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Deutsche Zementindustrie

Activity Report

2007 – 2009

Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie

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The cover picture shows a reflection of the VDZ logo on a concrete surface. The mirror effect is created by using fine-grain, ultra-high performance concrete in combination with very smooth formwork. Due to the optimised particle size composition of the concrete, its surface is almost as smooth as that of the formwork used.

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Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie

In this Activity Report the German Cement Works Association describes the joint projects which it worked on between 2007 and 2009. It thus continues the long-established tradition of reporting about the relevant topics of cement manufacture and applications which were significant for the cement industry and determined the work of VDZ during the period under review.

The global economy is currently facing challenges that would have seemed almost inconceivable in the past. At present, no one can say exactly how this situation will affect the construction materials industry in general or to what extent the cement industry will be affected. Consequently, joint projects that identify and efficiently deal with the topics that are important for cement manufacturers take on special significance against the background of tight budgets in the industry.

Through its Research Institute, VDZ offers an attractive portfolio of services along the complete cement and concrete value chains. The Institute has the support of a professional team of experts who are also involved in current research topics and who can rely on cutting-edge methods and equipment to conduct their investigations. The results of the research work that is carried out provide groundbreaking contributions in terms of further development in the areas of cement and concrete. In spite of the high cost pressure during the period under review, VDZ was still able to handle issues that are important for cement manufacturers. These include demands to reduce CO_2 emissions, requirements for the manufacture of durable and efficient concrete types and the challenges of reducing emissions in clinker manufacturer.

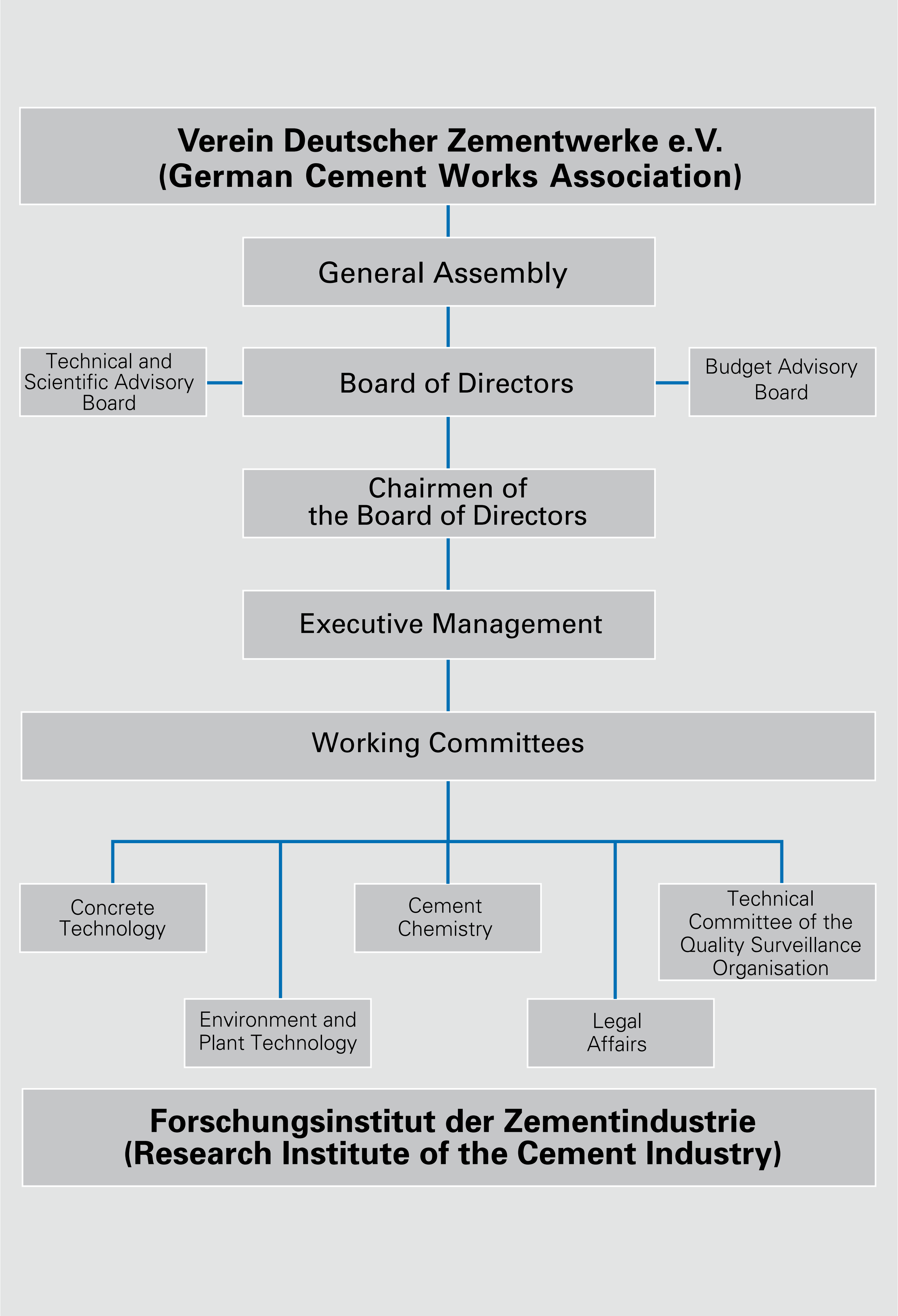
More than 130 years after it was founded, today VDZ is closely involved in the joint projects carried out in the cement industry at an international level. With its Research Institute it makes use of these contacts and, in return, acquires a wealth of experience for its own work. VDZ works together with the European Cement Research Academy on projects that have an overriding importance and which, because of this fact, cannot be pursued independently by single cement manufacturers. In particular, these include carbon capture and storage (CCS), examining the general status of this technology and predicting how it could develop in the coming decades.

