47: Adhesive tensile strength after 28 days of storage under various storage conditions

## Development of the adhesive compositions

Adhesion is being investigated in the research project by testing the adhesive tensile strength according to DIN EN 1348 and the shear adhesion strength in compliance with DIN EN 12003. An ordinary flexible thin-bed mortar according to DIN EN 12004 (flexible mortar) is used as a reference for the development of cement-based adhesives. The particle size distributions of the adhesives were optimised based on a UHPC composition [1]. Classified fine blastfurnace slag and classified fine fly ash as well as ordinary (coarse) fly ash were used for this purpose. A dispersing agent and a cellulose methyl ether were also added to the adhesives to improve the adhesive properties. The compositions of the adhesives modified with fine blastfurnace slag (S) and with fine fly ash (V) are indicated in Table V-9.

#### Test prodecure and results

Base plates made of  $TiO_2$ -modified fine concretes were manufactured in the ibac in order to determine the adhesive tensile strengths and the shear adhesion strengths. Ceramic tiles were adhered to the base plates using the adhesives to be tested. The tensile adhesion strength was tested pursuant to DIN EN 1348.

Two fine concrete plates with dimensions of 100 mm x 100 mm x 10 mm were adhered to each other with a 6 mm displacement in order to determine the shear adhesion strength in compliance with DIN EN 12003. All test specimens were stored in compliance with DIN EN 1348. For the dry storage, the adhered test specimens were stored in a 20/65 climate until the 28th day after adhesion. For the water storage, the test specimens were subjected to dry storage for seven days and then under water at 20 °C until testing after 28 days. The hot storage took place for 14 days in a drying cabinet at 70 °C after a 14-day dry storage period. The test specimens were cooled down to room temperature prior to testing. For the freeze-thaw-cycle storage, the test specimens were initially subjected to preliminary storage pursuant to the water storage. Twenty five freeze-thaw-cycles then took place at a rate of one freeze-thawcycle every day. **Fig. V-47** shows the adhesive tensile strengths after dry, hot, water and freeze-thaw-cycle storage. Adhesive S, modified with classified fine blastfurnace slag, exhibited up to 75 % higher tensile strengths than the reference adhesive in all the storage types.

**Fig. V-48** shows the shear adhesion strengths after dry, hot and water storage. The corrected average values pursuant to DIN EN 12003 are represented, as this test frequently (up to 50 % of all test specimens in a test series) led to bending failure of the test specimens instead of shear failure of the glue joint. Similar to the adhesive tensile strengths, adhesive S, modified with classified fine blastfurnace slag, exhibited a higher strength than the reference adhesive regardless of the storage type.

Besides the impact of classified fine blastfurnace slag and classified fine fly ash on the adhesive properties of UHPC-based mortars, the impact of UV irradiation of the TiO<sub>2</sub>-modified fine concrete test specimens on the adhesive properties of the mortar was also investigated. In this case, the concrete test specimens were irradiated with a UV lamp until they obtained superhydrophilic properties (contact angle of a water droplet on the surface  $\leq 10^{\circ}$ ). Ceramic tiles were adhered to the concrete test specimens immediately after irradiation and the adhesive tensile strength was determined after dry storage pursuant to DIN EN 1348. The adhesive tensile strengths after 2 and 28 days storage in a 20/65 climate are set out in Fig. V-49. The UV irradiation of the TiO2-modified fine concrete plates did not significantly influence the adhesive tensile strength at the age of 2 days and, in view of the high standard deviation, also at the age of 28 days.

#### Evaluation of the results

 $TiO_2$ -modified fine concrete test specimens can be adhered with cement-based adhesives based on organically modified UHPC compositions. The shear adhesion strength and, in particular, the adhesive tensile strength were greater than for the reference adhesive in the investigated storage types of dry storage in a 20/65 climate, hot storage at 70 °C, water storage at 20 °C and for freeze-thaw-cycle stresses.

Zilch, K., Mühlbauer, C.: Zum Fügen von Ultra-Hochfestem Beton (UHPC) durch Verkleben: Grundlegende Untersuchungen. VDI-Berichte, 1970, S. 37–46

The adhesive tensile strength correlated with the shear adhesion strength. The coefficient of determination  $R^2$  was approx. 0.8.

Superhydrophilic surfaces were reliably achieved when using TiO<sub>2</sub>-modified concrete compositions in a test series on the impact of UV irradiation on the concrete and adhesive properties. However, the superhydrophilic fine concrete surfaces had no significant impact on the adhesive properties when using cement-based adhesives based on organically modified UHPC compositions.

## Fair-faced concrete – Influences on the sedimentation stability

Fair-faced concrete is extremely popular. Building owners and architects use the concrete surface as element of style and creative expression of modern architecture. Smooth, low in pores and uniformly coloured fair-faced concrete surfaces having sharp edges are requested to an increasing extent. This becomes particularly obvious for representative structures.

## "Fair-faced concrete" joint research

Although much progress has been made in structural design, concrete technology and release agent manufacturing as well as formwork and construction technology over the past years, it was not always possible to manufacture uniformly coloured surfaces having low-porosity in a targeted manner despite the greatest care being taken in the planning and execution of fair-faced concrete. Phenomena such as marbling, clouding, patchy discolorations, pore accumulation and drag water effects can affect the visual properties of fair-faced concrete. There was a lack of systematically gained and scientifically based knowledge in order to explain the causes and mechanisms of these phenomena and to reduce effectively their occurrence. Two joint research projects were therefore performed on the issue of "fair-faced concrete" in an association of scientific experts and practical specialists. The "fair-faced concrete" joint research was conducted under the joint overall responsibility of the Deutscher Beton- und Bautechnik-Verein E.V. (DBV) and the Verein Deutscher Zementwerke (VDZ). The joint research was supported financially by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF) within the framework of Industrial Collective Research (IGF) of the Federal Ministry of Economics and Technology. The focus of the "fair-faced concrete" joint research was on the occurrence and reduction of discol-



Fig. V-48: Shear adhesion strengths after 28 days storage under various storage conditions



Fig. V-49: Adhesive tensile strengths with and without UV irradiation of the base plate prior to adhesion

orations in fair-faced concrete surfaces (VDZ) and on the integration of findings on the interactions between formwork, release agents and concrete surfaces in the process chain for the manufacture of fair-faced concrete (DBV).

## Research at the Research Institute of the Cement Industry

Influences of blastfurnace slag or limestone as main constituent of laboratory cements on rheological properties of cement paste and concrete as well as interactions with superplasticizers were investigated systematically in the Research Institute of the Cement Industry in a research project (IGF project no.: 15876 N) supported financially by the AiF. The investigations focussed on the reduction of discolorations in fairfaced concrete surfaces as a result of sedimentation. Investigations were carried out using cements with the same Portland cement clinker and sulphate agent components.

**Fig. V-50** displays the beneficial effect of the substitution of clinker in the cement with blastfurnace slag or limestone on the shear resistance of cement paste. When compared with the reference paste produced with Portland cement, the shear resistance of the respective cement paste was decreased with increasing proportion of blastfurnace slag S21 or limestone LL12 in the cement. The decreasing of the shear resistance was based mainly on a decreased yield value. The dynamic viscosity remained almost constant. A lower yield value of cement paste means an improved workability of the corresponding concrete.



Fig. V-50: Shear resistance of cement paste depending on the type and proportion of blastfurnace slag or limestone in the cement

Clayey components in limestone LL31, which is not generally used in practice, induced a relatively high water demand of the respective cements. This led to no significant beneficial effect on the shear resistance of the cement paste offset replacing the clinker in the cement of up to approximately 35 mass %. With an almost identical consistency compared to concrete produced with Portland cement, concretes made with cements with blastfurnace slag or limestone as additional main constituent besides clinker could be manufactured with lower water-cement ratio. A lower water-cement ratio improves the stability of concrete with regard to sedimentation when superplasticizer is used and therefore significantly reduces the risk of the occurrence of discolorations in fair-faced concrete surfaces. At the same water-cement ratio, cement pastes and concretes made with blastfurnace slag or limestone-containing cements were significantly more effectively plasticized than those made with Portland cement. But, the added quantity of superplasticizer must always be lower than the quantity necessary for maximum plastification (saturation point dosage) in order to achieve an optimal plastification and duration of plastification without sedimentation and discoloration in fair-faced concrete surfaces. The saturation point should always be determined using the applied raw materials and under practical conditions. The saturation point can be determined with the flow table test according to DIN EN 12350-5. The saturation point is exceeded if a clearly visible paste rim forms during the test.

## Concrete products

### Earth-dry concrete

Earth-dry concretes are used for paving blocks, plates, kerbs or concrete pipes, etc. Intensive vibration-compression compaction compacts the concretes in steel moulds and they immediately retain their form due to their green stability. If they are properly composed, the compacted concretes achieve a high strength and compactness as well as a high freeze/de-icing salt resistance.

#### Modified slab test

The regulations for concrete products, standard series EN 1338, 1339 and 1340, are currently being revised. The modified slab test is currently being trialled as a process for determining the freeze/de-icing salt resistance, in particular, due to large repeat comparison variations. The process is primarily distinguished from the slab test according to CEN/TS 12390-9 by the size and nature of the test areas, the preliminary storage of the test specimens, the testing age and the number of freeze-thaw cycles. Besides the test variation, it seems that primarily the sampling, the nature of the sample and the number of the samples are responsible for the, in part, large variation of the individual scaling. An increase of the number of test specimens from three to five and a representative sampling is therefore recommended. Experience and recommendations that lead to a high quality of concrete products are being intensely discussed together with the Betonverband Straße, Landschaft, Garten e.V. (SLG) in the VDZ/ SLG discussion group and should be considered in the regulations.

## Colour fluctuations and freezethaw resistance of concrete products

Barely any systematic findings exist on the causes of colour fluctuations. The above-mentioned discussion group therefore held extensive discussions on possible impacts by the concrete composition, the cement properties and the production technology on the colour fluctuations of concrete products. Systematic investigations were then performed by member companies and concrete product manufacturers.

Investigations on the impact of de-icing agents on the freeze-thaw resistance with de-icing agents of concrete products are currently in progress in a research project initiated by the SLG involving the SLG, VDZ and the Verband Beton- und Fertig-teilwerke (VÖB). Besides investigating the freeze/de-icing salt resistance, investigations on the resistance of concrete products to the crystallisation of de-icing agents in the event of alternating wetting and drying and to a chemical attack of highly concentrated chloride-containing de-icing agents and acetates at low temperatures are also scheduled.

## Screed mortar

The use of Portland-composite cements (CEM II) and blastfurnace cements (CEM III) is becoming increasingly important in the manufacture of cement bound screeds due to the constantly increasing environmental protection regulations. The VDZ investigated the influence of the cement type on the structurally relevant properties of screeds. Comparative investigations that were performed on cement bound screeds between 1998 and 2008 – with varying cement types but an otherwise similar composition of the screed and identical manufacturing and test conditions – were evaluated. For the investigations 40 screed mor-

tars manufactured with various compositions were used. 26 different cements of different origins were used. The determined properties provide an important data base for cement bound screed mortar.

In general, the higher meal fineness of CEM II and CEM III/A cements compared to CEM I may lead to a rise in the water demand of the cements in the standard testing. This effect generally has no influence on the water demand of mortar as the workability characteristics of mortar are predominantly defined by its composition and the properties of all the components. This was also confirmed for screed mortar. Other concrete technology-relevant properties were also confirmed for screed mortar, such as the fact that the stiffening, setting and hardening of the cement screeds can be delayed or accelerated by the temperature and regardless of the cement type, according to the recognised concrete rules.

Depending on the drying conditions, the screed has a moisture content that depends on the water content, the screed thickness and the environmental conditions. In practice, the moisture content is regarded as residual moisture. The moisture content was determined by kiln drying at 105 °C (Darr method) and using the calcium carbide method (CM method). The evaluation showed that the water-cement ratio has a significant influence on the drying of the screed under constant environmental conditions. The relative ambient air humidity is decisive for comparable water-cement ratios. As expected, the residual moisture determined using the CM method at the same test age under identical test conditions was lower than the residual moisture determined when drying at 105 °C. A clearly quantifiable correlation of the measurement results between the two methods could not be derived for different test specimens, storage conditions, test conditions and test ages. There is no systematic influence of the cement type. Fig. V-51 provides an example of the residual moisture in the event of kiln drying (105 °C) cement bound screeds. The results confirm the fundamental suitability of Portland cement, Portland composite cements and blastfurnace cements for the manufacture of screed mortar, as well as in other areas of concrete construction technology.

In May 2009, the results of the cooperation between the VDZ and the Bundesverband Estrich und Belag e.V. (BEB) led to a guideline for the manufacture of cement screed mortars for use in interior areas. This guideline secured the propagation of high



Fig. V-51: Residual moisture when kiln drying (105 °C) cement bound screeds (c between 270 and 320 kg/m<sup>3</sup>; w/c between 0.42 and 0.79; with and without additives)

quality cement screed construction and has been positively received in practice.

As part of the discussions between the VDZ and BEB regarding the technical exchange of experiences it was determined that issues relating to the drying behaviour of cement screeds and suitable measuring methods had still not been conclusively clarified. In light of this, in June 2011 the BEB commenced investigations on the drying of cement screeds with financial support and other involvement by VDZ member companies. Cement screeds with various mixture ratios, water-cement ratios and screed thicknesses were investigated. The influence of different cements and additives was reviewed. The final assessment is still outstanding. The VDZ is planning additional investigations in order to expand the data base (AIF project).

## Industrial concrete flooring

A requirement for the targeted manufacture of high quality industrial concrete flooring is a concrete composition that meets the particular demands of, for example, the sedimentation stability for this construction.

In the IGF research project no. 16328 N, the Research Institute of the Cement Industry is performing investigations with the aim of creating recommendations for the targeted manufacture of concrete flooring. Besides tests on the bleeding water of the concrete, investigations are also being carried out to determine the structure of the surface mortar and to clarify the stiffening and setting behaviour.

The preparation and evaluation of a practical database by surveying construction sites provided initial practical reference values for the concrete compositions with regard to laying and mixing stability. The construction required a laying consistency (flow table spread) of approx. 54 cm and a bleed water quantity (DBV Eimer test) of about 3 to 5 kg/m<sup>3</sup>. Some activities in the project, e.g. the site supervision, are performed by the Institut für Baustoffprüfung und Fußbodenforschung (IBF) in Troisdorf.

Concretes with varying cement contents, water-cement ratios, powder content and grading curves were investigated in the Research Institute of the Cement Industry. It was shown that the use of CEM II and CEM III/A cements prevented bleeding compared to CEM I cements. Increasing the paste content by increasing the cement content led to increased bleed water quantities, while the addition of quartz meals led to reduce the bleeding water. Increased bleeding was detected as the water-cement ratio increased. The bleeding water also in-



Fig. V-52: Comparison of an optimised concrete composition in the laboratory and for practical concreting in winter (CEM II/B-S 42,5 N; c = 340 kg/m<sup>3</sup>; w/c = 0.50; admixture: Combination of melamine and naphtalene sulphonates)



creased as the maximum particle size of the aggregate increased.

Systematic investigations on segregation propensity and stability were performed with a typical concrete composition for industrial concrete flooring by varying the cements, admixtures and grading curves. The optimisation of the concrete composition in order to reduce the sedimentation and segregation propensity with regard to the laying consistency and simultaneous compliance with the above-mentioned bleed water quantity was achieved by using concrete measures such as grading curve optimisation in the sand.

The manufacture and investigation of concrete plates with dimensions of 50 cm x50 cm in the laboratory were used to prepare for construction site tests.

The visual evaluation of the concrete cross-section showed paste accumulation on the surface in some cases depending on the grading curve applied. The concrete composition was then further modified in order to attempt to fulfil all the practical requirements up to the pumpability of the concrete.

In the context of a practical concrete manufacture, concrete was delivered to the IBF by a ready-mixed concrete works as recommended by the Research Institute of the Cement Industry. Test surfaces with dimensions of 4 m x 4 m were manufactured. The influences of the thickness of the areas, the manufacture (mixing and vibration times) and the smoothing were investigated. The results showed that the concrete composition optimised in the laboratory also met the requirements for construction in practice (**Fig. V-52**).

The overall assessment of all the investigation results is currently still outstanding. The end of the test series will provide practical recommendations for the targeted manufacture of industrial concrete flooring.

## Traffic route engineering

Forecasts predict a rise in passenger traffic and, in particular, the transport of goods (Fig. V-53). The major fraction of the transport of goods will be on the roads and lead to increased stressing of the German highway network by heavy-load traffic. Of particular importance in this regard is durable and economic construction with long service lives and low construction and maintenance costs, as well as high environmental compatibility. Concrete construction offers a solution. Concrete roads are distinguished by their high durability, deformation stability and grip, as well as noise reduction and economy (long service life and low maintenance expense) and are especially suited for the construction of highways with a high proportion of heavy-load traffic. Construction in municipal road areas should also continue to be developed for concrete construction, and asphalt/concrete combination constructions should be tested.