VDZ extends a cordial welcome to its guests who will be attending the International VDZ Congress in September 2009 and, at the same time, underlines its close contact with national and international cement manufacturers, research institutes and plant constructors. Despite all the challenges, with its Research Institute VDZ will continue to support competitive and environmentally friendly cement manufacturing methods and high-quality concrete manufacturing processes in the coming years.

Dr. Martin Schneider
Chief Executive

Verein Deutscher Zementwerke e.V.
Düsseldorf, September 2009

The Research Institute of the Cement Industry in Düsseldorf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The German Cement Works Association ■

The German Cement Works Association (VDZ), located in Düsseldorf, is the technical/ scientific association for the German cement industry. It continues the tradition of the Association of German Cement Manufacturers formed on 24 January 1877. As a result of differences of opinion between the Portland cement industry and the slag cement industry regarding the question of using granulated blast furnace slag, the technical/scientific interests of the German cement manufacturers were represented by the German Portland Cement Manufacturers Association founded in 1877, the German Portland-Slag Cement Works Association established in 1901 and the German Blast Furnace Cement Works Association formed in 1907, respectively. They amalgamated in 1948, initially under the name of Verein Deutscher Portland- und Hüttenzementwerke (German Portland and Slag Cement Works Association). In 1952 the Association was given its present name of Verein Deutscher Zementwerke e.V.

Object of the Association

VDZ has no political, profit-motivated or entrepreneurial aims. The object of the Association is to promote technology and science – including research and development – in the production processes and applications of hydraulic binders. The statutory functions of the Association include, in particular, the promotion of measures for quality assurance, environmental protection and workplace safety. The knowledge gained from scientific work or everyday practice in the industry is transferred in publications, colloquia, seminars, conferences and congresses. Another purpose of the Association is to promote 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.

VDZ membership

Any natural or legal person who manufactures cements or cement-type binders in the Federal Republic of Germany that are standardised or approved by the building authorities can become a full member. Cement manufacturers outside Germany can be admitted to the VDZ as associate non-voting members. Currently, 24 German cement manufacturers with 50 cement works are full members of VDZ, while 31 foreign cement manufacturers are associate members.

BDZ Chairman Andreas Kern (right), VDZ Chairman of the Board Gerhard Hirth (centre) and VDZ Chief Executive Martin Schneider at the general meeting 2009 in Baden-Baden

VDZ organs

The organs of VDZ are the General Assembly, the Board of Directors, the Executive Management, the Management of the Research Institute of the Cement Industry and VDZ’s quality surveillance organisation as a testing laboratory, inspection body and certification body. During the period under review, the Annual General Meetings provided for in the statutes took place on 10 May 2007, 29 May 2008 and 14 May 2009; all in Baden-Baden. The current Board of Directors was elected on 29 May 2008. In principle, the Board of Directors is responsible for all the functions of VDZ. It also appoints the executive management of the Association and the management of the Research Institute of the Cement Industry. In recent decades the Board has consistently succeeded in unifying the personnel of VDZ’s management and the Research Institute’s directorate. The General Assembly appoints VDZ’s chief executive as a special representative for the purposes of Section 30 of the German Civil Code (BGB).

Committees, working groups and commissions ■

The Board of Directors is given support and advice by advisory boards: the Technical and Scientific Advisory Board, which coordinates the tasks of the committees and plans, implements and evaluates research, and the Budget Advisory Board, which is in charge of financial matters concerning VDZ and its Research Institute. The Board of Directors can form committees for specific specialist areas. Experts from the members’ works and from the Research Institute work together in these committees. At present there are five committees (see organisational chart on page 6). The Legal Affairs Committee serves as a joint committee of both VDZ and the German Federal Association of the Cement Industry (BDZ). At the recommendation of the committees, the Board can set up working groups, which can also include specialists from non-members’ companies, to deal with specific issues. Moreover, the Board establishes commissions for important interdisciplinary questions, which are made up of Board members and specialists in the various disciplines. Like the working groups, these commissions are dissolved after their tasks have been completed.

Technical committee of VDZ’s quality surveillance organisation

According to the association’s statutes the technical committee (previously known as the quality surveillance committee) is the organ responsible for the functions performed as a testing laboratory, inspection body and certification body (PÜZ body) of the German Cement Works Association’s surveillance organisation, which is approved by the building supervisory authorities. Its members are elected by the VDZ Board of Directors. The Technical Committee also includes the director and one other representative from the Research Institute of the Cement Industry as well as the manager of the PÜZ body. The committee’s main function is to assess and evaluate the results of the certification carried out by VDZ’s quality surveillance organisation. This entails inspecting, assessing and evaluating factory production control procedures and third-party inspections of cement samples.

Numerous topics deriving from inspection work were dealt with, and corresponding instructions were compiled during the period under review. For example, members of the technical committee were regularly notified about the latest developments in the field of standardisation – especially as regards cement standards. This concerned, for instance, the European standard for cements with high sulphate resistance, the revision of EN 197-1, details about the inspection standard EN 197-2 and the completion of various standards for special cements and binders (super-sulphate cement, hydraulic road binders, etc.).

The EU Construction Products Law, introduced in 1988, is also significant for the surveillance organisation. The underlying European Construction Products Directive is currently being revised and transferred into a legally binding regulation. The existing draft regulation places particular demands on the independence of the notified bodies. VDZ's surveillance organisation anticipated this development at an early stage by having itself privately accredited and establishing a certification advisory board.

FIZ-Zert Certification Advisory Board

The Certification Advisory Board acts as a steering committee for the certification body for management systems, FIZ-Zert, which was established in 1998. In conjunction with the accreditation of VDZ's surveillance organisation under public law, it also acts as an advisory body for product certification (see Chapter IV). The advisory body consists of at least five members from the interested parties, all of whom have voting rights. It is convened at least once a year.

Concrete Technology Committee

Working groups: transport engineering, cement and admixtures, ad-hoc working groups and task groups: European standardisation, ASR investigations, sulphate resistance

The Concrete Technology Committee deals with current issues in the areas of concrete manufacture and applications. It supports the Institute's corresponding research work with due consideration of the correct, quality-conscious and cost-effective use of cement and concrete in practice.

Via the ad-hoc group "European standardisation", the committee intensively followed the standardisation work, especially the A2 change, the consolidated version of DIN 1045-2 and the discussions about the planned revision of the European concrete standard EN 206. The committee was also very involved with test methods for determining the frost and deicing salt resistance of concrete in terms of its suitability and transfer to practical conditions.

With the "transport engineering" working group the technical committee supported construction work with CEM III/A cements on German roads and motorways and the manufacture of washed concrete surfaces. The Technical University of Munich was commissioned to "Prepare a lifecycle assessment for the manufacture and use of a section of German motorway". Work started in July 2008. The technical committee also had a list drawn up of the potential applications for a "thin wearing layer of asphalt (porous asphalt or stone matrix asphalt) on a concrete sub-base.

The use of cements with several main constituents in concrete and other cement-based construction materials (such as screed) remains a focal point of the committee's work. The "CEM II- und CEM III/A-Zemente im Betonbau" [CEM II and CEM II/A cements in concrete constructions] brochure was compiled. The brochure describes the technical application properties of CEM II and CEM III/A cements, the ecological benefits of using them and a wide variety of practical areas of application. A joint statement on "Information to manufacture cement-based screeds" was issued in collaboration with the German Federal Association for Screeds and Coverings (BEB) and the Federal Specialist Group for Screeds and Coverings in the Central Association of the German Construction Industry (ZDB). The statement also contains information about using CEM II cements in screeds.

Regarding the updating of the Alkali Guidelines, performance tests to assess the alkali sensitivity of concrete were examined. These include the 60°C concrete test with external alkali supply and alternating climate storage. Investigations with which the alkali sensitivity of concrete for road surfaces using the washed concrete method can be assessed were also examined. The suitability of fly ash from bituminous coal to prevent damaging ASRs was discussed and the future definition of test cements was considered.

Within the scope of the Deutsche Bauchemie/VDZ coordination committee, the cement and admixture working group made preparations for a meeting between VDZ Board members and Deutsche Bauchemie (DBC), the central association in Germany for manufacturers of chemical products used in the building industry. The focus was on identifying measures to manufacture more sturdy concretes. Against this background, the stability of the admixtures and the basic rules of concrete engineering in terms of adequate paste content are very important as regards manufacturing sturdy, high-performance and durable concretes. In the "Interface issues" project group important cement-based parameters and constituents for construction chemical products whose interactions could affect the properties of the concrete were named.

The committee also examined the environmental effects associated with the manufacture of cement and concrete. It presented the latest environmentally relevant data for cement and concrete for Germany in the form of construction material profiles. The basis remains the average values for a metric tonne of cement or a cubic metre of concrete. There has been a considerable improvement compared to the data from the reference year 1996. This can be especially attributed to the general reduction in the amount of Portland cement clinker in cement. The development of a European environmental declaration for cement was also discussed. The committee continues to support attempts to evaluate construction materials in connection with their use. In this respect, consideration of the entire lifecycle is important.