## Asphalt on concrete combination construction method

Concrete and asphalt pavements with dense structures are classified as equivalent with regard to noise reduction, only open pore asphalts are quieter. One advantage of asphalt construction is that the pavements can be laid quickly and renewed by layers. Disadvantages include rut formations and the higher maintenance expenses. The VDZ "Traffic engineering" task force compiled a progress report "Thin asphalt paving on concrete surfaces (DAB)" in order to document previous experience with the combination construction. This construction has been used for many years and is now intended for the construction of new highways. In contrast to road maintenance, the asphalt protective coating (e.g. open pore asphalt or mastic asphalt) will be applied to a new concrete pavement rather than an old, damaged pavement. The concrete pavement assumes the load bearing function over a long period, while the easy-toreplace wear layer determines the pavement properties (grip, noise reduction). The addition of an open pore asphalt protective coating on top of the concrete pavement allows concrete to be used in particularly noise-sensitive areas. This is not currently possible with the conventionally dense standard concrete construction method with exposed aggregate texture. When the acoustic properties or the grip of the asphalt protective layer no longer correspond to the requirements, the wear layer can be milled off and replaced. As a result of the low layer thickness of the asphalt paving of only about 3 to 5 cm, there is no risk of rut formation as is the case for conventional asphalt paving. The construction of a trial route is planned in order to gain additional experience. Continuously reinforced concrete paving has already been covered with an asphalt layer in the BAB A5 area.

## Concrete in municipal road construction

Concrete construction in Germany is currently poorly represented in municipal areas. The expansion of the area of application could therefore unlock a great market potential. This includes concrete road pavements in inner city areas such as roundabouts, bus stops and bus lanes. Additional examples include inner city intersections, heavily trafficked access roads into large cities or covering damaged asphalt pavements with concrete (whitetopping). Ruts or deformations in the wearing course often arise during periods of high temperature in congested areas (e.g. at crossings, bus bays or bus lanes) on heavily stressed asphalt roads. Restorations require the milling off and relaying of the asphalt wearing course. An alternative is the permanent reconstruction of damaged asphalt layers using whitetopping construction. This removes the old, damaged asphalt coating. The surface is then cleaned and a high quality paving concrete is laid in accordance with the cutting depth, which ensures a good bond. This technique uses the bearing capacity of the remaining asphalt layers and ensures deformity resistance by overlaying with the thin concrete paving (approx. 10 cm). Joints are cut into the concrete after laying in order to prevent the formation of cracks. Fig. V-54 displays an example of an overlayed entry and exit ramp at a motorway junction, whose damaged asphalt paving was overlayed using whitetopping construction.

Bus bays or intersections of heavily used roads can also be produced in concrete construction. Roundabouts have been increasingly laid with concrete road paving in previous years. The reason for this is that roundabouts and the entry and exit areas of bus bays are exposed to high shear deformations due to the heavy traffic. Asphalt constructions are frequently not able to withstand these stresses, requiring resurfacing work. In contrast, concrete pavements are deformation-resistant and guarantee a long service life with low maintenance requirements. They therefore represent an economic solution, even if the initial investment is slightly more expensive. Due to the high shear loads, the concrete pavement thickness in roundabouts is increased compared to customary dimensions. The concrete is laid with a road paver or manually inserted into a mould. After laying, the concrete surface is textured with a broom and cured.

Codes of practice are being prepared in the FGSV task force "City and country roads and special road pavements" in order to simplify the construction. Regulations are being prepared for roundabouts, bus lanes and whitetopping constructions, etc. Pilot projects will be implemented in order to gain experience in all areas, from planning through to execution. The equipment technology must be adapted to the local conditions. The construction measures can be implemented by regional construction



Fig. V-54: Whitetopping concrete pavement for a motorway connection

companies. However, this requires sufficient experience in concrete construction. The findings will be documented and published after the conclusion of the pilot projects.

## Regulations

The current regulations for concrete constructions in road construction are divided into three parts. The first two parts "Technical supply conditions for construction materials and construction material mixtures for road bases with hydraulic binders and concrete pavements" (TL Beton-StB 07) and "Additional technical contractual conditions and guidelines for the construction of road bases with hydraulic binders and concrete pavements" (ZTV Beton-StB 07) were provided in mid-2008. In 2010, an FGSV task force, under the leadership of the Research Institute of the Cement Industry, prepared the third part of the regulation, the TP Beton-StB 10 (Technical inspection requirements for road bases with hydraulic binders and concrete pavements). The TP Beton regulations contain the inspection requirements for all hydraulically bound layers for the construction materials, construction material mixtures, laying mixtures, the execution and the ultimate performance. The compressive strength of pavements was determined on drill cores after 60 days pursuant to the TP Beton regulations. The test result is adjusted by time factors for a subsequent test period. The time factors consider the re-hardening of the concrete at a later test age by multiplying the test result with the factor. They were determined as PZ 35 F as standard, given that pavement cement was used. Additional requirements have since been determined with regard to the cement properties as blastfurnace slag-containing cements can now also be used. Cements in strength class 42,5 are now predominantly used. The old factors (Table **V-10**) were therefore not transferred to the TP Beton. The time-dependent compressive strength development of concretes were determined in an experimental program by the Ruhr Universität Bochum and the Research Institute of the Cement Industry in order to review the validity. Eight concretes ( $c = 350 \text{ kg/m}^3$ ) were produced with eight current pavement cements with various cement types and strength classes and the compressive strengths were determined after 28, 60, 120, 180 and 360 days. After 28 and 60 days, the four concretes with CEM II or CEM III cement had a

 Table V-10: Time factors when considering the testing age

Testing	Time factors							
age in days	Old factors	New factors						
	(standard cement PZ 35 F)	CEM I	CEM II/III					
60	1.00	1.00	1.00					
120	0.94	0.92	0.95					
180	0.90	0.88	0.93					
≥ 360	0.85	0.82	0.92					



slightly higher average strength than the four concretes with CEM I cement (**Fig. V-55**). This is due to the finer grinding of the CEM II and CEM III cements to reduce the curing sensitivity and the comparably low alkali content of the CEM I cements. A rapid strength development is beneficial as the concrete fulfils the desired requirements as quickly as possible and traffic approval can then be provided. The adopted, updated time factors in the FGSV "Road construction materials" committee will be introduced by the BMVBS.

## Standardisation

## Revision of the European concrete standard EN 206-1

At the time of publication of this Activity Report, the draft of EN 206 was at the CEN-Enquiry stage. As part of this survey, CEN member states are required to indicate whether the draft standard would be acceptable in the formal vote, or what would have to be changed in order to be accepted by the relevant country. A series of previously unpublished CEN documents will therefore have to be quoted and obviously no statements can yet be made about the final version of the standard. Some fundamental points that are highly likely to be incorporated into the standard are explained in the following by way of example. These are based on the draft standard currently in the enquiry stage. The present Part 9 (self-compacting concrete) is expected to be integrated into the standard pursuant to the current draft, which will result in the removal of the additional number "1" in the EN 206 designation. New included was a table on the basic aggregate requirements and a reference to the technical report for the prevention of a damaging alkali-silica reaction. The annexes have also been revised and supplemented. Examples include annexes D (additional

concrete requirements for special foundation engineering activities), E (use of coarse recycled aggregates), F (concrete composition limit values), G (self-compacting cement), H (application of "control charts") and J (Special Spanish rules for proof of conformity).

#### Use of cements

Section 5.1.2 of EN 206 specifies the general suitability of cements according to EN 197-1 (common cements) for manufacturing concrete according to EN 206. Furthermore, the cements of EN 14216 (very low heat special cements) and EN 15743 (supersulphate cement) can also be used depending on the application requirements (e.g. exposure class, component dimensions). EN 206 does not contain any additional, specific, standardised determinations on the application of individual cement types. The cement must be selected from cements whose general suitability has been verified pursuant to 5.2.2 "Selection of cement", whereby the following must be considered:

- execution of the work
- intended use of concrete
- curing conditions (e.g. heat treatment)
- dimensions of the structure (the heat development)
- environmental conditions to which the structure is to be exposed
- potential reactivity of the aggregate to the alkalis from the constituents.

The recommendations for the concrete composition contained in the informative Appendix F will now presumably apply to CEM I and CEM II cements. This would implement at least part of the practice already employed for many years in Germany with the normative tables F.3.1 to F3.4 of using cements with several main constituents – sometimes even beyond the

currently valid German regulations – in the form of a recommendation at the European level. With the revision of EN 206 and the adjustment of DIN 1045-2 that will then be necessary the areas of application for cements will also in future be laid down precisely at the national level in Appendix F of DIN 1045-2.

## Use of concrete additions

In the CEN member countries additions are used in concrete within the framework of different principles or concepts. Working group (TG) 5 of the CEN/TC 104/SC1 has summarized the principles and concepts in a report that will be published as a CEN Technical Report (CEN/TR) [2]. A precondition for application of the principles and concepts is conformity of the concrete addition to one of the product standards harmonized at the European level and listed in **Table V-11**.

#### k-value concept

As a descriptive regulation – i.e. without further tests other than proof of conformity of the concrete – the k-value concept allows a stated addition content to be counted towards the (equivalent) water-cement ratio or minimum cement content. The present draft of EN 206 provides for k-values given in Table V-11 to be used with CEM I and CEM II/A cements.

## *Principle of "equivalent concrete performance"*

In all probability the principles of the "equivalent concrete performance concept" (ECPC) will be included in Section 5.2.5.3 of EN 206. This concept permits specific deviations from the descriptive requirements specified at the national level for the

<sup>[2]</sup> CEN/TC 104/SC1 N717: Draft CEN/TR "Use Of k-Value Concept, Equivalent Concrete Performance Concept And Equivalent Performance Of Combinations Concept" (Status as of 26.10.2011); unpublished

Concrete addition	Permissible types of cement acc. to EN 197-1 (c)	k-value	Amount of addition that can be counted towards the $(w/c)_{eq}$		
Fly ash (f) acc. to EN 450-1	CEM I	0.4 1)	$f/c \le 0.33$		
	CEM II/A		$f/c \le 0.25$		
Silica fume (s) acc. to EN 13263-1	CEM I and CEM II/A (without CEM II/A-D)	2,0 <sup>1)</sup> for $(w/c)_{eq} \le 0.45$ 2,0 <sup>1)</sup> for $(w/c)_{eq} > 0.45$ except for XC and XF where ks = 1.0	s/c ≤ 0.11		
Ground granulated blast furnace slag (h) acc. to EN 15167-1	CEM I and CEM II/A	0.6 <sup>2)</sup>	$h/c \le 1.0$		

 Table V-11: Proposal for the k-value concept EN 206 in accordance with [5]

<sup>1)</sup> normative

2) recommended value

maximum water-cement ratio and the minimum cement content during joint use of a cement and an addition with clearly defined origin and properties. The proof of equivalent performance is obtained with the aid of durability tests on concrete with the appropriate material combination compared with a reference concrete for the corresponding exposure class(es). In the Netherlands, for example, the procedures, criteria and test methods for the ECPC are laid down in the national guideline CUR Recommendation 48 [3]. The ECPC has been used for about fifteen years in the Netherlands for the use of fly ash and cement (CEM I or a parallel use of CEM I and CEM III) and for about ten years for ground granulated blastfurnace slag and cement. The methods and requirements for using fly ash or ground granulated blastfurnace slag and fly ash are described [2] in the Netherlands assessment guidelines for the BRL 1802 certification [4].

## Principle of "Equivalent performance of cement/addition combinations"

The "Equivalent performance of combinations concept" (EPCC) lays down a procedure with which the basic requirements are established for using a combination of a certain cement (as a rule CEM I Portland cement) and a certain addition in the same way as a type of cement of comparable composition conforming to EN 197-1. In

[4] Dutch assessment procedures for certification BRL 1802. Kiwa-BMC, PO Box 150, 2800 AD Gouda NL Great Britain and Ireland the concept includes compressive strength tests on mortars as defined in EN 196-1. In Portugal, however, the amount of the combination of a cement and addition that corresponds to a cement type conforming to EN 197-1, is determined mathematically for the combination. The respective application rules stipulated at the national level for this cement type are then applied. The "Equivalent performance of combinations concept" (EPCC) differs fundamentally from the "Equivalent concrete performance concept" (ECPC) in that the proof of durability is not provided in the specific case by durability testing but is based on the practical experience of the country in which it was used within the framework of the corresponding national application rules (concrete composition, concrete cover and curing) and under the corresponding climatic conditions, building traditions and safety requirements.

## Use of aggregates

In a similar way to the German DIN Technical Report 100 "Concrete", Appendix U of the current draft standard [5] contains a table of "minimum requirements" for the aggregates that are regarded as "generally suitable" for concrete conforming to EN 206. In particular, the proposals for the minimum requirements for the particle shape "FI<sub>40</sub>" and for the particle strength "LA<sub>50</sub>" (prEN 206, Table 15) still need to be discussed. There are comments on this from some countries (including Germany) and from ERMCO, the European Readymixed Concrete Organization. Basically, however, there is agreement in the CEN/ TC 104/SC1 technical committee that "minimum requirements" are necessary because in the course of its onward development the European aggregates standard now permits aggregates with a general suitability for producing concrete conforming to EN 206 that has not yet been proved or about which the CEN/TC 104/SC1 has doubts. The relevant working group (TG) 19 is also to draw up minimum requirements for light-weight aggregates conforming to EN 13055.

## **Conformity control**

The relevant working group (TG) 10 had started its work with the stipulation that the rules for factory production control and the conformity control of concrete in EN 206-1 have in principle proved successful and that there is therefore no need to make any fundamental changes to the system. In spite of this the TG10 has looked more closely again at the following aspects [6]:

- possible adoption of definitions for "production day" and "production week"
- number of test results and evaluation period
- use of control charts as an alternative to the "classical" conformity control
- conformity control and identity testing for parameters other than compressive strength
- conformity criteria and factory production controls for fibre content.

The current draft standard [5] contains, among other things, the recommendations listed in **Table V-12** with respect to the above-mentioned aspects.

Also worth mentioning is the new informative Appendix J of EN 206 that allows Spain to stipulate coefficients greater than 1.48 for the conformity control of the concrete compressive strength in Method B. In practice, Spain continues to use the value of 1.64 that earlier was also stipulated in Germany. The reason for this is that according to a notified Spanish rule the consumer's risk must never be greater than 50 %.

<sup>[3]</sup> CUR-Aanbeveling 48:2010: Assessment of the suitability of new cements for use in concrete and of the equivalent performance of concrete with additions. Procedures, criteria and test methods

<sup>[5]</sup> prEN 206:2012:E Concrete – Specification, performance, production and conformity (March 2012); unpublished

<sup>[6]</sup> CEN/TC 104/SC 1 N 687: Report to CEN TC 104 SC1 on activities in TG 10 "conformity evaluation" (June 2011); unpublished

## Table V-12: Proposed alterations to the topic of "conformity control" [5,6]

Production day	The definition "production day" will not be included. No unanimity was obtained at the European level. The definition will be at the national level as before.
Production week	The term "production week" has been replaced by a given number of production days.
Number of test results and evaluation period	EN 206-1 had previously contained no limit to the number of test results. Due to this vagueness the concrete producers have sometimes used standard deviations that are not representative of the proof period.
	Recommendation for plants with low testing frequency:
	number of test results in three months $\leq 35$ :
	proof with $15 \le n \le 35$ in twelve months at most
	Recommendation for plants with high testing frequency:
	number of test results in three months $\geq 35$ :
	proof period three months at most
Introduction of Method C: control charts	It is recommended that the system of "control charts" should be integrated into the standard as Method C alongside the "classical" methods of conformity control for the "initial production" (Method A) and for "continuous production" (Method B). Method C combines the proof of conformity in the classical sense with an instrument of factory production control [7]. It may only be used if the concrete production is subject to third-party inspection or the application of the method has been expressly agreed between the specifier and the concrete producer. For the system that is to be introduced it must be proved that the average outgoing quality limit (AOQL) is not greater than 5.0 %. This condition is considered to be fulfilled if the targets and requirements of the newly introduced Appendix H are met.
Conformity control and iden- tity testing for parameters other than compressive strength	Conformity criteria and criteria for the acceptance test based on individual values in the form of limit de- viations, relative to the specified value or class at the point of delivery, are proposed for the consistency, including that of self compacting concrete, the air content and the proof of fibre content/distribution (Table 23 and Sections B.4 and B.5)

Table V-13: Comparison of the application regulations for cements given in the national appendices to the European concrete standard EN 206-1 based on the example of a concrete for exposure class XF1

		·				CE	II M			CEN	M III	CEN	A 137	CE	ΜV
Country	max (w/c) <sub>eq</sub>	min c in kg/m <sup>3</sup>	CEM I	5	5	L	L	N	M	CEr	VI 111	CEN	110	CE	VI V
	( e)eq			А	В	А	В	А	В	А	В	А	В	А	В
Austria	0.55	300	х	х	х				(x)	х	(x)				
Belgium	0.55	300	х	х	х	х	х	х	х	х	х			(x)	
Denmark	0.55	150	(x)			(x)									
Finland	0.60	270	х	х	х	х		х		х	х				
Germany	0.60	280	х	х	х	х	О	(x)	(x)	х	х	О	(x)	(x)	(x)
Ireland	0.60	300	х			х									
Italy	0.50	320	х	х	х	х	х	х	х	х	х	х	х	х	х
The Nether- lands	0.55	300	х	х	х	(x)	(x)	(x)	(x)	х	х	(x)	(x)	(x)	(x)
Norway	0.60	250	х	х		х									
Great Britain	0.60	280	х	х	х	х				х	х	(x)	(x)		
x permitted				not mentioned											
(x) with restrictions				0	not	permitte	d								

## Compressive strength versus durability

The question about the extent to which the compressive strength of the cement, of the cement/addition combination or of the concrete can be used as a proxy criterion to provide information about the durability characteristics was also discussed during the preliminary work for the revision of EN 206. The question arose from the practice of dispensing with a specific check on

the durability in the context of descriptive application rules (e.g. use of the cements as specified in DIN EN 197-1 in accordance with Tables F3.2 to F3.4 in DIN 1045-2 or the use of combinations as specified in British Standard BS 8500-2 in accordance with the application rules in BS 8500-1) on the basis of strength-related proof of conformity for cement, combinations and concrete. In both cases this seems justified because of the extensive practical experience of the countries involved with which the materials have been used successfully within the framework of the respective national application rules (concrete composition, concrete cover and curing) as well as under the corresponding climatic conditions, building traditions and safety requirements.