Cement Chemistry Committee

Working groups: Analytical chemistry, performance of cement constituents

During the period under review, apart from the Research Institute's research activities, the committee's work also focused on topics such as sulphate resistance of concrete, blast furnace slag reactivity, chromate reduction in cementitious mixtures, crystalline silica, safety data sheets for cement clinker and cement, alkali reactivity of test sands, REACH and geopolymers.

Investigations into the effects of blast furnace slag reactivity/quality on the sulphate resistance of concretes and mortars containing blast furnace slag have shown that with CEM III/A and CEM II/B-S cements there is a relationship between the chemical composition of the blast furnace slags and the sulphate resistance of the mortars. According to these investigations, low aluminium, silicon rich blast furnace slags are advantageous for achieving high sulphate resistance.

During hydration of cements containing blast furnace slag with relatively low early strength, it is possible that hydrogels rich in silicates are released from the blast furnace slag glass. These are plastic phases that reduce the standard compressive strength of the respective cements. Adding reactive aluminates can reduce corrosion of the blast furnace slag during hydration, which also reduces the extent of hydrogel formation. The reason for corrosion inhibition is believed to be the formation of aluminosilicates. Adding aluminate can certainly improve relatively low early strength – in some cases it can even double it. Cements that already exhibit high early strength cannot be influenced positively in this respect as they do not tend to form hydrogels.

Even if chromate-reducing cements are used, cementitious preparations may still exhibit higher chromate contents since other components in the mixture, such as finely ground calcium carbonate, can affect the dissolving behaviour of the chromate. It seems that the long-term stability of tin (II) sulphate as a chromate reducer is still not being achieved in some cases. The German Industry Association of Factory-Made Mortars (IWM), Deutsche Bauchemie (DBC) and VDZ have informed their members about the facts and have recommended that in the case of cementitious preparations which, in spite of chromate-reducing cement, still exhibit high chromate content they should independently add more chromate reducer.

In June 2008 the first reporting phase for the European social dialogue agreement on crystalline silica was completed. With this agreement in which 15 different industries are participating, technical workplace safety measures are aimed at improving the health protection of employees against silicosis and lung cancer caused by alveolar silica dust (crystalline silica dust). If this is a success, it may not be necessary to introduce a European limit value for crystalline silica dust. All cement works participated in the study. Experience has shown that in cement manufacture no or only very small crystalline silica dust loads occur.

To assess the alkali reactivity of aggregates the corresponding regulations define test methods using an "inert" test sand in combination with the aggregate under assessment. The initial results of a research project into the influence of quarzitic or not fully inert sand fractions on the assessment of the alkali reactivity of aggregates (chippings) would suggest that no incorrect assessment of the aggregates in use is caused by any of the test sands that have been investigated to date.

The REACH regulation – Registration, Evaluation, Authorisation and Restriction of Chemicals – came into force on 1 June 2007. Cement clinker has been included in Annex V of the regulations and is likewise exempt from the obligation to be registered. Cements are formulations and are thus also not obliged to be registered. However, substances that do have to be registered include chromate reducers and grinding aids (assuming they are not a preparation).

The representative organisation of the cement industry in Europe, CEMBUREAU, has created new sample REACH-compliant safety data sheets for cement clinker and cement. The Research Institute is working on the corresponding German versions.

The Research Institute prepared a literature study on geopolymers. Geopolymers form during the alkaline stimulation of reactive constituents, such as metakaolin, fly ash, blast furnace slag and natural pozzolans. Polycondensation reactions cause the formation of amorphous to semi-crystalline inorganic, aluminosilicate polymers. In the past, geopolymers were only used for special applications. Research is needed into the reaction mechanisms and products, controlling the reactivity of the starting materials and the durability of geopolymers.

Over the last few years, the "Analytical chemistry" working group has carried out various comparative trials to determine metal/semi-metal trace constituents. As expected, analysis of already decomposed samples (bypass dust, cement containing tin sulphate) showed a better correlation than the previous comparative trials where the participants decomposed the samples themselves.

The working group envisages providing a standard for chromate determination. For this purpose, in a long-term study a hydrophobed cement is being investigated roughly every six months to assess its water soluble chromate content. Compared to the first tests, in the third test – after approx. one year of storage – 1 ppm higher values for water soluble chromate content were determined. The tests are being continued.

The "Performance of cement constituents" working group is supporting investigations aimed at preventing a damaging ASR in concrete by using cements with several main constituents. The cement constituents blast furnace slag, fly ash and silica fume bond to alkalis early in the reaction. The extent to which these could be released again at a later time is still unclear.