<sup>[7]</sup> CEN/TC 104/SC 1 N 686: Use of control charts in the production of concrete (October 2010); unpublished

This procedure is not permissible with new materials without further testing of the durability characteristics. Direct transfer of the application rules of one country to the conditions in another country is also out of the question for the above-mentioned reasons. This is vividly illustrated by comparison of the application rules for cements in different countries using the example of exterior component concretes (**Table V-13**).

This shows that on the basis of nationally available and proven raw materials Italy permits the use of a significantly wider range of cements in exterior components than, for example, Germany. However, comparison of the concrete technology conditions shows that the preconditions for this in Italy (max. w/c = 0.50) are also different from those in Germany (max. w/c = 0.60).

Another example is the use of sulphate-resisting cements containing granulated blastfurnace slag as specified in DIN 1164-10 (HS) or EN 197-1 (SR) compared with combinations of ground granulated blastfurnace slag, used as a concrete addition, and Portland cement [8]. In contrast to the German experience with blastfurnace cements containing granulated blastfurnace slag (HS or SR cement with a granulated blastfurnace slag content  $\geq$  66 mass %) various investigations from Great Britain and the USA provide evidence that the joint use of ground granulated blastfurnace slag (proportion > 65 mass %) and Portland cement does not by any means always produce a higher sulphate resistance of the concrete than the sole use of a Portland cement. Results from long-term investigations by D.C. Stark [9] over a period of up to 16 years under both laboratory and outdoor conditions are shown as an example in [8]. The concrete test specimens were exposed to severe sulphate attack and a wetting-drying cycle. The diagram in Fig. **V-56** shows the scaling behaviour of test specimen based on Portland cement and on mixtures of Portland cement and ground granulated blastfurnace slag. The test specimen containing ground granulated blastfurnace slag exhibited more severe scaling than the test specimens based on Portland cement (= "without ggbs") [9].



Fig. V-56: Visual scaling rates of concrete test specimen based on Portland cement ("without ggbs") and mixtures of Portland cement/ground granulated blastfurnace slag (h) [w/c = 0.37 - 0.39, (c+h) = 390 kg/m<sup>3</sup>, ground granulated blastfurnace slag 40 and 65 mass %], sulphate concentration of the storage solution 65,000 ppm [8, 9]

## Report from CEN/TC 104 "Concrete and associated products"

Since 2003 the Research Institute of the Cement Industry has been committed to heading CEN/TC 104 "Concrete and associated products". In 2009, Dr. Christoph Müller succeeded Professor Gerd Thielen in this function. CEN/TC 104 is the superior and controlling European standardisation committee on concrete as building material. Apart from the European concrete standard EN 206 - whose revision in CEN/ TC 104/SC1 is being prepared under the leadership of Professor Rolf Breitenbücher (Ruhr-University Bochum) - the CEN/TC 104 task forces and committees also deal with the standards for concrete additions, concrete admixtures, the execution standards and concrete repair. The following represents some examples of the CEN/TC 104 activities to supplement the explanations with regard to the revision of EN 206:

## Working group (WG) 4: "Fly ash"

The revision of EN 450-1 "Fly ash for concrete" was initially rejected in a preliminary enquiry prior to the start of the "formal vote". Many CEN members had not responded and these votes were assessed as abstention. France and Italy rejected the start of the "formal vote" as their comments with regard to the abolition of the lower class limits for loss on ignition (LOI) "were not sufficiently considered". The abolition of the lower class limits for loss on ignition (LOI) was considered necessary by the WG4 in order to enable the manufacture of a category B (2 to 7 mass % loss on ignition) while maintaining the statistical evaluation (such as for cement, silica fume and ground granulated blastfurnace slag). The rejection by France and Italy and the low participation of other countries meant that the approval required to start the "formal vote" for the weighted voting was lacking. The matter was discussed in the CEN/TC 104 once again but no mutual agreement was reached. The draft standard was not changed, adopted in the "formal vote" and ultimately confirmed by the majority. In the formal vote, a 74.05 % weighted majority voted for the standard – 71 % was required. EN 450-2 with the conformity regulations remained unchanged.

Greece made an application to standardise calcareous fly ash (e.g. lignite fly ash). The composition of the ash deviated from the provisions of EN 450-1. In its meeting in November 2011, CEN/TC 104 did not see any compelling reason to standardise this fly ash. The European fly ash organisation ECOBA was requested to first provide additional information on the use of calcareous fly ash.

## *WG 15: "Ground granulated blastfurnace slag"*

In the enquiry on the cyclical revision of EN 15167 "ground granulated blastfurnace slag", many countries proposed the revision of the standard with the objective of creating a classification for ground granulated blastfurnace slag. The Netherlands also, once again, proposed the option of standardising the addition of a sulphate carrier to the ground granulated blastfurnace slag. A classification may be important if ground granulated blastfurnace slag is to be applied under the k-value concept.

<sup>[8]</sup> Deutscher Ausschuss für Stahlbeton (DAfStb): Hüttensandmehl als Betonzusatzstoff – Sachstand und Szenarien für die Anwendung in Deutschland. Schriftenreihe des DAfStb, Heft 569, Berlin 2007

<sup>[9]</sup> Stark, D.: Performance of concrete in sulphate environments Portland Cement Association, Skokic, USA 2002

The currently recommended k-value is k = 0.60, without any additional ground granulated blastfurnace slag requirements exceeding EN 15267. Significant data that can be used to identify a correlation between classes for ground granulated blastfurnace slag and that can generate a variable k-value on this basis to illustrate the corresponding performance in concrete have not yet been provided. The addition of a sulphate carrier is fundamentally impossible as part of the standardisation of concrete additions. The existing version of EN 15167 was therefore confirmed. In order to clarify the actual need for revision, the CEN/TC 104 members have been asked to formulate the precise requirements of possible classes and to display the relation to the performance of the concrete.

#### Standing Committee (SC) 8: "Protection and repair of concrete structures"

Germany raised several concerns regarding the standard series EN 1504. From a German perspective the standards do not fully comply with the mandate. A number of requirements are lacking. The specific concerns were restated in CEN/TC 104 in November 2011. A solution could not be found. A discussion between representatives of CEN/TC 104 (German delegation) and CEN/TC 104/SC 8 took place in March 2012, under the leadership of the Research Institute of the Cement Industry, based on a CEN/TC 104 resolution, in which the German position on EN 1504-3 was expressed once again. The majority of the SC 8 representatives present were of the opinion that the additional performance features requested by Germany should not be incorporated into the European standard. The additional performance features predominantly originate from traffic route engineering (ZTV-ING, ZTV-W, ZTV-SIB, ZTV-RISS, etc.) that contain both technical content as well as contractual requirements and, in the opinion of the majority of the SC 8 representatives present at the meeting, could therefore not be seen as regulations that necessarily have to be observed in the CEN standardisation activities, despite notification. At the meeting an agreement was reached that the mandate M/128and the associated business plan should be supplemented by additional performance features so that the traffic route engineering requirements, which are specified as an application area for EN 1504-3 in the mandate, is fully taken into account. Germany was asked to ask for the mandate adjustment via the SCC (Standing Committee on Construction). In this regard, NABau, with support from the NA 005-07-06 AA "Protection and repair of concrete components" as a mirror committee for CEN/TC 104/SC 8, was asked to provide the German members in the Standing Committee on Construction (BMVBS, DIBt) with a corresponding letter containing a substantive justification.

## Joint working group (JWG) of CEN/ TC 250/SC 2 "Eurocodes" and CEN/ TC 104/SC 1 "Concrete"

The joint working group of CEN/TC 250/ SC 2 "Eurocodes" and CEN/TC 104/SC 1 "Concrete" is working on a new approach for future standardisation of the impacts from environmental influences and the corresponding concrete resistances. The impact classes (exposure classes) are currently described in normative terms and their ultimate regulation takes place in the national annexes. A combination of impact classes (exposure classes) and resistance classes (e.g. different carbonation depths after 50 or 100 years) is now envisaged. This requires relevant test methods that are not currently available for all properties at a European level. Alternatively, a table with guidelines for the composition of the concrete (w/c values, cement types, additions) could be developed. The limit values would then be declared as "deemed to satisfy". This approach seems promising with regard to the further harmonisation of the technical regulations.

## German Committee for Structural Concrete (DAfStb) guidelines German Committee for Structural Concrete guideline "Concrete structures for the handling of substances hazardous to water"

The revised version of the Federal Water Act (WHG), the planned amendment of the Federal Ordinance on plants handling substances hazardous to water (VAUwS) and the adjustments to Eurocode 2 made it necessary to revise the German Committee for Structural Concrete guideline "Concrete structures for the handling of substances hazardous to water" from 2004. In addition to the revision for the reasons mentioned above, the list of available cement types was also supplemented (CEM II/A-M (T-LL), and adapted (with regard to the updated cement standards) and the minimum compressive strength class requirement for FDE concrete was removed in order to enable the application of light-weight concrete. Finally, a detailed process description for the application of the thermography for determining the penetration depths of substances hazardous to water in uncracked concrete (in particular for n-hexane and di-chloromethane) was incorporated. The guideline is currently being notified in Brussels.

## German Committee for Structural Concrete guideline "Self compacting concrete"

Supplementary rules for self compacting concrete have been specified in DIN EN 206-9 since 2010. These do not cover the degree of legislation provided in Germany. The "self compacting concrete (SVB)" guideline was therefore revised and changes or supplements DIN EN 1992-1-1 in connection with DIN EN 1992-1-1/NA, DIN EN 206-1 and DIN EN 206-9 in connection with DIN 1045-2 and DIN EN 13670 in connection with DIN 1045-3. The process for testing the cone slump flow and the cone flow using the flow cone was added. Publication is expected at the start of 2013.

German Committee for Structural Concrete guideline "Reinforcement quality – Supplementary determinations on the further processing of reinforced concrete and for installation of the reinforcement" Notification and printing took place in 2011.

## German Committee for Structural Concrete guideline "Steel fibre concrete"

The first issue of the German Committee for Structural Concrete guideline "Steel fibre concrete" was published in March 2010. The conversion of DIN 1045-1 to EC 2-1-1 and the related publication of DIN EN 1992-1-1 and the national annex (DIN EN 1992-1-1/NA) at the start of 2011 meant that the "Steel fibre concrete" guideline had to be edited. Changes to the punching shear verification in EC 2-1-1 with regard to DIN 1045-1:2008 also meant that the relevant passages in Part 1 of the "Steel fibre concrete" guideline had to be revised. There was also another discussion regarding the area of responsibility that the washout trial would have to be performed to determine the steel fibre content according to Annex M of the guideline. The manufacturer is responsible for ensuring the fibre quantity and homogenous fibre distribution in the truck mixer.

The test in Part 2 of the guideline was therefore integrated into the initial test and the manufacturer's factory production control. On the other hand, Part 3 of the guideline was changed so that the acceptance test (wash-out test or, alternatively, the bending beam test) only has to be performed in cases of justified doubt, while the current acceptance criteria remain in place. It was ultimately decided to once again enter the draft of the German Committee for Structural Concrete guideline "Steel fibre concrete" converted to EC 2-1-1 into an objection proceeding. The reason for this decision is the planned issue of an amendment and a draft of an A1 change to DIN EN 1992-1-1/NA that may impact the "Steel fibre concrete" guideline. Furthermore, the new DIN 1045-3 has now been published as the national code of practice to DIN EN 13670. Part 3 of the guideline was therefore converted to the new execution standard DIN EN 13670:2011-03 and DIN 1045-3:2012-03 without any changes to content.

## German Committee for Structural Concrete guideline "Preventative measures against damaging alkali reactions in concrete (alkali guideline)"

The alkali guideline is currently being revised in working groups of the "Alkali reaction in concrete" sub-committee of the German Committee for Structural Concrete. The objective is the complete restructure of the guideline (discontinuation of the current three part guideline) and adaptation to the structure of the European standards. The following restructure is currently scheduled:

- 1 Scope
- 2 Normative references
- 3 Terms
- 4 Aggregate evaluation
- 5 Proof of conformity for aggregates
- 6 Preventative measures

#### Annexes

- A (normative) Aggregate tests with opaline sandstone including siliceous chalk and flint
- B (normative) Tests for additional aggregates
- C (informative) Mortar rapid test (alternative method)
- D (informative) Concrete test at 60 °C over water (60 °C concrete test)

The two amendments to the alkali guidelines from 2010 and 2011 and some amendments to the Construction Products List A/ Part 1 are included in the new edition of the guideline. The activities in the "Alkali reaction in concrete" sub-committee are expected to conclude in 2012 in order to allow for the publication of the revised alkali guideline in 2013 (cf. Alkali-silica reaction section).

## Construction Products Regulation – Effects of extended basic requirements

#### Introduction

The Construction Products Directive (CPD) was replaced by the European Construction Products Regulation (CPR, see

Chapter IV), which is directly applicable in all member states. The regulation aims to remove technical trading barriers for construction products and thereby improve the functioning of the internal European market for construction products. This objective will be achieved through harmonising technical specifications, including product standards. However, in contrast to other products, the construction product requirements do not primarily relate to the product itself, but rather to its application in construction works. Both the CPD and the CPR specify basic requirements for construction works. Among other things, the new CPR contains an extension of the basic requirements for construction works (BWR - Basic Work Requirements) no. 3 (hygiene, health and the environment) and a newly introduced no. 7 (sustainable use of natural resources).

The effects of these basic requirements for construction works on harmonised construction products standards were investigated in a research project under the leadership of the VDZ on behalf of the BBSR (The Federal Institute for Research on Building, Urban Affairs and Spatial Development). The research project inspected several examples of construction products and compared them with the current legal construction work requirements in Europe. Possible future regulations were also included as examples, which particularly affected the sustainability assessment of construction works. The extent to which the environmental product declarations (EPD) can be used to implement such requirements was also investigated.

## Content of BWR 3 and BWR 7

The basic requirements for construction works no. 3 were extended with the new CPR. The changes primarily targeted the consideration of the entire life cycle of a construction work. Furthermore, both the impact on hygiene and health as well as on the environment and climate were addressed.

The basic requirements for construction works no. 7 was a new addition and relates to the sustainable use of natural resources, particularly, in order to take account of the recyclability of the construction work, its building materials and parts after demolition, the durability of the construction work and the use of environmentally friendly raw materials and secondary building materials for the construction work – i.e. recital 55 of the CPR. The basic work requirement no. 7 therefore relates to a partial aspect of sustainable construction. According to Article 3, paragraph 2, essential characteristics of construction products are to be derived from the basic requirements for construction works and specified in the harmonised technical specifications. The essential characteristics of construction products will then be listed in the declaration of performance (Article 4 to 6 of the CPR) of the construction product and in the CE marking (Article 8 to 9 of the CPR). However, values only have to be provided for those essential characteristics that are required at the intended place of use. NPD ("no performance determined") can be declared for the remaining product characteristics.

## Construction product requirements in Europe

Existing legal requirements for construction products with regard to BWR 3 and BWR 7 were determined based on an inquiry by the associations responsible for the construction products under consideration. Pursuant to the available information, requirements for construction products regarding BWR 3 exist in Germany, the Netherlands, Austria, Poland and the Czech Republic. These relate to requirements regarding the radioactivity of construction products (Austria, Poland and the Czech Republic) and requirements regarding hazardous organic substances and the release of hazardous inorganic substances from construction products (The Netherlands, Germany). However, the requirements in Germany do not generally apply to standardised construction products, or those which are previously technically approved, but only come into effect as part of the approval process of the German Institute for Building Technology (DIBt).

CEN/TC 351 has established task forces to develop a harmonised European standard for the determination and assessment of radioactive radiation exposure by building materials and to harmonise the test methods for hazardous substances and their release (cf. Chapter VI Environment and Health, European Construction Products Directive).

With regard to the newly added BWR 7 in the Construction Products Regulation, traditional requirements already exist on the aspect of durability, even if the durability has not been mentioned in any of the basic requirements of the Construction Products Directive. For example, in Germany they are derived from the model building code and the Federal State Building Codes. The durability requirements are included in national as well as in some harmonised stand-



Fig. V-57: Implementation of legal requirements for the sustainability assessment of construction works

ards and are also applicable in European technical approvals.

Two national regulations seem to be in the pipeline with regard to the assessment of the sustainability of construction works. The Scottish construction regulation will be amended so that buildings generally have to meet a "sustainability value". It has not yet been confirmed how this will be achieved and what will be required from construction products. A new version of the Durch building decree is currently being prepared in the Netherlands, which will also result in the assessment of the sustainability of construction works. An official draft version is not yet available.