Environment and Plant Technology Committee

Working groups: safety at work, refractory materials, environmentally compatible quarrying, NO_x abatement, training courses advisory board, rotary kiln burners and the ad-hoc working group BAT

The focus of the Environment and Process Engineering Committee's work was again operational requirements for safe, energy-efficient, cost-efficient and environmentally friendly cement production. Much of the work was summarised at a meeting of the full committee in Düsseldorf on 31 January 2008.

During the period under review, the safety at work working group again looked at the occupational safety situation in the members' works and the latest accident statistics. This included an analysis of the accident statistics at German cement works, which were generally positive over the last years. There were some changes in the accident statistics compared to the 2008 reporting year; accordingly, a works is no longer deemed to be accident free if an employee is unable to work on the day after the accident. In future, the data will be recorded only electronically. Other focuses of the working group were hazard assessments, the CE conformity statement, updating the code of practice for "Handling hot meal", the instruction matrix, the "Series of seminars for the statutory accident insurance fund for the quarry industry for foremen and assistant foremen in the cement industry", the "New version of the Machinery Directive" and "New technical rules for handling dangerous materials (TRGS)". Together with StBG a symposium on "Working safely in hot areas in cement works" was organised (Göttingen, Germany 24 April 2008). A meeting of instructors was held to prepare the new series of seminars for foremen and assistant foremen in the cement industry (Fulda, 17 September 2008) in which the content of the new series was planned.

The "refractory materials" working group has summarised its work in a guideline. For this purpose, a survey of the companies represented in the working group was evaluated to record their operating experience and refractory consumption. The guideline deals with delivery methods, occupational safety while working with refractories, drying and heating procedures and incoming goods checks for refractory materials. Other focuses were the cause of damage to refractory materials, measuring and adjusting the rotary kiln and the effect that the conditions of use have on the consumption of refractory materials. Refractory consumption among the member companies is to be surveyed regularly in future. The committee will decide on this when the guideline is complete. The working group's work should be completed by the middle of 2009.

The "Environmentally compatible quarrying" working group summarised the results of its work in a guideline for the environmentally compatible recovery of raw materials and was then dissolved. 2,500 copies of the guideline were printed and provided to VDZ members in August 2008.

The "NO_x abatement" working group discussed various operational experiments in which the abatement potentials of the SNCR (selective non-catalytic reduction) method were examined. In addition, in Germany and Austria SCR (selective catalytic reduction) projects have been started which are supported by the working group in close collaboration with the Austrian Cement Association. In this regard, contact with companies that build SCR plants and that manufacture catalysts has been extended. In a workshop entitled "Status of NO_x abatement in the cement industry", experts from the cement industry and VDZ and also from plant construction companies, universities and the area of environmental management summarised current and future requirements for NO_x abatement processes in the cement industry.

Under the responsibility of the training courses advisory board, the training certificates are currently being revised within the scope of a research project and provided on VDZ's new e-learning platform. The first 15 training certificates are already available and are being tested by 5 pilot works. After the test phase the other training certificates will be reviewed by the VDZ and the working group and will then also be implemented. The platform should be available to all VDZ member works by the start of 2010.

During the period under review, the 23rd industrial foreman training course was completed in March 2009 and the 14th production controller training course was completed in September 2008.

The "rotary kiln burner" working group commenced its work successfully. In the 1990s the rotary kiln systems were fitted with so-called low-NO_x burners so that the kilns could operate with relatively low NO_x emissions using low volumes of primary air and a low oxygen flame core. However, the increased use of alternative fuels requires higher quantities of primary air and excess air for rapid ignition and good incineration of the alternative fuels. A new generation of burners with modified burner design thus allows the use of alternative fuels even with high levels of substitution. However, at present there is no common agreement as regards optimum burner design or optimum operation for high volumes of alternative fuels. Because of this, the working group will especially gather experiences from the works with the following focuses: operational experience with new and modified rotary kiln burners, effects on clinker quality, use of alternative fuels, wear and tear, burnout, CO and NO_x formation and kiln operation. A corresponding research project from the Research Institute is being supported.

During the period under review, the "BAT" ad-hoc group discussed drafts for the BREF document (Best Available Technique Reference Document) for cement and the main changes desired for the revision process. The work of the Technical Working Group in Seville has almost been completed. From the point of view of the cement industry, the revision of the BREF document has achieved the following considerable improvements: energy efficiency, specific energy consumption for new/modern kilns with cyclone pre-heaters or calciners, dust emissions and NO_x emissions.

Legal Affairs Committee

The Legal Affairs Committee has been following initial experiences with the new EU Environmental Liability Directive which is to be implemented into national law. For the first time, the directive introduces a liability regime governed by public law for so-called biodiversity damage. For the cement industry the liability risks can be especially in the operation of the quarries, but also as regards emissions in connection with the manufacture of clinker and cement and in handling dangerous materials.

VDZ Alkali-Silica Reaction Commission

In 2000, the Concrete Technology Committee and the ASR Commission deployed the ad-hoc working group "ASR investigations" with the aim of aggregating the results of investigations in the various works and to coordinate other programmes of experiments with one another in order to promote research in the area of ASR. The activities focused on:

- organisation and evaluation of round robin tests,
- modification of the test method according to Part 3 of the Alkali Guidelines and, if necessary, development of new methods (rapid test) for aggregate tests,
- developing regional solutions to prevent damaging ASRs in order to introduce these in the contact working group with the aggregate industry and in the DAfStb's sub-committee "Alkali reaction in concrete".

Regarding the updating of the Alkali Guidelines, the commission has been monitoring performance test methods to assess the alkali sensitivity of concrete via the ad-hoc working group in coordination with the Concrete Technology Committee. This includes the 60°C concrete test with external alkali supply and alternating climate storage. Investigations with which the alkali sensitivity of concrete for road surfaces using the washed concrete method can be assessed are also being examined. The suitability of fly ash from bituminous coal to prevent damaging ASRs was discussed and the future definition of test cements was considered.

VDZ/BDZ Emissions Trading Commission

The underlying conditions for CO_2 emissions trading for the period after 2012 were defined in the revision of the EU Emissions Trading Directive. At the start of 2008 the EU Commission presented a draft with the following goals: auctions as the general method for allocating emission rights, gradual introduction of auctions as the allocation method for the industry, reduction target of 30% by 2020 for the entire EU, reduction target of 21% for the emissions trading sector by 2020 (basis 2005). In this regard, the Emissions Trading Commission has developed various analyses which, in particular, will enable free allocation of emission rights for energy intensive industries based on benchmarks. One of the main elements of this was a study by McKinsey & Company, which highlighted the extent to which the cement industry would be affected by carbon leakage. In December 2008, the European Parliament and the EU Council finished their work on the directive and considered how CO_2-intensive industries would be affected. Under certain conditions the affected sectors will not be allocated emission rights by auction but instead on the basis of benchmarks. Consequently, how these benchmarks will be structured at an European level will now be very significant. The Research Institute is involved in the corresponding discussions through its work in CEMBUREAU.

Regarding the cement industry's voluntary commitment to reduce CO_2, monitoring of CO_2 emissions was also continued during the period under review and the fuel and production data of the cement companies was surveyed and aggregated.

VDZ Ready-Mixed Concrete Commission

During the period under review, the Ready-Mixed Concrete Commission was involved with the revision of the European concrete standard EN 206-1, the interactions of cements and admixtures in ready-mixed concrete and the amount of fly ash from bituminous coal that will be produced in future.

In Task Groups TG 5 and TG 17 of CEN/TC 104/SC1 the focus was on the use of concrete admixtures and how these are counted, as well as the concept of equivalent durability. Different experiences and regulations have been reported from the countries that are involved in reviewing the European concrete standard. For example, in some cases combinations of cements and admixtures can be used on the basis of individual certificates, while in other countries the descriptive k-value concept has been established and proved reliable for many years.

With modern concretes the interactions of cements and admixtures in ready-mixed concrete are dependent on a whole range of factors. Optimising cements for individual super plasticisers is not possible because it must be possible to combine cements with many different super plasticisers. To avoid difficulties when using superplasticisers other concrete engineering aspects have to be considered, especially that there is an adequate paste content.

The volume of fly ash from bituminous coal is likely to rise considerably over the coming years as new coal-fired power plants are built. The potential of employing fly ash from bituminous coal in cement and concrete will thus become very important. This applies especially to the quality of the fly ash, which is extremely important for the durability of concrete.

The commission is also examining the requirements for concrete used in bridge caps, aggregating environmentally-relevant data for concrete (environmental data sheet) and aspects of third-party inspection of concrete.

Cooperation with other organisations ■

VDZ and its Research Institute cooperate closely in many different areas with public authorities, universities, material testing institutes and numerous professional associations, standards committees and organisations of related industries at national, European and international levels. This cooperation usually involves institute staff or member companies being represented on the committees of these organisations. This cooperation again achieved very good results on many issues in the period under review.

Federal German Association of the Cement Industry

The Federal German Association of the Cement Industry (BDZ) is the economic-political trade association of German cement manufacturers. It is the successor organisation of the "Central Agency for the Promotion of the German Portland-Cement Industry", which in turn originated from the "Association of German Cement Manufacturers" back in 1911.

BDZ represents 21 cement-producing companies and groups with 49 cement works. It is one of the association's key functions to represent its members' economic interests before politicians, the business community and the general public in the Federal Republic of Germany. At an international level BDZ is a member of CEMBUREAU, the association of European cement manufacturers. At a national level it is involved in the German Building Material Association and the Federal Association of German Industry (BDI).

In the period under review, BDZ's Concrete Information Department performed the countrywide tasks of the former Cement Building Information Board. To pool their marketing activities, BDZ, the Federal German Concrete and Precast Components Industry Association and the Federal German Ready-Mixed Concrete Industry Association founded BetonMarketing Deutschland GmbH, a limited liability company designed to promote concrete marketing.