## Scenario: Sustainability assessment of construction works as established law

Research projects considered a scenario of how a legal requirement regarding the assessment of sustainability of construction works would affect the construction product standards. The selected scenario describes the implementation of the sustainable construction assessment system (BNB) into established law. Only aspects that related to BWR 3 and BWR 7 of the Construction Products Regulation were considered. Also investigated was whether these requirements could be implemented with the help of the Environmental Product Declarations (EPD). The sustainable construction assessment system (BNB) of the Federal Ministry of Transport, Building and Urban Development for federal buildings is an assessment process for office and administration buildings. This considers the entire life cycle of buildings with regard to the ecological, economic and socio-cultural quality as well as technical and procedural aspects. The system is comparable to that of the German Sustainable Building Council (DGNB).

Requirements for the construction products considered in the research project were derived from the BNB assessment mechanism profiles: The impact of the construction work on the environment over its entire life cycle is considered the environmental quality of the construction work and described with indicators. These indicators are primarily those that are also used in the EPDs and described in the relevant CEN/ TC 350 "Sustainability of construction works" (EN 15804 (construction products) and EN 15978 (construction works)) standards. The potential effect for the manufacture of the products, the installation, use and potential disposal must be determined for the construction products. Possible additional uses of the construction products, whether this is as a secondary product or fuel, would also be included. As this scenario would generate requirements for construction works relating to the BWRs, the resulting essential characteristics of construction works would have to be calculated according to the above-mentioned standards and converted into harmonised technical specifications (product standards). This would place requirements on the provision of information that would potentially have to be responded to as part of the declarations of performance of the construction products. The Construction Products Regulation enables alternatively "Appropriate Technical Documentation" (Article 36) to be used. The data in the declarations of performance could therefore also originate from a product EPD, for example, if this document is referenced. For the proof of conformity, in this case, the producers verify that their construction product corresponds to those for which the applied results were determined. Both specific product EPDs as well as association or average EPDs are suitable. The process for the implementation of legal requirements for the sustainability assessment of construction works is represented in Fig. V-57.

#### Research project conclusions

The replacement of the Construction Products Directive with the Construction Products Regulation does not change the objective or the principal responsibilities. The regulation's objective remains the removal of the technical trading barriers on the European construction products market by means of harmonised technical specifications. The regulation specifies the basic requirements for construction works, similar to the directive. The specification and implementation of the construction product requirements remains within the responsibility of the member states. These specify the essential characteristics of construction products that they consider to be important in order to build construction works so that they fulfil the basic requirements, regardless of the formulations in Annex I of the Construction Products Regulation. The basic requirements for construction works specified by the Construction Products Regulation do not automatically necessitate new product characteristics. If new requirements are established, these must comply with the harmonised standards to the greatest possible extent. If no harmonised standards exist for a (new) product requirement, then these must be established. Also, the harmonised product standards do not necessarily require the individual member states to apply all of the product characteristics described in these standards or to implement these into legal regulations. There is the option of declaring "no performance determined" (NPD option).

Essential characteristics of construction products with regard to hazardous substances, which arise based on legal regulations in relation to BWR 3, will presumably need to be declared with the test methods harmonised in the activities of the CEN/TC 351 after their completion. Information on the presence of hazardous substances, or to the leaching of these substances, could be provided in the declaration of performance of a construction product. Alternatively, "NPD" could also be declared in this case.

However, requirements for construction works also exist, which cannot be directly transferred into product requirements. This includes requirements that relate to BWR 3 (e.g. "greenhouse gases") and BWR 7 ("sustainability and recycling") of the CPR. For example, if a requirement for compliance with certain greenhouse gas limit values has been specified for a construction work, this does not necessarily mean that construction products also have to comply with a limit value with regard to greenhouse gases. However, the construction product manufacturer would then have to provide relevant information for the building assessment. In this example, this would be the greenhouse gases that arise during the manufacture and transport of the construction product, as well as parameters such as the thermal conductivity of an insulating material that enables the energy consumption and the greenhouse gas emissions during the construction work's service life to be calculated. All parameters would have to be determined according to harmonised standards. However, the specification of all parameters in the CE marking of a construction product - as stipulated in the CPR - is not useful for a number of reasons. One the one hand, the number of possible parameters, as would be required for assessing the sustainability of a construction work, would increase the scope of the CE marking to an unnecessary extent. Also, the specification of these values on the CE marking would suggest a quality criterion of the relevant construction product, even though this is not the purpose of this parameter.

It remains to be seen how the sustainability evaluation of buildings in Europe will develop. It seems possible that the demand for construction product data for these types of sustainability assessments will increase.

## Fire safety

With regard to fire safety, a distinction is generally made between preventative and protective measures. Protective fire protection only takes effect when a fire has already started and is mainly comprised of extinguishing activities by the fire brigade. In contrast, the preventative measures aim to prevent or limit the occurrence and spreading of fires. Apart from fire protection technology, such as fire alarm systems and automatic fire-fighting systems, structural fire protection is the key element for the necessary safety in the field of preventative fire protection. Constructed fire protection measures are permanent and provide the necessary protection without having to be triggered by operational/mechanical processes that have a risk of failure. Protective fire protection depends on the operation of the fire brigade, which also has a risk of failure.

Building elements made of concrete can easily fulfil the structural fire protection requirements, generally without any significant additional costs. Concrete, a non-combustible construction material, allows building elements with a high fire resistance and continuous insulation properties. This means that concrete structures retain their integrity for a long period in the event of a fire and that the fire can be restricted to certain areas. These protective effects of concrete and concrete elements help to safeguard the safety of people, which is the top priority in the statutory fire protection regulations. But the preservation of the building is also important for reasons of asset protection. Even if the legislator has transferred asset protection into the individual responsibility of the building owner and user, asset safety is both in the private as well as in the public interest. Furthermore, by reducing the smoke and gas emissions as well as the volume of extinguishing water used and by retaining the most contaminated water, structural fire protection measures also contribute to environmental protection.

## Implementation of the Eurocodes in Germany

According to the "Guidance Paper L" on the use of the Eurocodes, which the European Commission issued in November 2003, a complete implementation of the Eurocodes was scheduled for 2010. This goal could not be achieved in Germany as well as in many other EU member states. The final versions of sections of Eurocode EN 1992-1-1 (general rules and rules for buildings), EN 1992-1-2 (structural fire design) and EN 1992-3 (liquid retaining and containment structures) relating to reinforced concrete construction with their national annexes have been available since December 2010 and January 2011 and may be applied parallel to the present national regulations in Germany since then. The final introduction of the Eurocodes by the German federal states took place on 01.07.2012. Accordingly, the Eurocodes were recorded as technical rules in the changes to the "Musterliste der Technischen Baubestimmungen" (model list of technical building regulations) in December 2011, to be implemented by the federal states from June 2012.

In addition to the "traditional" design of building members using tables, Eurocode 2, part 1-2, which regulates fire design, also allows the application of so-called "simplified" or "advanced" design processes. The advanced design methods correspond to Fire Safety Engineering. These methods have been developed over the past 10 to 15 years. Their objective is to provide a realistic, integrated estimate of the impacts of fires on a building or building

part and thus expand the traditional design of individual building elements for standard fires. A typical design using fire safety engineering initially defines protection objectives. The primary protection objective is the life and health of individuals, but asset protection objectives can also be specified. Fires are modelled in consideration of the actual fire loads present and the geometry of the fire compartments. Moreover the thermal and mechanical impacts on the surrounding building parts are determined. The impact of automatic fire detection, active fire fighting using automatic fire extinguishing systems or the fire brigade can be considered. Computer programs are often used in order to simulate the effects of a fire or the behaviour of groups of people when evacuating a burning building. In many cases FSE reduces the fire protection requirements of individual building elements.

The decision on whether the use of advanced calculation methods is permitted in a member state is regulated in the national annexes. Many member states only permit their use with restrictions. For example, some national annexes specify that their application remains restricted to specialists with sufficient experience. These restrictions should be approved since an improper approach when applying FSE can easily lead to incorrect estimates and evaluations in the calculations and therefore to incorrect results for the requirements.

## National residual standard for fire safety design

As a member of the European Committee for Standardisation (CEN), DIN is obliged to withdraw the national planning and design standards that contradict the Eurocodes. However, the content of DIN 4102-4, according to which fire design was previously carried out in Germany, is not completely covered by the Eurocodes for fire safety design. For example, the Eurocodes do not regulate non-load bearing and enclosing components and only a limited amount of information is included on structural design. The industry and its associations therefore still require DIN 4102-4 regulations and produced a "DIN 4102-4 residual standard" in order to continue to provide comprehensive standardisation regulations for their products. The VDZ is also involved in preparing the supplementary standard for the fire design of concrete. This standard will continue to provide the important regulations and information that do not contradict the Eurocodes. Examples of supplementary regulations that do not contradict the Eurocodes include:

- Consideration of plaster as replacement for concrete for the cover of the reinforcement when determining the fire-resistance class of a reinforced concrete component
- Information on the structural design of concrete components such as brackets, supports, etc.
- Information on the design of joints and connections for pre-cast concrete elements
- Design of reinforced concrete hollow core slabs and ribbed slabs
- Design of segmented reinforced concrete walls

It is expected that the "DIN 4102-4 residual standard" will be published towards the end of 2012/start 2013.

#### **Revision of the Eurocodes**

According to the CEN regulations, standards must be reviewed five years after publication.

The current Eurocode revision time frame is as follows:

- March 2013: Launching of the review of current Eurocodes five years after their publication; new Eurocodes are also planned for the evaluation of existing structures and for designing glass and fibre-reinforced plastics.
- October 2015: Start of the CEN-enquiry by the national mirror committees on the revised and new Eurocodes (CEN Enquiry)
- October 2017: Start of the formal vote on the revised and new Eurocodes (CEN formal vote)
- October 2018: Publication of the second Eurocodes generation

The standardisation committee CEN/TC 250/SC2 for the revision of the concrete Eurocodes has been organised so that several task groups are formed under an overarching coordinating working group (WG1). Each of these task forces is focussed on individual problems within the development of the next generation of Eurocodes. A task force (TG 5) will focus on the revision of the Eurocodes for the fire design of concrete. As part of the European cooperation at the level of the European Concrete Platform (ECP), the European Cement Research Academy (ECRA) will actively support the additional work on the Eurocodes that relate to the fire design of concrete in TG 5 of CEN/TC 250/SC2.

## Expert's reports

## Examples of concrete reports and consultation

The demand for concrete consulting and verification activities by the Research Institute of the Cement Industry continued unabated during the reporting period. Focal points include the following:

- Technical approvals for new cements
- Assessment of drinking water reservoirs
- Evaluation of aggregates and concretes with regard to the prevention of a damaging alkali-silica reaction (cf. section Alkali-silica reaction)
- Development of optimised concrete and mortar mixtures for the customer's relevant area of application

Specialists for all concrete issues, who are represented in national and international committees and have extensive laboratory and practical experience, prepare efficient solutions to the often complex problems. The interdisciplinary cooperation with experts from the specialist areas of mineralogy, chemistry, physics and the process engineering of the other departments of the Research Institute of the Cement Industry is a particular advantage in this regard.

#### **Approval tests**

Approval tests enable the suitability of construction products (e.g. cements) to be investigated for certain product and application areas. The Research Institute of the Cement Industry has performed assessment procedures to obtain national technical approvals (abZ) for the use of cement, European Technical Approvals (ETA) and KOMO attestations with product certificate in accordance with CUR 48 for the use of cements in the Netherlands. All the levels of the assessment procedure, such as the application, preparation and implementation of the test program, the test report and a report on the suitability of the product, are carried out in the approval process. The sampling of the cement main constituents, secondary constituents and the cement subject to approval as part of this approval process is generally performed by a representative of the Research Institute of the Cement Industry at the cement manufacturer's plant. The cement and the cement constituents are characterised according to the approval body guidelines. The cement is used to manufacture concretes to be tested for their mechanical and durability properties. The results of the testing are summarised in a test report. Additional questions on the suitability of the product can be answered by expert reports.

## Rehabilitation of drinking water reservoirs

The Research Institute of the Cement Industry has been supporting the rehabilitation works of Heisterberg drinking water reservoir by the Hannover public utility company since 2003. The Heisterberg drinking water reservoir is an elevated reservoir that consists of three chambers. The chambers have a combined volume of approx. 45,000 m<sup>3</sup>. The chamber surface area is about 240 m<sup>2</sup> with a total of 230 columns. Condition analyses were initially performed in the chambers as part of the reporting activities of the Research Institute of the Cement Industry. Drilling cores were obtained, from which the layer structure, the concrete cover of the reinforcement, total porosity, concrete compressive strength of the reservoir floor, wall and roof construction and the columns were determined as part of laboratory tests. The adhesive tensile strength of the coatings was also determined. Investigations were also performed on concrete test specimens that exhibited efflorescence or spalling for example. These investigations provided the basis for the subsequent rehabilitation works of the drinking water reservoirs. The Research Institute of the Cement Industry also performed quality assurance investigations during construction as part of the rehabilitation measures (Fig. V-58). The adhesive tensile strength was determined in a pull-off test on blasted and coated surfaces in order to assess the suitability of the concrete subsurface and the coating. The porosity of the coating was determined using mercury intrusion porosimetry in order to evaluate the coating with regard to the requirements of the DVGW technical rules W 300.

#### Alkali-silica reaction reports

Sufficient non-reactive aggregates and concretes must be used to prevent damage as a result of an alkali-silica reaction (ASR). The alkali reactivity of aggregates can be investigated with tests according to the German Committee for Structural Concrete's (DAfStb) Alkali Guidelines or RILEM. In the cases in which the Alkali Guidelines specify that the aggregate needs to be replaced or that low alkali cements must be used, the alkali reactivity of a concrete composition may also be verified by a performance test. The risk of a damaging alkali-silica reaction is particularly high for concrete road pavement (e.g. on aviation runways or motorways), as additional alkalis may penetrate into the cement from outside due to the use of de-icing agents. In many cases it is now customary to evaluate the alkali reactivity of concretes for



Fig. V-58: Experts from the Research Institute of the Cement Industry in action in drinking water containers – component consultation and testing of the compliance with the requirements pursuant to the technical rules of the DVGW W 270, W 300, W 347.

Photo: enercity/Hannover public utility

motorways and aviation runways in a performance test performed by an expert. The Research Institute of the Cement Industry is recognised as an expert by the Federal Highway Research Institute (BASt) and the Ministry of Transport (BMVBS). The Research Institute of the Cement Industry prepared expert reports for various construction projects in the reporting period:

- 24 concretes for moisture class WS (18 performance tests and six expert opinions)
- 6 concretes for aviation runways and precast components to be used at airports and that come into contact with airport-specific de-icing agents (four performance tests and two expert opinions)
- Four expert reports on damage to concrete constructions (two bridges, seven lots of a motorway and one radio tower)
- Four concretes in moisture class WA

# VI

## Environment and health



Photo: HeidelbergCement

# Environmental criteria for cementitious building materials

Cement is the most important binder for the construction sector and it is produced in extremely large quantities in order to establish reliable, durable and environmentally friendly concrete components and buildings. Global cement consumption amounted to about 3 billion tonnes in 2009 and it is expected that this consumption will increase significantly in the coming years – especially in emerging markets. Due to the extremely large production quantity, the environmentally compatible production and use of cement is a top priority.

The German cement industry has intensely investigated the environmental compatibility of cement and concrete in all stages of life for many years. The focus was initially on the environmentally compatible production of cement. Extensive investigations by the Research Institute of the Cement Industry have shown that the immission situation is not significantly affected at a cement work location.

The increasing use of alternative raw materials and fuels in cement production has shifted the focus to the product cement. Extremely strict quality criteria are applied for the use of alternative materials in German cement works. This ensures that the emissions, the homogeneity and the structural properties of the cement as well as its environmental compatibility are not impaired. For example, the trace element content of German standard cements has the same order of magnitude as the content in natural rocks, soil or clays. This applies regardless of whether the cement production has used alternative materials or not.

## Use of alternative raw materials and fuels

The clinker burning process is a highly energetic material conversion process, which is distinguished by high kiln feed temperatures of about 1 450 °C, an intense contact between the solids and the kiln gas with temperatures of up to 2000 °C and a strongly basic kiln feed. As a result of these process conditions, rotary kilns in the cement industry are very well suited for the reliable and environmentally compatible recycling and energy recovery of a multitude of alternative materials.

Depending on the raw material situation that exists at a cement work, alternative



Fig. VI-1: Development of the use of alternative fuels in the German cement industry

raw materials can be used as raw material components and as corrective material for the raw mix. Industrial lime used foundry sand, pyrite cinder, fly ash and waste materials from the iron and steel industry are predominantly used for clinker production. Granulated blastfurnace slags as well as gypsum from flue gas desulphurisation are primarily recycled in cement grinding.

The use of alternative fuels in the German cement industry continued to increase in the reporting period (Fig. VI-1). In 2010 about 61 % of the total fuel energy consumption was covered by treated industrial and commercial waste, animal meal, used tyres, waste oil, treated municipal waste, sewage sludge, etc. The energy recovery contributed to CO2 reduction without resulting in any production-specific residues. Regardless of the fuels used, the emission concentrations of organic compounds are extremely low, as the high temperatures in the rotary kiln firing system ensure that organic substances are almost completely converted to carbon dioxide landwater.