Two BDZ subsidiaries, namely the Concrete Information Centre (IZB) and the Verlag Bau+Technik are in charge of certain aspects of joint work associated with boosting the image of concrete as a building material.

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

AiF, of which VDZ is a founding member, promotes joint industrial research, especially in medium-sized companies, with funds provided by the Federal Ministry of Economic Affairs. To be eligible for sponsoring, the research associations have to contribute funds that match the respective grants.

In the past years, VDZ received several AiF grants for various large research projects. The assistance of AiF and the Federal Ministry for Economic Affairs is gratefully acknowledged.

VDZ is represented in the AiF scientific council by the chief executive and by several employees in various expert committees.

Cement production and environmental protection

In the fields of cement production and environmental protection, close professional contact was maintained with the Federation of German Industries and the German Mineral Building Materials Association. Given the wide range of technical fields it covers, VDZ also cooperates with a number of other organisations. These include the German Engineers' Association (VDI), the German Combustion Research Association (DVV), the Technical Association of Power Station Operators (VGB PowerTech), the Association of German Metallurgists (VDEh), the Building Materials Research Institute FEhS, the German Water Management, Sewage and Waste Association (ATV-DVWK) and the German Gas and Water Engineering Association (DVGW), the German Sustainable Building Council (DGNB) and the German Construction Technology Platform (GCTP). Cooperation with the Federal German Association of the Lime Industry and its research association chiefly relates to the joint training and development of industrial foremen in the field of lime and cement as well as a wide variety of activities in the areas of environmental protection and occupational health and safety. VDZ conducts an active exchange of views on various topics with many state and federal ministries, including the environmentally compatible use of alternative fuels, CO_2 abatement and the trade in emissions certificates. Furthermore, institute staff members are involved in various bodies of the German Institute for Standardisation (DIN). In this context, especially the standards committees for "Construction" (NABau) should be mentioned. Both at national and international levels, VDZ cooperates very closely with the Federation of Industrial Cooperative Research Associations.

Use of cement

VDZ is represented on the board and the steering committees of the German Committee for Structural Concrete (DAfStb), on the advisory board and various working committees of the Standards Committee for Construction, in various bodies of the Standards Committee for Materials Testing, and in the Road and Transport Research Association (FGSV). Moreover, Research Institute employees are members of various bodies and expert committees of the German Institute for Building Technology. Cooperation in external bodies primarily covers the discussion, coordination and evaluation of research projects, the development of standards, guidelines and codes of practice, as well as consulting services regarding the granting of building inspectorate approvals.

Traditionally, VDZ has had a close, mutual trust relationship with technical and scientific cement consumer associations, particularly with the German Concrete and Construction Engineering Association (DBV), the Federal German Ready-Mixed Concrete Industry Association (BTB) and the Federal German Concrete and Precast Components Industry Association (BDB). Furthermore, close professional ties have been maintained with the manufacturers and producers of other basic materials for cement-based building materials, such as the Technical Association of Power Station Operators (VGB PowerTech), the German Industry Association for Construction Chemicals and the Federal German Gravel and Sand Industry Association.

The professional contacts maintained with the German Gas and Water Engineering Association (DVGW), the DIN Standards Committee on Water (NAW) and the Wastewater Treatment Association (ATV) relate to the application of cement-based building materials in the areas of drinking water supply and wastewater disposal. Close professional contact also exists with the Association of German Concrete Engineers (VDB). For many years now, a contact committee with the BTB has served to discuss issues regarding the application of cements in ready-mixed concrete and to find a common basis with regard to general issues. The Concrete Admixtures Coordination Committee was set up jointly with the German Industry Association for Construction Chemicals back in 1990, and a contact group involving the gravel and sand industry was formed in 2000.

The Joint Concrete Working Group – (GAK)

The Joint Concrete Working Group (GAK) regards the preparation of joint initiatives in the field of standardisation as one of its primary tasks – with the strategic goal of promoting concrete engineering. In the working group members of the Federal German Ready-Mixed Concrete Industry Association (BTB), the German Concrete and Construction Engineering Association (DBV) and the German Cement Works Association (VDZ) are represented. Chairmanship of the GAK rotates annually; in the period under review, VDZ and BTB chaired the working group.

In the period under review, the associations sponsored and supported jointly initiated research projects, such as on fair-faced concrete and sulphate resistance – in some cases helped by government funding. In the area of standardisation, a number of enquiries on the interpretation of the new concrete standards had to be commented on. In the coming years the GAK will especially have to monitor standardisation activities at European level.

VDZ/German Industry Association for Construction Chemicals Coordination Committee

The coordination committee, which is composed of specialists from the cement and admixtures industries, is currently chaired by the German Industry Association for Construction Chemicals. Chairmanship rotates every two years.

The committee is intensively involved with issues relating to the interactions between cement and admixtures. During the period under review, the focuses of the committee's work were cementitious mixtures, the way in which natural and synthetic air-entraining admixtures work and interactions between air-entraining admixtures and super plasticisers based on polycarboxylate ether (PCE).