#### **Trace elements in cement**

All building materials produced from natural raw materials contain low amounts of trace elements. The trace element content in cements is comprised of the content in the main constituents of Portland cement clinker, pozzolana, fly ash, burnt shale, limestone and silica fume as well as the minor additional constituents. The trace element content in Portland cement clinker is predominantly determined by content in the raw materials used to produce the clinker. This content may differ according to the geochemical composition of the raw material deposits.

If primary feed material is replaced by suitable alternative raw materials and fuels in clinker production, their trace element content is an important quality criterion as, depending on their volatility and the process conditions, these remain in the clinker more or less completely. It must be remembered that the alternative materials only replace a corresponding fraction of trace element-containing primary materials. In today's customary use of carefully selected and monitored alternative materials in the German cement industry, both minor increases or decreases of the trace element content may occur in the cements. However, these changes are generally covered by the natural concentration fluctuations in the primary feed materials.

In 1995 the Research Institute of the Cement Industry first investigated about 100 Portland cements from the 1994 monitoring period with regard to the content of ten trace elements. In 1999, 2002 and 2006 all of the cements produced in Germany and monitored by the Research Institute from a test period in 1998, 2001 and 2005 were analysed with regard to the content of the elements specified in the national Clean Air Act plus beryllium and zinc. Another investigation of all cements from a 2011 test period was commenced during the reporting period in order to update and enhance the data base. The evaluation of the existing analyses shows that the average value of trace element contents of the investigated standard cements have not changed significantly in the five production periods (**Fig. VI-2**), even though the use of alternative fuels has more than sextupled from 1994 to 2011 (cf. Fig. VI-1).

## **Release of trace elements**

The leaching behaviour of environmentally relevant constituents from cementitious building materials has been well researched and numerous scientifically proven results are available. These show that only extremely low quantities of trace elements or critical organic compounds are contained in cementitious building materials and that the release of these trace substances during the use of the structures is extremely low. This also applies for cements and concretes for which alternative raw materials. fuels as well as concrete additives, such as hard-coal fly ash, were used in production. However, only a small amount of information was previously available on whether and how concrete admixtures influence the leaching behaviour of trace elements. To fill this knowledge gap, the Research Institute of the Cement Industry carried out a research project "Impact of concrete admixtures on the leaching behaviour of trace elements from hardened concrete" supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF).

Modern concrete technology is largely aligned to the use of concrete admixtures. This means that numerous concrete properties cannot be achieved without concrete admixtures and many construction activities can only be managed with the use of these admixtures. Accordingly, these days more than 90% of all concretes in Germany are produced with concrete additives. In many cases, the active substances in these agents are organic or inorganic compounds with several functional groups, such as sulphate, sulphonate, hydroxyl, or carbonyl groups that can interact strongly with positively charged particles or trace elements (complexation). These reactions may lead to flocculation as well as increased solubility/leaching.

The research project used eleven common concrete admixtures and two raw materials for chromate reducers (**Table VI-1**). Two Portland cements CEM I 42,5 R and one blastfurnace cement CEM III/A 42,5 N with high barium, chromium, nickel and



Fig. VI-2: Comparison of the average trace element contents in German standard cements for 5 production periods

#### Table VI-1: Overview of the concrete admixtures and active substances used for the investigations

No.	Concrete admixture or active substance	No.	Concrete admixture or active substance
1	Lignosulphonate	8	Phosphonic acid
2	Melamine sulphonate	9	Pyrophosphate
3	Naphthalene sulphonate	10	Sugar
4	Polycarboxylate ether A	11	Methyl cellulose
5	Polycarboxylate ether B	12	Tin(II) sulphate
6	Wood rosin	13	Iron(II) sulphate
7	Alkyl polyglycol ether sulphate		

vanadium contents were used. The concretes were produced and stored based on the German Institute for Building Technology (DIBt) principles, Part II "Concrete starting materials and concrete". The maximum permitted concentration and double the maximum permitted concentration of the concrete additives and active substances were used. The leaching investigations were carried out on concrete cubes (10 cm x 10 cm x 10 cm) according to the German Committee for Structural Concrete's (DAfStb) guideline "Determination of the release of inorganic substances by leaching from cementitious building materials".

The comparison of the leaching results for the 98 produced concretes did not provide any clear correlations between the admixture type or concentration and the determined release quantity. The leaching value of the concretes with admixtures correlated to the level of the reference concretes without admixtures. For the elements mercury (Hg), molybdenum (Mo), selenium (Se) and tellurium (Te), in all cases, the content in the eluates was below the determination limit of the applied and extremely powerful method of analysis. For the elements arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), tin (Sn) and thallium (Tl), most eluate contents were below the determination limit.

The leaching investigations were assessed pursuant to Part II of the DIBt-principles. This showed that, in most cases, the accumulated leaching quantities were less than 25 % of the maximum permitted release quantity. Higher accumulations, which exceeded 50 % of the maximum permitted release quantity, were only recorded for the elements nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn). No elements exceeded the maximum permitted release quantities. Overall, these results once again confirm the extremely good binding capacity of cementitious building materials for trace elements. This is particularly the case, if the fact that cements with the highest possible trace element contents were consciously used in the investigations is considered, and that in some cases the excessive additive concentrations led to severely distorted concretes, e.g. with air void contents of more than 20 % by volume or 56 day compressive strengths of about 2 N/mm<sup>2</sup>.

## Product-related occupational health and safety

Product-related occupational health and safety has become more important due to updated legislation, regulations and provisions at both the European and national level. These regulations (see. Fig. VI-3) are intended to protect employees as well as private users against the risks that may be posed by the products. A part of these regulations also covers possible ecotoxicological effects. Cement industry companies are affected as both producers and distributors of materials and mixtures, which are predominantly used in the construction industry and in the private sector. Portland cement clinker and flue dust (dust from clinker production) are among the materials produced. Cements and all other formulated products, such as fresh mortar or premixed mortar, are considered mixtures. End products, i.e. articles such as buildings and structural elements, must also be considered.

The requirements for cement industry companies specified by the regulations are regularly reflected in the VDZ bodies, in particular, in the cement chemistry committee and in the REACH task force.

## **REACH and CLP regulation**

Although the REACH regulation has been in force since 01.06.2007, some implementation obligations only arose during the reporting period. Cement industry companies were particularly affected by the following:

- The notification of Portland cement clinker,
- The registration of flue dust and
- The update of the safety data sheets.

## Portland cement clinker

Portland cement clinker is exempt from the registration obligation pursuant to Annex V of the REACH regulation. Cement companies were therefore not required to prepare an expensive registration dossier and

**REACH** Regulation (EC) no. 1907/2006 on the registration, evaluation, authorisation and restriction of chemical substances (REACH) from 18.12.2006 including regulation (EU) no. 453/2010 to change regulation (EC) no. 1907/2006 of 20.05.2010

**CLP** Regulation (EC) no. 1272/2008 on the labelling, identification and packaging of substances and mixtures as part of the Global Harmonised System (GHS) introduced in the EU on 16.12.2008

**ChemG** – Chemicals Act, law on the protection against hazardous chemicals in the new version of 02.11.2011

GefStoffV – Hazardous substances ordinance of 26.11.2010

TRGS 559 – Technical rules for hazardous substances 559 Mineral dust of February 2011

Construction Products Regulation (EU) no. 305/2011 to specify harmonised conditions for the marketing of construction products from 09.03.2011

Fig. VI-3: New and updated national and European regulations on product-related occupational health and safety protection

	Portland cement clinker (EC: 266-043-4; CAS: 65997-15-1)
	HAZARD
	H315: Causes skin irritation. H317: May cause an allergic reaction. H318: Causes severe damage to eyes H335: May irritate the respiratory system
	P280: Wear protective gloves/protective clothing/eye protection/face protection P305+P351+P310: IN CASE OF CONTACT WITH EYES: rinse with plenty of water and immediately seek medical attention.
Zement AG	P302+P352+P333+P313: IN CASE OF CONTACT WITH THE SKIN: rinse with plenty of water and soap. In case of irritation or rash: seek medical attention.
Klinkerstr. 4	P261: Do not inhale dust
D-12345 Zementhausen Tel +49 (9876) 54321 Fax +49 (9876) 54322	P304+P340+P312: IN THE EVENT OF INHALATION: Move the affected person into fresh air and steady them in a position that facilitates breathing. Immediately seek medical attention if they feel unwell.

Fig. VI-4: Classification and labelling of Portland cement clinker according to CLP/GHS

submit this to the European Chemicals Agency (ECHA). However, as a hazardous substance, Portland cement clinker had to be notified with the European Chemicals Agency in the newly established classification and labelling inventory by 03.01.2011. This notification was issued by the CEMBUREAU jointly for all cement producers. In this regard, looking forward, every producer must maintain the information on the physical, toxicological and ecotoxicological hazard end points, such as test reports, publications, etc. required for the notification. The REACH and CLP regulations have required that substances be classified and labelled pursuant to the Global Harmonised System (GHS) since 01.12.2010. A corresponding classification and labelling is required for Portland cement clinker. **Fig. VI-4** displays the new identification. In place of the previous "St. Andrew's cross" hazard symbol (with code letters Xi), two pictograms are now required for labelling; the pictogram with the exclamation mark and the pictogram with the test tube. It also includes the signal word "HAZ-ARD". The risks are communicated by H statements (hazard statements) instead of R(risk) statements and the safety information by P statements (precautionary statements) instead of S(safety) statements.

Furthermore, each producer of Portland cement clinker, if they distribute the substance, also requires a safety data sheet that complies with REACH and CLP. A template prepared by the VDZ has been available since November 2010. The current version can be downloaded from the VDZ homepage. The VDZ template is based on the template prepared by the CEMBU-REAU expert group "TF REACH SDS C&L".

## Flue dust

Most German cement producers registered the substance flue dust at the end of 2010 in accordance with the REACH regulation. Flue dust was jointly registered by a consortium of about 80 European companies. Flue dust is the term used in the European inventory of existing substances (EI-NECS). This includes all process dusts that may arise in cement clinker production, for example bypass dusts or filter dusts. The bandwidth of dusts specified as flue dust may contain a large number of different components. The important components are the Portland cement clinker phases, calcium oxide, potassium chloride, alkali sulphates and calcium carbonate as well as other minerals from the raw meal. To complete the registration, the producers had to know the precise mineralogical composition of their flue dust in order to demonstrate that the substance identity requirements from the joint registration dossier had been met. This required measurements on the phase composition and chemical composition (primary and secondary elements and trace elements), whereby the REACH regulation did not provide any information on the testing frequency. Each producer takes independent responsibility in this regard.

The joint registration dossier with the integrated chemical safety report also required the investigation of numerous physical, toxicological and ecotoxicological properties (so-called hazard endpoints). The necessary tests were assigned and financed by the consortium and completed in 2010. The documents, such as test reports, studies and publications, submitted for the registration dossier must be maintained by every registrant in their company and may need to be presented to the official representatives as part of a REACH



Fig. VI-5: Timetable for the classification and labelling of substances and mixtures according to the previous EC system and CLP/GHS

inspection. An evaluation of the flue dust registration dossier by ECHA started in 2012 and will be finished in 2013. This will show whether the registration can be brought to a successful conclusion or whether additional tests in the form of animal tests are required.

Pursuant to the CLP regulation, the classification and labelling of flue dust must be performed according to the GHS, similar to Portland cement clinker. The cement clinker phases and calcium oxide contained in the dust are decisive for the hazards presented by the process dusts. Flue dust therefore has a classification and label with the same hazard pictograms and H and P statements as for Portland cement clinker.

However, the safety data sheets for flue dust and Portland cement clinker differ considerably. As flue dust has to be registered, the safety data sheet must also contain exposure scenarios apart from the usual general section. These must be indicated in the chemical safety report in the registration dossier. This has resulted in the size of the safety data sheet expanding from about 10 to 60 pages. A VDZ safety data sheet template, which is aligned to the CEMBUREAU template, is available on the VDZ homepage.

#### Cement

Cements and other cementitious products are mixtures. No registration or notification is required for mixtures pursuant to the REACH regulation. However, mixtures now also require a REACH-compliant safety data sheet. Labelling currently still takes place according to the previous preparation guideline with R and S statements. However, at the European level, the cement industry has agreed not to wait until the end of the transition period available for mixtures (see Fig. VI-5). A switch to the GHS labelling is expected to take place by mid-2013. This recommendation was decided by the CEMBUREAU board. The changed labelling must then also be used on packaging, and not only in the safety data sheet. The mid-2013 deadline was selected as other changes based on the updated cement standard EN 197-1 and the new construction products regulation become effective at this time. All of the changes can then be jointly implemented as part of a single process. Cement producers therefore only have to update the information printed on the bags on a single occasion.

The future CLP/GHS labelling of cements predominantly corresponds to the CLP/ GHS labelling of Portland cement clinker. If the cement is chromate-reduced then statement H317 "May cause allergic reactions" is not required. However, this is the general rule. As the previous restriction rules regarding the content of water-soluble chromate continue to apply under the REACH regulation, a corresponding labelling with effective date of the reducing agent is still required on the packaging.

# Duty of notification for hazardous mixtures in accordance with the Chemicals Act

Until the new version of the German Chemicals Act 2011, the duty of notification pursuant to § 16 of the Chemicals Act only applied for certain hazardous products that were placed on the market and were accessible to everyone. The new version now also affects those products classified as irritants and this duty now also applies regardless of whether the product is distributed to professional or private end users. There are two possible approaches to fulfil the duty of notification in the transition phase. The VDZ has recommended the following version to its members in a circular:

- Transmission of the existing safety data sheets to the Institute for Occupational Safety and Health (IFA) for the German Statutory Accident Insurance (DGUV) by 01.05.2012 and
- Notification pursuant to § 16e ChemG (Chemicals Act) to the Federal Institute for Risk Assessment (BfR) as soon as the identification of the products has been switched from the previous system (preparation guideline 1999/45/EC) to the Global Harmonised System (GHS) pursuant to regulation (EC) no. 1272/2008, however, before 01.07.2014.

## **Hazardous Substances Ordinance**

An updated version of the Hazardous Substances Ordinance (GefStoffV) has applied in Germany in addition to the REACH and CLP regulations since the end of November 2010. The reason for this lies in the additional aspects covered by the Hazardous Substances Ordinance but not by the two European regulations. Risk assessment is a key point of the Hazardous Substances Ordinance. This also means that the employer must complete a risk assessment for every workplace at which hazardous substances are handled. The necessary protective measures must then be determined. The risk management measures listed in the safety data sheets and exposure scenarios must be used as a guideline for identified uses by so-called downstream users. However, the employer's risk assessment is ultimately also decisive for the risk management and occupational protection meas-

		end 2011
General dust, respirable fraction (A dust)	until 2010: 3 mg/m <sup>3</sup> since 2011: 0.3 mg/m <sup>3</sup>	$3 \text{ mg/m}^3$
General dust, inhalable fraction (E dust)	until 2007: 10 mg/m <sup>3</sup> since 2008: 4 mg/m <sup>3</sup>	10 mg/m <sup>3</sup>
Portland cement dust, E fraction	until 2007: 10 mg/m <sup>3</sup> since 2011: $-^{1)}$	$5 \text{ mg/m}^3$

MAK value

until 2003: 0,15 mg/m3

since 2004:

Occupational ex-

Table VI-2: MAK values and German occupational exposure limit values (OEL)

<sup>1)</sup> MAK value withdrawn or not available

Fine quartz dust, A fraction

(respirable crystalline silica)

ures to be taken. The employer must confirm whether the measures they have taken are covered by the safety data sheet and the measures described therein. If an activity deviates from the uses considered in the chemical safety report and described by exposure scenarios or categories, the downstream user must also fulfil the REACH obligations in addition to their risk assessment. For example, this may include the preparation of a chemical safety report for the activities for which the substance is used by the downstream user.

## **TRGS 559 Mineral dust**

The TRGS 559, published in 2010, protects employees and other persons during activities in which mineral dust may occur, in particular, if fine quartz dust fractions are present. The TRGS contains provisions for the risk assessment to be performed by the employer at workplaces that may be exposed to dust. Apart from the actual dust exposure, the occupational exposure limit values (OEL) applicable in Germany are decisive for the risk assessment. The limit values specified in **Table VI-2** apply for dust that does not have any carcinogenic, fibrogenic (organ-damaging), allergenic or toxic effects.

In order to evaluate the dust exposure, the TRGS 559 refers to the dusting tendency, which can be divided into four dust classes, from low-dust to extremely dusty, based on the dusting values measured based on two processes according to DIN EN 1505. The dusting value is the ratio of the respirable or inhalable dust mass in mg released in the dusting test and the mass of materials used in kg. Although no dusting values have yet been determined, based on experience it can be assumed that cements are extremely dusty. Previously, there was no obligation to determine the dusting value of a powdery product and to forward this to customers. However TRGS 559, Section 4.1 "Replacement substances and alternative processes" specifies that a test must be carried out to confirm whether changing the work process could prevent or reduce the occurrence of dust prior to starting activities with materials that may release mineral dust. A GISBAU task force and a BG BAU discussion group are currently looking into these relationships. This is where representatives of professional associations, authorities and industry (BBS, DBC, IWM, VDZ, etc.) meet to discuss practical measures to implement the TRGS 559.

#### New MAK values

The cement industry is scrutinising the MAK values for general dust and Portland cement dust that were changed by the DFG senate commission for testing harmful materials in 2011. The previous MAK value for the respirable fraction of general dust (A dust) of 3 mg/m<sup>3</sup> was replaced by a new value. This refers to a value for respirable granular biogenic dusts of 0.3 mg/m<sup>3</sup>. It is therefore expected that this new 2012 MAK value will be introduced as a new workplace limit value by the Committee for Hazardous Substances (AGS). It is possible that the value may be 0.75 mg/m<sup>3</sup> for inorganic particles and therefore 4 times lower than the current occupational exposure limit value. Presumably, the limit value for inhalable general dust (E dust) will also be reduced from  $10 \text{ mg/m}^3$  to  $4 \text{ mg/m}^3$ .

The senate commission has withdrawn the previous MAK value for Portland cement dust as they have now classified Portland cement dust as a potential carcinogen (level 3B). The VDZ submitted a written statement to the senate commission at the end of 2011 in this regard. This referred to the investigation results of the CEMBUREAU studies on the health effects of cement.

According to these results, a classification as a potential carcinogen is not reasonable. However, any further development is still unclear. But it is not expected that the classification by the senate commission will be transferred into an applicable classification by the Committee for Hazardous Substance in 2012 or 2013.

#### **Respirable crystalline silica**

Fine quartz dust has been suspected of being a carcinogen for many years. The issue of exposure to fine quartz dust is therefore a top priority. Activities or processes in which employees are exposed to respirable dusts of crystalline silicon dioxide in the form of quartz and cristobalite are already considered carcinogenic pursuant to TRGS 906. Only the minimisation requirement applies as there are no occupational exposure limit values in place for fine quartz dust in Germany. This type of approach is also taken by the European social agreement on crystalline silica (NePSi). In this case, fine quartz dust exposure at the workplace is minimised by the implementation of the best and established technology and improved awareness (e.g. by employee training). A reporting phase takes place every two years in which a review of the extent to which measures on exposure minimisation, training and health monitoring have been implemented in companies takes place. The cement industry sets a positive example with a participation rate of almost 100 % at the European level in 2010. However, as not all sectors of industry actively participate in NePSi, some social partners continue to demand a uniform European workplace value or an official classification as a carcinogen.

However, a classification of fine quartz dust as a carcinogen is controversial. While it is known that there is an increased risk of silicosis diseases as a result of repeated exposure to fine quartz dust, this is not the case for cancers. In light of this, the European Industrial Minerals Association (IMA Europe) introduced a new CLP/GHS classification and identification for products that contain fine quartz dust. Pursuant to this self-classification, fine quartz dusts and products that contain more than 10 mass % of fine quartz dust are classified as STOT RE 1, while products with a fine quartz dust fraction of 1 to 10 mass % are classified as STOT RE 2. STOT stands for specific target organ toxicity and RE 1 and RE 2 stand for repeated exposure category 1 and 2. The fine quartz dust content of the product must be known in order to apply this classification. One method of determination is the SWeRF method (Size-weighted Respirable Fraction). The respirable quartz fraction can be calculated based on the phase analysis and particle size distribution. Numerous measurements on Portland, Portland limestone and other standard cements from the VDZ member companies have shown that the fine quartz dust fractions are below one percent. An additional STOT RE classification is therefore not generally required for cements and other cementitious products.

## European Construction Products Directive / Regulation

Both the European Construction Products Directive (CPD) as well as the legally binding Construction Products Regulation (CPR) that was published on 04.04.2011, and which replaces the previous CPD, make specific references to hygiene, health and the environment. However, as currently only two member states of the European Union, the Netherlands and Germany, have set quantitative requirements regarding the environmental compatibility of construction products in contact with soil and ground water, the currently adopted harmonised European product standards only contain general information on existing national requirements.

Appropriate assessment methods are now expected to be prepared for the future preparation and revision of harmonised technical specifications (harmonised European standards or European technical approvals). The European Commission issued mandate M/366 "Development of horizontally standardised assessment methods for harmonised approaches relating to dangerous substances under the Construction Products Directive - emissions to indoor air, soil, surface water and ground water" on 16.03.2005. The mandate provides for the development of horizontal test and assessment methods by the European Committee for Standardisation (CEN), while the specific requirements of the construction products continue to be specified nationally by the individual Member States.

## Standardisation activities in CEN/TC 351

In order to provide the necessary generic, horizontal test and assessment methods to implement mandate M/366, the CEN established the technical committee CEN/TC 351 "Construction products: Assessment of release of dangerous substances" in 2006. The two following working groups were set up under the TC according to the various conditions of use:

- Working group 1: Release into soil and ground/surface water
- Working group 2: Emissions from construction products to indoor air

Three additional working groups have now also been established:

- Working group 3: Radioactivity
- Working group 4: Terminology
- Working group 5: Content determination

The main result of the CEN/TC 351 activities over the past years have been three drafts for harmonised test standards. Two of these test standards are intended for determining the leaching of inorganic and organic substances from construction products. The third test method deals with the release of volatile compounds to indoor air. It is intended to apply for all emission-related construction products; however it is only of secondary significance for purely inorganic cementitious building materials.

In order to consider the fundamentally different leaching behaviours of granular and monolithic construction products, working group 1 prepared a leaching test "Generic horizontal dynamic surface leaching test (DSLT) for determination of surface dependent release of substances from monolithic or plate-like or sheet-like construction products" and a percolation test "Generic horizontal up-flow percolation test for determination of the release of substances from granular construction products" (Fig. VI-6). Robustness tests and, as a second step, interlaboratory tests, are required before the test methods prepared by CEN/TC 351 can obtain the status of European standards (EN).

The objective of the robustness tests is to determine how sensitively the test method reacts to changes in the test conditions by varying selected testing parameters. After the robustness tests, the draft standards may be adapted according to the test results and published as technical specifications (TS). Robustness tests for the leaching and percolation tests are currently being performed by a European consortium for a multitude of different construction products.

Once the test results are available and if the votes in the CEN have a positive outcome, the draft standards could be available as technical specifications in 2013.

Mortar and concrete are not being investigated by the European consortium as a corresponding research project was assigned to the Verein Deutscher Zementwerke together with the Intistut für Bauforschung der RWTH Aachen by the Federal Environment Agency (UBA) in 2009 in order to support the validation process – as the financing for these validation investigations



Fig. VI-6: Concrete cube in long-term leaching test (left); granular construction product in the percolation test (right)

Table VI-3: Variation of the test conditions for the concrete tests

Variation no.	Description
1	Decrease of the preliminary storage period to 28 days
2	Increase of the preliminary storage period to 91 days
3	Decrease of the test temperature to 15 °C
4	Increase of the test temperature to 25 $^{\circ}$ C
5	Contact times according to the DAfStb long-term leaching test
6	Contact times according to the Dutch standard NEN 7375
7	Decrease of the ratio of eluent volume to the test specimen surface of 40 $\ensuremath{l/m^2}$
8	Increase of the ratio of eluent volume to the test specimen surface of 120 $l/m^2$
9	Decrease of the pH value of the test water to a value of 4
10	Increase of the pH value of the test water to a value of 10

Table VI-4: Relative standard deviations (variation coefficient V) for the eightfold determinations for all investigated parameters

Parameter	Relative standard deviation (variation coefficient V) in %
Barium (Ba)	36.30
Lead (Pb)	19.80
Chloride (Cl <sup>-</sup> )	89.60
Chromium (Cr)	17.20
Potassium (K)	6.86
Copper (Cu)	56.60
Sodium (Na)	14.40
Selenium (Se)	7.16
Sulphate (SO42-)	33.80
Vanadium (V)	6.55
Zinc (Zn)	34.90

by the European Commission had not yet been specified. The project objective, which was established in cooperation with CEN/TC 351, was to perform the robustness tests for the leaching test with mortars and concretes. For the mortar tests, a mineral reinforcement plaster with a high fraction of organic components was used in order to additionally determine the suitability of the leaching test for investigating the release of organic substances (TOC release). The mortars and concretes were produced and stored based on the DIBtprinciples. Cubes with dimensions 10 cm x 10 cm x 10 cm were provided as test specimens in both cases.

For the concrete tests, the leaching test was initially performed as an eightfold determination according to the European draft standard (DSLT, 36 day long-term leaching test). The test conditions were then varied pursuant to Table VI-3. These investigations were each performed as duplicate determinations. The eluates were investigated regarding the inorganic parameters according to the DIBt-principles, for which an insignificance limit value is defined. The sodium and potassium concentrations, the pH value and the electrical conductivity in the eluates were also determined. The TOC release was also investigated for the reinforcement plaster.

The results of the eightfold determination for potassium and sodium, i.e. for elements for which large quantities are present and dissolved in pore water and whose leaching is predominantly diffusion controlled, displayed extremely good correlation. In contrast, large distributions were recorded for some trace elements. This relatively large bandwidth of results is attributable to the fact that, in most cases, only extremely low substance quantities were leached, which were generally near or under the determination limit of the extremely powerful analysis method applied. Table VI-4 provides a summary of the relative standard deviations (variation coefficient V) of the cumulated release quantities in the eightfold determination for all of the investigated parameters. The size of these variation coefficients are similar to those determined in studies by other authors.

Fig. VI-7 provides an example of the time dependence of the cumulated sodium release from concrete for the variation of the test conditions according to Table VI-3, including the average value of the eightfold determination. Only the test conditions that had the largest impact in the concrete tests were varied for the mortar tests and the DSLT tests were only executed as a duplicate determination. The leaching results for the reinforcement plaster confirm the results of the concrete investigations. The cumulated releases for the investigated parameters are of the same order of magnitude. Fig. VI-8 shows the time dependence of the cumulated TOC release from the reinforcement plaster when the test conditions were varied, including the average value of the duplicate determination.

The results for the potassium, sodium and TOC leaching show that there was only a low distribution when the test conditions were varied for these parameters. It can therefore be concluded that the leaching test (DSLT) as such is robust and that it is also suitable for investigating the release of organic substances. Another important result of the research project is that the leaching result for the above-mentioned parameters, which were obtained according to the Dutch standard NEN 7375 and the DAfStb long-term leaching test, were in the centre of the scatter range for all the test versions performed. This shows that it should be relatively easy to transfer the existing results to the 36 day leaching test pursuant to the European draft standard (DSLT).

The investigation results also show that no changes to the European draft standard (DSLT) are required with regard to the permitted ranges of the test conditions provided. The comprehensive final report on the research project with all of the investigation results was published by the Federal Environment Agency and can be downloaded from http://www.uba.de/uba-infomedien/4153.html.

## Effects on cement and cementitious construction products

The standardisation activities in CEN/TC 351 on the test methods are progressing rapidly. If the European Commission and other stakeholders, such as the member states and industry, promptly provide the funds for the necessary interlaboratory tests, it is possible that the publication of the first three CEN/TC 351 test standards will be published as harmonised European standards in 2015/2016. However, the implementation of the entire concept of mandate M/366, including the necessary assessment methods and the legislative requirements, will take several years. The Research Institute of the Cement Industry is represented in the key committees and brings essential experience in cement and concrete, which has been established over decades for components in contact with soil, surface, ground and drinking water, into the standardisation activities. The European concrete platform is currently working on a dossier for concrete which will ensure (based on existing scientifically proven investigation results) that cements according to EN 197 and concrete according to EN 206 can continue to be used, preferably without separate environmental tests, for the production of construction products or components in contact with soil and surface water and ground water.



Fig. VI-7: Time dependence of the cumulated sodium release from concrete when the test conditions are varied according to Table VI-3 including the average value of the eightfold determination



Fig. VI-8: Time dependence of the cumulated TOC release from reinforced plaster when varying the test conditions according to Table VI-3 including the average value of the duplicate determination

## DIBt-principles: Assessment of the effect of construction products on soil and ground water

In Germany, standardised or building inspectorate approved construction products meet all of the environmental protection requirements. However, possible soil and ground water risks must be considered for all new, unknown construction products that require building inspectorate approval. The DIBt-principles for the "Assessment of the effects of construction products on soil and ground water" summarise the scientific, technical and legal principles in this regard. The principles are divided into three parts. Part I describes the concept for the assessment of construction products in consideration of the concerns regarding damaging change to soil or ground water. This general concept applies for all construction products and was initially published in the November 2000 issue. In Part II, the evaluation concept for selected construction products is specified by the relevant DIBt project groups in order to properly consider the material-specific properties of the various construction products.

Part III summarises the analytical methods to be used for the evaluation of construction products according to Part I and Part II.

For concrete and concrete starting materials the responsible project group developed an evaluation model with which the 137

results of laboratory investigations (DAfStbguideline: Determination of the release of inorganic substances by leaching from cementitious building materials) can be transferred directly to groundwater pollution in the direct vicinity of a structure. The substance concentrations in the ground water calculated for defined boundary conditions based on the model have to comply with the defined limit values (insignificance threshold, GFS value). Investigations by the Research Institute of the Cement Industry on concretes produced with specific cements with high trace element content showed that these requirements were fulfilled. However, the distance to the GFS values was very low for some trace elements.

The general Part I and the special Part II for concrete and concrete starting materials were notified at the European level in 2006. The contents of both these parts have already been extensively presented and discussed in the previous Activity Report. There have been no changes for concrete and concrete starting materials in the reporting period. However, Part II has been extended by curtain injections and sewage pipe restoration materials. The revised version was notified at the European level in 2011 and can be downloaded on the internet from the European Commission's "Technical Regulation Information System" (TRIS).

The DIBt project group "Modelling: Roof and facades" has been engaged in deriving an evaluation model for components exposed to rain, such as concrete stone roofs, metal roofs or external rendering, since 2012. These activities are expected to take some time. The DIBt has targeted 2019 for the overall concept.

## Cementitious materials in the drinking water sector

#### **European activities**

Drinking water is vital for survival. Therefore only materials that do not unduly influence the drinking water quality may be used for materials that come into contact with drinking water. Cementitious products have established themselves in all areas of drinking water supply for decades. The European Drinking Water Regulation specifies the minimum requirements of drinking water for all the EU member states. It therefore seemed logical to also harmonise the hygienic requirements of materials in contact with drinking water across Europe. Drinking water hygienists authorised by the member states worked on a uniform European Acceptance Scheme (EAS) in the Regulators Group from 1999 to 2004. The EAS was intended to apply for all materials that come into contact with drinking water, and ensure that the existing consumer protection level remained in place and that all the established materials could continue to be used without restriction.

The Regulators Group activities were stopped in 2004 as the EU Commission determined that the Construction Products Directive (CPD) did not provide a legal basis for this type of group. The Regulators Group was therefore changed into an Expert Group with no regulation or decision-making power, rather only established to advise the Commission. It was also clarified that the CPD only included construction products that meet a harmonised technical specification and that these product requirements would remain with the member states. This resulted in the so-called CPD-EAS.

The CPD-EAS activities were also discontinued in 2007. Since then, drinking water regulators in the 4 Member States Group (4MS) from France, Great Britain, the Netherlands and Germany have been consulting on how the European activities can be continued. The objective of these activities is the neutral recognition of test results on a voluntary basis. A declaration of intent was signed by the authorised representatives of the 4 member states in January 2011.

The activities by the 4MS for metals and plastics are already at an advanced stage. A draft report for the evaluation of cementitious products in contact with drinking water has been available since February 2012. This draft provides that at this time only factory-made products and finished products for site applications will be assessed. The assessment will take place according to the attestation of conformity system 1+, for which the following parameters will face certain requirements:

- Complete description of the composition
- Compliance with the drinking water positive list (organic substances)
- Organoleptic parameters
- Migration of metals
- Migration of organic substances (TOC determination)
- Migration of specific organic substances

- GC/MS screening (if required by the approval body)
- Microbial growth

These extensive tests can be considerably reduced if the relevant certificates are available for all the initial constituents. In this case, only the organoleptic parameters and the TOC release of the end product need to be determined. It is also expected that the metal migration will not have to be tested if the cement and additives do not exceed certain trace element contents. The trace elements for which content values will be defined, and the size of these values, will be clarified this year by relevant migration trials. The Research Institute of the Cement Industry is closely involved in these investigations.

## **DVGW worksheet W 347**

Worksheet W 347 "Hygiene requirements of cementitious materials in contact with drinking water - Testing and evaluation" of the German Technical and Scientific Association for Gas and Water (DVGW) specifies the requirements of cementitious materials that come into direct or indirect contact with drinking water or raw water for drinking water production. The May 2006 issue of the worksheet provided adaptations to the state of technology and the relevant European test methods. There have been no changes to the worksheet in the reporting period. However, it was intended that the positive list in the worksheet would be discussed by the DVGW project group 3.4.12 "W 347" in the future and that the supplemented lists would be published on the internet. The body responsible for the drinking water sector, the Federal Environment Agency (UBA), objected to this procedure as the maintenance of the positive list was their "sovereign" duty.

However, it was also determined that the Federal Environment Agency did not currently have the personnel capacity to maintain the positive list. This means that no new substances can be added to the positive list. This situation is not acceptable for the affected industries, in particular building material chemistry companies. It is hoped that a solution that is acceptable for all parties is found as quickly as possible.

The DVGW steering committee has now resolved to revise worksheet W 347. The positive list will be released from the worksheet and formally assumed by the Federal Environment Agency for future maintenance.



Fig. VI-9: Overview of the standards published by CEN/TC 350 and those currently in development

## Sustainability of construction works

Sustainable development meets the needs of the current generation, without compromising the opportunities of future generations. The building trade complies with this mission statement if functional structures are established at low cost, if they represent a low burden on the environment and if they can be used for a long-lasting period.

## Standardisation of sustainability assessment

Over the past years, the European Standardisation Organisation CEN has prepared standards for evaluating the sustainability of construction works in technical committee CEN/TC 350 "Sustainability of construction works". The VDZ was involved in the development of these standards via the international cooperation with CEM-BUREAU. **Fig. VI-9** provides an overview of the published standards and the standards that are currently under development.

An assessment of the sustainability of buildings according to the standards developed by CEN/TC 350 includes all three dimensions of sustainability (environmental, social and economic) and considers the entire life cycle of a building. Technical and functional requirements of buildings generally have to be defined prior to a sustainability evaluation as they impact the result of the assessment. Some of the relevant technical properties (fire protection, noise protection, etc.) are considered when assessing the social performance of a building. The so-called framework documents define the general principles and indicators for the assessment of environmental, social and economic performance (see Fig. VI-10), while evaluation standards provide the methods for assessing these indicators. Standards have also been developed for the environmental quality, which enable construction product producers to provide environmental information on their products so that these can be included in a sustainability assessment at the building level (see the following section "Environmental product declaration"). Sustainability com-

#### Indicators for the evaluation of environmental quality (examples):

- Global warming potential
- Acidification of soils and water resources
- Eutrophication
- Ground-level ozone formation
- Destruction of the stratospheric ozone layer
- Abiotic resource depletion potential
- Use of primary energy

## Indicators for the evaluation

## of the economic quality:

Life cycle costs
 Financial value (income minus costs)

#### Indicators for the evaluation

- of social quality:
- Accessibility
- Adaptability
- Health and comfort
- Stresses for the neighbourhood
- Maintenance
- Safety/Protection

Fig. V-10: Indicators for the sustainability assessment according to the CEN/TC 350 standards

parisons are not sensible at the product level but may only take place at the level of a "functional equivalent", i.e. a building or building part.

The standards developed by CEN/TC 350 do not contain any minimum sustainability requirements for buildings, but only provide the indicators to be investigated and the assessment methods. Information on the evaluation of the assessment results or the specification of benchmarks, performance classes, etc. have deliberately not been provided. This type of evaluation can take place at the national level for the sustainability certification of structures and is outside the scope of the standards developed by CEN/TC 350.

In addition to the standards for the sustainability assessment of buildings, corresponding European regulations will also be developed for civil engineering works in the future. The VDZ will support these standardisation activities.

## Environmental product declaration for cement

Quantified environmental information on the construction products used is required in order to assess the environmental sustainability of construction works. The standardised format to be used to communicate this information is the so-called Environmental Product Declaration (EPD). The standard EN 15804 developed by CEN/TC 350 specifies rules for the preparation of EPDs. The objective is that the product manufacturers provide verifiable and consistent data that is determined based on comparable rules. The Environmental Product Declarations are verified by independent third parties in order to ensure the credibility of the information that they communicate.

Based on a resolution by its Executive Board, the VDZ prepared an EPD for a cement with a composition that represents the average of cements produced in Germany in 2010. Datamining from the German cement works was the basis for determining the environmental impact of cement production. 51 works, almost all the German cement and grinding works, provided information on the material and energy resources. The results of the statutory emission measurements from rotary kiln plants were also evaluated. The EPD for cement is a so-called "cradle to gate" EPD and includes all the environmental burdens of cement production, including the burdens from raw material mining and fuel extraction/processing and from transporting the raw material and fuels to the cement work.

According to ISO 14025, Environmental Product Declarations must be managed in an environmental declaration program. The program operator must ensure the transparency and comparability of the EPDs published in their program by so-called product category rules. The operator must also establish a suitable verification procedure by independent verifiers. The most established EPD program in Germany is that of the Institute Construction and Environment (IBU), which the VDZ joined in the context of the preparation of the cement EPD.

For many years the calculation of the life cycle analysis for cements involved the dispute of how the environmental burdens from secondary products from other industrial processes could be considered in the calculation if these materials are used in cement production. For the environmental product declarations for cement, this particularly relates to blastfurnace slag as a secondary product of the blastfurnace process and hard-coal fly ash as a secondary product of electricity generation. In these cases, the issue relates to the share of the burdens from these processes that are to be allocated to the primary product (pig iron for the blastfurnace process and electricity for the coal-fired power plant) and the share allocated to the secondary product. According to the new EN 15804, in these cases, an "economic allocation" has to be carried out; this means that the environmental burdens must be distributed to the primary and secondary products according to the economic revenue generated. Following these rules only a small share of less than 1 % of the environmental burdens of the blast furnace process and electricity production are allocated tu blast-furnace slag and hard-coal fly ash. This was taken into account in the EPD when calculating the environmental impact of cement production.

The Environmental Product Declaration for an average German cement was published in March 2012 and is available from the IBU and VDZ internet sites. **Table VI-5** shows a selection of the environmental information contained in the EPD.

The VDZ will subsequently prepare an EPD for concretes of various strength classes based on the EPD for cement. This will take place in close cooperation with the Bundesverband der deutschen Transportbetonindustrie (BTB) and the Fachvereinigung Deutscher Betonfertigteilbau (FDB).

## Sustainability certification in Germany

A system for the integrated consideration and evaluation of sustainability aspects for buildings was developed in a two year cooperative collaboration between the Federal Ministry of Transport, Building and Urban Development (BMVBS) and the German Sustainable Construction Council (DGNB) in which ecological, economic, social and technical criteria are all equally considered. This resulted in the development of two separate certification systems, the sustainable construction evaluation system for federal buildings (BNB) and the DGNB certification system, according to which industrial buildings and hospitals or residential buildings can now also be certified apart from just office and administration buildings. A bronze, silver or gold certificate is awarded depending on the result.

The VDZ used the example of a fictitious office building with a reinforced concrete structure to investigate the impact that the environmental burdens of cement production can have on the result of a sustainability certification according to the DGNB system. The example showed that the production of cement and concrete can have a significant effect on the life cycle assessment of the construction phase. However, the environmental burdens of the building utilisation (particularly from energy supply) and the consideration of economic, socio-cultural and technical criteria ultimatively lead to the fact that the environmental burdens caused by cement production only have a minor impact on the overall result of a sustainability certification according to the DGNB system.

The DGNB system currently values some technical criteria such as fire protection or noise protection higher than indicators from the life cycle assessment such as the global warming potential.

## Measuring and testing methods

The Research Institute of the Cement Industry has been using powerful analysis technologies to determine main, minor and trace elements for many years. These technologies were originally primarily used for research projects and to process analytical problems. These days the Institute is increasingly being sought as a service provider for analytical tasks. The associated increased sample throughput requires analysis techniques that ensure both high quality and rapid order processing. In order to ensure this, the Research Institute's equipment is constantly reviewed and updated.

## Determination of the carbon, hydrogen, nitrogen and sulphur content of fuels

Due to the constantly increasing use of secondary fuels in the cement industry, their analysis is one of the main areas of responsibility of the Research Institute's Quality Assurance and Analytics department. A new elementary analyser was acquired in 2011, which allows for the simultaneous determination of the carbon, hydrogen, nitrogen and sulphate content of fuels in just a few minutes.

A high number of carbon measurements are also required for determining the biogenic carbon according to the selective dissolving method. Despite the relatively inhomogeneous samples, low repeatability standard deviations are achieved with the new device for sample weights of only approx. 20 mg. This was proven by the positive results achieved when performing appropriate round-robin tests. Certified reference materials are measured every working day prior to every sample series in order to ensure the quality of the results. The analyser is stable over long periods and only needs to be calibrated once a year (Fig. VI-11).

Table VI-5: Overview of the key indicators on the environmental effects and resource use for the production of one tonne of average German cements

Parameter	Unit	Value
Global warming potential	kg CO <sub>2</sub> equi.	691.7 <sup>1)</sup>
Destruction of the stratospheric ozone layer	kg CFC11 equi.	$1.50 \cdot 10^{-5}$
Acidification of land and water resources	kg SO <sub>2</sub> equi.	0.83
Eutrophication potential	kg (PO <sub>4</sub> ) <sup>3-</sup> equi.	0.12
Potential for the formation of ground-level ozone	Kg ethane equi.	0.10
Potential for the depletion of abiotic resources (elements)	kg Sb equi.	$1.30 \cdot 10^{-3}$
Potential for the depletion of abiotic resources (fossil fuels)	MJ	1901.4
Total use of non-renewable primary energy	MJ	2451.3
Total use of renewable primary energy	MJ	65.8

<sup>1)</sup> This figure contains 98.1 kg CO2 equi. from the burning of waste during clinker production. According to the polluter pays principle (EN 15804), these would be allocated to the product system that caused the waste. However, the cement EPD refrains from substracting this share. This allows the comparability of calculated global warming potentials for cements to be ensured across countries in the event that the secondary fuels used during the clinker production do not have a waste status in other countries.

Fig. VI-11: Elementary analyser for the determination of carbon, hydrogen, nitrogen and sulphur





#### Fig. VI-12: Analyser for the determination of organic carbon (TOC)

solid samples

**Determination of TOC in liquid and** 

The sample throughput for the determina-

tion of organic carbon (TOC) has also con-

tinued to increase. As a result, a new

analyser for determining the TOC content

in liquid or solid samples was also acquired

(Fig. VI-12). Solid samples are determined

after digestion with hydrochloric acid according to DIN EN 13639. Repeatabilities

of less than 1 % can be achieved for sam-

## ple weights of only approx. 30 mg. The determination limit of the process is 0.01 mass %.

The analyser also enables the simultaneous determination of the organic and inorganic carbon in a sample by first determining the organic carbon at 500 °C and then the inorganic carbon by additionally heating the sample up to 950 °C.
# VII

# **Responsibility for employees**



Personal support for participants in simulator training using Simulex®

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# Occupational safety

# Safety work result

The constant improvement of occupational health and safety protection in cement industry works is one of the statutory duties of the VDZ. Efforts by the works and the Research Institute of the Cement Industry are therefore a top priority in the joint activities. The VDZ Environment and Process Technology committee, which is effectively supported by the VDZ occupational safety task force, develops and introduces measures to improve occupational safety. The common objective of all the efforts is to provide safe workplaces and work equipment, as well as to motivate employees in the cement works to work safely, provide regular information on opportunities for improving occupational safety and to ensure that safety at the workplace is constantly monitored.

The occupational safety measures in the works and the cooperation with the VDZ and its Research Institute have made a vital contribution to reducing the accident frequency rate based on reportable accidents pursuant to the BG RCI definition to less than a fifth of the original number in German cement works since 1969. Fig. VII-1 shows the course of the accident frequency rate since 1969. The value was 8.1 for the current reporting period for accidents with more than three working days lost and 12.9 for accidents with more than one working day lost.

The economic impact of occupational safety can best be illustrated by the percentage of days lost as a result of industrial accidents. While there was an average relative downtime of 0.8 % caused by reportable industrial accidents in 1969, this was reduced to only 0.16 % in 2011.

Apart from the evaluation of the accidents, intensive efforts have been made to provide safer workplaces and equipment over the past few years. The occupational safety task force, in several subgroups, prepared a recommendation for the machinery directive and an extensive test matrix to inspect work equipment. These measures are supported by constant endeavours to increase the awareness of safe work among management and employees. Personal behaviour and the avoidance of negative routines are key criteria for a continued sustainable reduction of the accident figures.



Fig. VII-1: Development of the accident frequency rate for reportable accidents with more than three working days lost pursuant to the BG RCI definition

### Table VII-1: Accident figures for the workforce in the VDZ member works from 2008 to 2011

Year	2008	2009	2010	2011
Number of works	47	47	46	44
Cement production in millions of tonnes	33.6	30.4	29.9	33.5
Workforce				
Number of employees	4975	5063	5081	5093
Hours worked	8178699	8 3 2 1 8 2 4	8236481	8 283 691
Production-related wage hour expense in h/d	0.24	0.27	0.28	0.25
Reportable industrial accidents	109	132	111	67
Total industrial accidents (includ- ing non-reportable accidents)	176	182	151	107
Accident frequency rate (definition until 2007, reportable accidents per 1 million working hours)	13.3	15.9	13.5	8.1
Accident frequency rate (definition from 2008 / total industrial acci- dents per 1 million working hours)	21.5	21.9	18.3	12.9
Calendar days lost due to industrial accidents	3 363	3 2 6 2	2806	1 668
Work days lost per employee	0.7	0.6	0.6	0.3
Calendar days lost per industrial accident	19.1	17.9	18.6	15.6
100-person ratio (old definition / reportable accidents per 100 em- ployees)	2.2	2.6	2.2	1.3
100-person ratio (new definition / total industrial accidents per 100 employees)	3.5	3.6	3.0	2.1

# VDZ accident statistics

The reportable occupational and commuting accidents in the German member works have been recorded and statistically evaluated by the Research Institute of the Cement Industry since 1965. The most important results and accident statistics figures from 2009 to 2011 are summarised in Table VII-1. The 2008 values have also been provided by way of comparison. In order to take the development of the personnel structure in the operations into account, from 1993 the entire workforce in the operation forms the basis for calculating the accident statistics rather than just the industrial employees. From 2008 onwards, a work is only considered free of accidents if it has not recorded any working days lost as a result of an accident, i.e. including no lost working hours caused by accidents that do not have to be reported. The day on which an accident occurs is not included. The key evaluation criterion is also calculated differently under the new boundary conditions for competition: From 2008 the accident frequency rate describes the number of all industrial accidents with working days lost for every million working hours.

The workforce has risen slightly since 2008 (+2.4 %). The number of annual working hours per employee was 1 644 h/a in 2009 and, after dipping to 1621 h/a in 2010, rose slightly to 1626 in 2011. Table VII-1 shows that the production of approx. 30 million tonnes in 2009 and 2010 rose to 33.5 million tonnes in 2011. The production-related working hours expense sank from 0.27 h/d to 0.25 h/d. The number of reportable industrial accidents fell from 132 in 2009 to 67. The overall number of industrial accidents also reduced during the reporting period: While 182 industrial accidents were registered in 2009, this value reduced to 151 in 2010 and 107 in 2011. The average accident frequency rate developed accordingly.

The average number of calendar days lost per operational accident was between 15.6 and 18.6 during the reporting period. The economic impact of industrial accidents can also be evaluated using the annual loss of production. This figure shows the number of calendar days lost with regard to the number of employees. The average annual loss of production reduced from 0.6 in previous years to 0.3 in 2011. The 100-person ratio, i.e. the number of industrial accidents per 100 employees, continued to decrease from 2009 to 2011. Based on the new definition (i.e. total industrial accidents per 100 employees), the value fell by

 Fig. VII-2: Awarding the winners of the occupational safety competition for 2010 at the Technical/Scientific cement conference in Düsseldorf from 27 to 28.09.2011

about 42 % from 3.6 in 2009 to 2.1 in 2011. The 100-person ratio in line with the old and new definition is presented in Table VII-1 to provide a better comparison.

# Promoting occupational safety

Nine safety codes of practice (no. 110 to 118) describing typical and especially noteworthy industrial accidents, as well as nine safety checklists (no. 90 to 98) for inspecting equipment and measures to improve occupational safety were released over the past three years. A new edition of the VDZ code of practice Vt 12 "Health and safety in hot areas of cement plants" was completed in 2011 and published in January 2012. Since January 2013 it is also available in English.

Fig. VII-2 shows the winners of the VDZ occupational safety competition for 2010 after being presented their plaques in September 2011. The member works with clinker production with the lowest accident frequency rates have been recognised every year for over 30 years. The award consists of a plaque with the VDZ's symbol for work safety and the inscription "Work safe - VDZ". The plaque is a symbol of recognition of all the efforts by work management and employees to ensure work safety. The distinction is also intended to motivate employees and to promote safety awareness in the works. In 2011, 13 clinker works and 7 grinding plants were distinguished for their accident-free operation. Due to their differing hazards, grinding works are distinguished in a separate competition to clinker works.

### Safety seminars

The course of the accident figures over previous years illustrates that occupational safety has improved enormously thanks to the considerable efforts of the works with support from the task force and the Research Institute of the Cement Industry. However, to continue to improve occupational safety, employees must constantly strengthen rather than relax their efforts. The key in this regard is the motivation of employees to correctly apply and implement the safety regulations in the operation. Company management, works managers, operation managers and supervisors and foremen bear particular responsibility in this respect. The exemplary behaviour of management, with constant contact with employees, has the largest influence in improving occupational safety in the operation. This knowledge has induced the VDZ, at the recommendation of the work safety task force, to offer intensive training for supervisors and foremen. The objective of the seminars is to improve knowledge of work safety, especially in areas with high accident risks, and to provide suggestions for internal measures to improve occupational safety. The seminars each take two days and are organised and executed outside the operations by BG RCI seminar leaders in groups of 15 to 20 participants.

Table VII-2: Number o	f graduates :	from the industrial	foreman course
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Course		Year	Cement	Lime	Total
Cement	1 to 8	1958/1959 to 1964/1966	229	45	274
Lime/Cement	1 to 11	1965/1967 to 1985/1987	225	65	290
	12 13 14 15 16 17 18 19 20 21 22 23	1987/1989 1989/1991 1991/1993 1992/1994 1993/1995 1995/1997 1997/1999 1999/2001 2001/2003 2003/2005 2005/2007 2007/2009	22 20 20 24 26 24 21 21 13 13 13 11 15	3 10 10 6 3 2 2 2 2 2 0 1 2	25 30 30 29 26 23 23 15 13 12 17
Total	24	2009/2011	18 702	1 154	19 856



Fig. VII-3: Successful graduates of the 24th Industrial foreman course lime/cement

The seminars have been offered as a permanent institution since 1993.

# VDZ education and training

# Industrial foreman course

The qualification and training of employees in member companies is one of the core tasks of the VDZ. Cement producers have taken advantage of this since the very beginning and place great importance on targeted training measures, especially in times of tight economic conditions. The VDZ offer is targeted at various groups. The Education Advisory Board and the knowledge exchange with the works ensure efficient and practical training with modern content. The industrial foreman course continues to represent the central element of the VDZ training offer.

The Verein Deutscher Zementwerke has been providing foreman training together with the Bundesverband der deutschen Kalkindustrie e.V. for over 53 years. A total of 856 foremen and women have completed their foremen training (see Table VII-2 and Fig. VII-3). The 24<sup>th</sup> Industrial Foreman course lime/cement ended in March 2011. The 19 course participants, 18 from the cement industry and one from the lime industry, received their foreman certificate after successfully testing their knowledge in eight written tests and one final oral test in front of the examination board of the Düsseldorf Chamber of Industry and Commerce.

The industrial foreman candidates had to study theoretical know-how for their subsequent activities in the cement and lime works in a total of 28 subjects with just under 1000 hours of lessons. The fundamental subjects of mathematics, physics, chemistry and material basics were taught first during a 7-month boarding period. They were then subject to targeted training in specific subjects such as extraction technology, preparation technology, firing technology, environmental technology and machinery and energy technology in two 4 and 6-month correspondence courses at their local works. The training also focussed on the topics of occupational safety and behaviour in the operation. For example, operational situation tasks on individual topics (e.g. conduct in the event of an accident or a dispute between colleagues) were extensively covered and explained. Finally, the recognised training measures were rounded off by acquiring the trainer qualification (AEVO).

After passing the test, the foremen are then also qualified to train employees.

In the 18-month training, participants don't just cover the theoretical fundamentals of the lime and cement processes, they are also specifically trained in interdisciplinary topics such as the management of employees and leadership. A particular focus is on teamwork and mutual support.

The 25<sup>th</sup> industrial foreman course started in October 2011 with 20 participants.

# Production controller course

The increasing complexity of the process plants in connection with the high demands of environmental protection and occupational safety require increasing knowledge of the safe, environmentally-friendly and energy-efficient operation of plants for today's operators of modern rotary kiln plants and grinding mills. In order to satisfy these increasing requirements regarding the qualification of operators, the VDZ has been successfully providing production controller courses for over 20 years. The entire course includes a theoretical part, which is offered by the VDZ as boarding classes at the Hilden training centre and a practical part to be completed at the cement work. Participants at the Hilden training centre are subject to intensive training in three sections by experienced lecturers with the objective of teaching the control room staff the current state of knowledge in process and environmental technology of cement production and the requirements for an efficient and safe operation. In these seven weeks of theoretical training, participants obtain a deeper understanding in the fields of material science, burning technology, environmental technology, process technology, metrology and control engineering and the basic subjects of mathematics, chemistry and physics. The knowledge is enhanced by training with the Simulex® simulator. Participants are intensively prepared for normal and unplanned operational situations in the cement work. The students are extensively trained from start-up training of individual units and the entire plant through to diagnosing complicated faults. Apart from numerous lessons, the course also focuses on the practical exchange of experiences and group work.

More than 350 people in 17 courses had been trained as cement production controllers until 2011. The extremely good boundary conditions provided by the Hilden training centre also make a significant contribution to the successful completion of the course. Lecturers and participants con-



tinue to be extremely satisfied with the learning conditions and the full board.

# Cement knowledge 2.0 –

Multimedia knowledge transfer Between 1997 and 2008 VDZ and a task force of VDZ and the German cement plants developed a total of 47 training materials for the education of technical personell. During the ongoing development of the learning methods, the so-called tutorial notes were transferred to web-based online courses as part of the BMBF "Vocational training for sustainable development in the German cement industry" research project. The project was successfully completed in 2009. At the end of the project, more than 90 % of those surveyed were in favour of the continued use of the VDZ learning platform (www.elearning-vdz.de). The surveyed users especially highlighted the innovative visualisation and animations that help trainees better understand the issues and connections (Fig. VII-4). Reviewing and documentation of the learning outcomes is also possible thanks to the self-control questions and computer-based tests. The VDZ learning platform, with 48 online courses and 4 information assignments, has been available to all interested parties since the start of 2010. The technologies applied allow for individual configurations of separate topics and factory-specific supplements and tests. A large part of the courses has also been translated into English and can therefore be better used for international training. A Russian version is currently being prepared.

The VDZ, together with partners in the BMBF joint project "Cement/Lime/Concrete knowledge network", have been

### Table VII-3: Seminar topics 2012

Z-IML	Industrial foreman - lime/cement
Z-PSL	Production controller - cement
Z-GDP	Basics of cement production and utilisation
Z-IMP	Innovations for industrial foremen and production controllers
Z-INS	Maintenance in cement works
Z-ASI	Practical occupational safety knowledge for cement industry foremen and supervisors
Z-FOB	Modern kiln and firing technology
Z-GMT	Basics of grinding technology
Z-FMT	Advanced grinding technology
Z-GZC	Basics of cement chemistry
Z-TMI	Technical mineralogy
Q-QSI	Quality monitoring according to DIN EN 196
Q-RFA	X-ray fluorescence analysis (RFA)
Q-HSÜ	Determination of the blastfurnace slag content - method
Q-HSM	Determination of the blastfurnace slag content - microscopic/chemical process
Q-INA	Internal auditors
U-EUT	Introduction to environment technology (basic course according to 5 <sup>th</sup> BImSchV)
U-FIB	Further training for immission protection representatives (further training according to 5 <sup>th</sup> BImSchV)
B-MUP	Practical seminar: Grinding operation and product properties
E-AUT	VDZ learning platform authoring course
E-TUT	VDZ learning platform tutoring course

its previous offer for a 2-year period since 2010. The member works were informed of the current course offer in the form of a brochure as well as via the internet at www. vdz-online.de/weiterbildung. The internet site also provides the option of registering for the online newsletter and purchasing a newsletter that provides information on upcoming VDZ seminars three to four times a year (**Table VII-3**).

The process technology of cement production is covered in three annual seminars including "Modern kiln and firing technology", "Basics of grinding technology" and "Advanced grinding technology". Practical professional training was expanded with the seminars "Maintenance in cement works" and "Innovations for industrial foremen and production controllers" held for the first time in 2012. This particularly targets current industrial foremen and production controllers.

The objective of the 4-day "Basics of cement production and utilisation" seminar is to provide a comprehensive overview of all areas of cement production through to cement application in concrete. Accordingly, process technology issues, chemical/ mineralogical matters, environmental law, environmentally-compatible cement production, environmental monitoring, quality assurance and concrete construction technology are intensely discussed. The seminar is offered every two years.

The two 2-day seminars "Technical mineralogy" and "Basics of cement chemistry" take place on an annual basis. The first seminar covers how the chemical/mineralogical properties of cement raw materials, clinker, cement and concrete are determined based on microscopic and x-ray diffractometry investigation methods and how the results are evaluated. In particular, practical exercises are performed and the technical bases of the analytical system are discussed. The second seminar provides an overview of the basics of cement chemistry and the connections between cement production and cement properties.

Pursuant to the 5<sup>th</sup> Federal Ambient Pollution Protection Regulation (5. BImSchV), immission protection representatives must participate in training courses at least every two years. While the basic courses for immission protection representatives cover all areas of environmental protection, specific issues may be selected at further training events. The events are offered every two years with up-to-date topics that are specially tailored to cement industry mat-

working on expanding the learning platform to a cross-sector platform for exchanging knowledge and information since March 2011. The platform is expected to be completed and trialled by March 2014. The platform structure provides for the coverage of the four application scenarios of informing, consulting, learning and networking. Additional areas from the building materials/stone/earth industry are also incorporated. The opportunity to receive up-to-date industry information at central locations, to search for certain information, people and interest groups, to create knowledge together with others and to promptly obtain new knowledge in online courses should ensure that the platform is attractive for all groups and that it promotes knowledge in the industry. The project represents a significant development for the VDZ learning platform.

# **Training seminars**

Since 1998, the VDZ has been holding a series of single- or multi-day seminars as part of its training offer, in addition to the industrial foreman and production controller courses and the occupational safety seminars. Besides issues regarding process technology for cement production, chemical analysis, immission and environmental protection, the monitoring of cement quality and the fundamentals of concrete technology and concrete processing, two seminars have also been offered on the VDZ learning platform since 2010. These VDZ seminars are primarily intended as an introduction for young employees and as continued training for employees of VDZ member works that have been active in the cement industry for an extended period. The seminars are also available for employees from other companies and industries. Due to the, in part, long-term training planning in companies, the VDZ has extended ters. The focus is therefore on the current developments in German and European environment law, emissions of inorganic and organic compounds and trace elements and the reduction of  $CO_2$  emissions in the clinker burning process. The seminar is recognised as a further training course in terms of the 5<sup>th</sup> Federal Ambient Pollution Protection Regulation by the Ministry for Climate Protection, Environment, Agriculture, Nature Conservation and Consumer Protection of the German State of North Rhine-Westphalia.

The seminar "Introduction to environment technology" is also held every two years, alternating with the preceding seminar. The seminar provides an introduction into all the subareas of environmental protection and environmental technology. It discusses the issues of environment law, emission metrology, reduction of gas, dust and heavy metal emissions, noise and vibrations, ecological recycling of waste and production-integrated environmental protection. The lectures are supplemented by practical exercises regarding emission and immission metrology. The seminar is recognised by the state as a fundamental course for future immission protection representatives.

Four seminars are offered on the topic of "Monitoring cement quality" every year. These seminars are intended for laboratory supervisors and responsible laboratory work employees. The single day "X-ray fluorescence (RFA)" seminar provides participants with in-depth knowledge of x-ray fluorescence analysis technologies. The 2-day "Tests according to DIN EN 196" seminar presents the physical and chemical testing of cements and cementitious binders specified in the standard as well as the testing of raw materials and initial con-



stituents. Particular importance is placed on compliance with the standardised working method and the determination and prevention of sources of error. The focus of a further single day seminar was the determination of the blastfurnace slag content in cements in line with the combined microscopic/chemical process. This seminar was supplemented by a single day "Determination of the blastfurnace slag content method overview" seminar. This provides participants with an overview of the possible processes to determine the blastfurnace slag content in cement. The "Internal auditors" seminar has now also been added to the program. This seminar is intended for cement industry employees that audit energy, quality or environmental management systems in their company. On completion, participants receive an "Internal Auditor according to ISO 19011" certificate.

The single day "Grinding operation and product properties" practical seminar is also offered in the area of "Concrete technology". This provides an overview of the impact of the operation of cement grinding and mixing plants on important cement and concrete properties. The complex connections between cement production and the granulometric properties of cements with several main constituents are also explained. It provides the opportunity to discuss current practical issues.

Overall, an average of 20 seminars, with changing focal points, have been offered by the Research Institute of the Cement Industry every year since 2009. It is expected that this will increase to 23 in the future. Overall, the number of seminars held and the number of participants has developed positively since 2009, as illustrated by **Fig. VII-5**. Together with the consistent and rising number of participants in the industrial foreman and production controller courses and the VDZ learning platform, this provides a positive overall view of the further training activities in the cement industry. 149

# **Publications**

# Publication series of the cement industry (Schriftenreihe der Zementindustrie)

Eickschen, E.	Wirkungsmechanismen Luftporen bildender Betonzusatzmittel und deren Nachaktivierungspotenzial. Düsseldorf: Verlag Bau + Technik, 2009 (Schriftenreihe der Zementindustrie 73)
Bokern, J.	Betonprüfungen zur Beurteilung einer Alkali-Kieselsäure-Reaktion: Auswirkungen der klimatischen Bedingungen auf die Übertragbarkeit von Prüfergebnissen. Düsseldorf: Verlag Bau + Technik, 2009 (Schriftenreihe der Zementindustrie 74)
Seemann, S.	Einfluss des Mahlsystems und der Mahlatmosphäre auf die Zementeigenschaften. Düsseldorf: Verlag Bau + Technik, 2010 (Schriftenreihe der Zementindustrie 75)
Tigges, V. E.	Die Hydratation von Hüttensanden und Möglichkeiten ihrer Beeinflussung zur Optimierung von Hoch- ofenzementeigenschaften. Düsseldorf: Verlag Bau + Technik, 2010 (Schriftenreihe der Zementindustrie 76)
Eppers, S.	Assessing the autogenous shrinkage cracking propensity of concrete by means of the restrained ring test. Düsseldorf: Verlag Bau + Technik, 2011 (Schriftenreihe der Zementindustrie 77)

# Codes of practice and checklists (Merkblätter und Prüflisten)

Safety codes of practice (Sicherheits-Merkblätter)

- Nr. 110 Verbrennung durch defekte Schläuche an Gasflaschen
- Nr. 111 Absturzunfall durch Defekt an einem Gabelstapler
- Nr. 112 Verbrennung durch einen Unfall mit Rostlöser-Spray
- Nr. 113 Beinahe-Unfall bei Feuerfest-Arbeiten am Ofenauslauf
- Nr. 114 Schwerer Unfall bei Transport mit Gabelstapler
- Nr. 115 Tödlicher Unfall bei Lkw-Entladung
- Nr. 116 Augenverletzung durch Staubablagerung
- Nr. 117 Unfall bei Demontage eines Ausmauerungsgeräts
- Nr. 118 Sturz mit dem Fahrrad auf Glatteis

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# Safety checklists (Sicherheits-Prüflisten)

- Nr. 90 Verwendung von Ausrüstung zum Autogen-Schweißen
- Nr. 91 Tätigkeiten auf mobilen Arbeitsbühnen
- Nr. 92 Tätigkeiten in Bereichen mit hoher Umgebungstemperatur
- Nr. 93 Feuerfest-Arbeiten
- Nr. 94 Arbeiten mit Flurförderzeugen
- Nr. 95 Abkippvorgänge mit Fahrzeugen
- Nr. 96 Persönliche Schutzausrüstung (PSA) zum Augenschutz
- Nr. 97 Geräte und Ausrüstungen für Bau- und Montagearbeiten
- Nr. 98 Fahrradfahren im Zementwerk

# VDZ Codes of practice (Verfahrenstechnische Merkblätter)

- Vt 12 Sicheres Arbeiten beim Umgang mit Heißmehl (Neuaufl.)
- Vt 16 Feuerfeste Materialien

## VDZ Newsletter (VDZ-Mitteilungen)

Nr. 139 (Mai 2009) – 147 (Dezember 2011) Three issues per annum (May, September, December)

# Monitoring report (Monitoring-Bericht)

Verminderung der  $CO_2$ -Emissionen: Monitoring-Bericht 2008–2009; Beitrag der deutschen Zementindustrie. Düsseldorf, 2010

# Environmental data (Umweltdaten)

Umweltdaten der deutschen Zementindustrie 2008. Düsseldorf, 2009

Environmental Data of the Cement Industry 2008. Düsseldorf, 2009

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The use of superplasticisers can be optimized still further: Cements containing granulated blastfurnace slag or limestone, and their interactions with PCE superplasticizers. In: Cement International 9 (2011) 6, S. 21

Belite clusters in clinker caused by aluminium? Effects of raw materials and fuels on the clinker microstructure. In: Cement International 9 (2011) 6, S. 22

From the VDZ learning platform to the Web 2.0 knowledge network: The learning platform is being extended to include new possible ways of co-operation, referencing and learning. In: Cement International 9 (2011) 6, S. 23

# Congress proceedings (Kongressband)

Verein Deutscher Zementwerke, VDZ (Hrsg): Process Technology of Cement Manufacturing: 6<sup>th</sup> International VDZ Congress (Düsseldorf 30.09.-02.10.2009). Düsseldorf: Verlag Bau + Technik, 2009

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	Leitfaden zur Herstellung von Zementestrichmörteln im Innenbereich. In: Forum Lafarge Zement (2010) 1, S. 8–9
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Alonso, M. T.; Müller, C.	Verwendung von CEM II- und CEM III/A-Zementen in zementgebundenen Estrichen. In: Beton-Informationen 50 (2010) 6, S. 85–90
Baetzner, S.; Glöckler, J.; Israel, D.; Paul, M.	Long-term effectiveness of tin (II) sulfate as a chromate reducer. In: Cement International 8 (2010) 5, S. 67–76
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Bauer, K.; Hoenig, V.	Energy efficiency of cement plants. In: Cement International 8 (2010) 3, S. 50–57
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