The "Interface Issues" working group discussed the interactions between cements and the constituents of construction chemical products in detail. The goal is to establish key parameters for cements and admixtures that are suitable for the stable interaction between cement and admixtures in construction products.

Universities

Promoting university activity in the fields of construction research and structural engineering has always been a priority for VDZ. Once again, VDZ provided funds for research at university institutes in the period under review. Together with the Federal Association of the German Lime Industry, VDZ contributed to an endowment professorship at the Technical University of Clausthal, thus supporting the chair of "Binders and Building Materials". Furthermore, Research Institute employees give lectures at technical universities.

International cooperation

CEMBUREAU is the European umbrella organisation in which 26 national cement associations cooperate at an international level. VDZ has contributed its technical and scientific expertise to this joint work for many years. In the period under review, issues relating to environmental protection and CO_2 reduction were given top priority. The Europe-wide trade in emissions certificates that started in 2005 created tremendous challenges for the cement industry. This applies especially to the continuation of emissions trading in the third trading period from 2012. Other focal points of the joint European work included the BAT reference document for cement production and the revision of the IPPC Directive (Integrated Pollution Prevention and Control).

VDZ has been intensely involved in European standardisation work for many years. The main emphasis in this context is placed on the work of CEN/TC 51 (cement standardisation) and CEN/TC 104 (concrete standardisation). The CEN/TC 350 standardisation committee is establishing requirements for the sustainability of construction work. Standardisation committee CEN/TC 351 examines harmonised test methods with which the release of constituents from construction products can be investigated. The background to this is the discussion about substances that may be significant for the environment, particularly in terms of soil and groundwater.

CEPMC, the European confederation of national "umbrella" organisations, con-

Klaus Dyckerhoff commits a research funding to the VDZ for the support of young scientifics at the research institute at the general meeting 2007

tinues to be an important platform for the cement industry, allowing European developments to be identified at an early stage. All producers of construction materials have shared interests as regards the environmental effects of their materials. The same applies to building energy requirements. Supported by VDZ, the German Building Materials Association is also working on the establishment of German positions for the discussion in Brussels.

VDZ continues to be involved in scientific projects in which synergies arise from supranational cooperation. VDZ has worked in the European research and training consortium NANOCEM since it was formed. NANOCEM consists of 30 partner organisations. These include universities, national research facilities and industrial partners. More than 120 scientists work together in NANOCEM. The aim they pursue is to enhance knowledge about the nanostructures and microstructures of hardened cement paste in order to gain a better understanding of the macroscopic properties of cement-based construction materials.

In addition to the cooperation with the international organisations mentioned above, VDZ and its Research Institute maintain contacts with other European and international organisations. These include amicable relationships with the associations of the cement industry and their technical and scientific organisations in neighbouring European countries. Cooperation takes place in diverse ways, with the bodies of the European Standardisation Committee CEN and the European cement association CEMBUREAU forming the primary platform. VDZ also works continuously with the Indian National Council for Cement and Building Materials (NCB), the China Building Materials Industry Association (CBMIA), the Korean Cement Association (KCIA), the Hungarian Research Institute CEMKUT and Bandung Technical University in Indonesia. During the period under review, there was once again lively discussion with the US Portland Cement Association (PCA) on various topics. The focus was on environmental issues, concrete durability and CO_2 reduction. VDZ also maintains contact with the International Standardisation Organisation (ISO), Fédération Internationale du Béton (fib) and the International Association of Testing and Research Laboratories (RILEM), the International Institute of Flame Research (IFRF), the American Concrete Institute (ACI) and the American Society for Testing and Materials (ASTM). It is also in contact with numerous research institutions worldwide.

European Cement Research Academy (ECRA)

The European Cement Research Academy can once again look back on its successful work during the period under review. The roughly 40 members include cement producers and cement associations that cooperate at the ECRA level in specific advanced training measures and in research projects for selected topics. The focus was, again, issues in relation to cement production and cement use; two large research projects were initiated for the first time. The issue of carbon capture and storage (CCS) is being handled in a combined research project involving ECRA members and plant manufacturers. Determining the biogenic CO_2 content in waste gases of rotary kiln systems with the help of the ^{14}C method is being developed in collaboration with research institutes and universities. In addition, ECRA was involved in work related to fire protection in buildings, environmental data sheets and recarbonation of concrete. At the international ECRA Conference in Prague various topics were presented that are of superordinate interest for the cement industry. These include sustainable concrete manufacture with the help of innovative cements and reducing CO_2 emissions through the appropriate use of alternative fuels. ECRA is supported by a Technical Advisory Board that includes representatives from leading cement producers. These include the companies Buzzi, Cemex, CRH, HeidelbergCement, Holcim, Italcementi, Schwenk, Titan Cement, Vicat and Aalborg.

Dissemination of findings

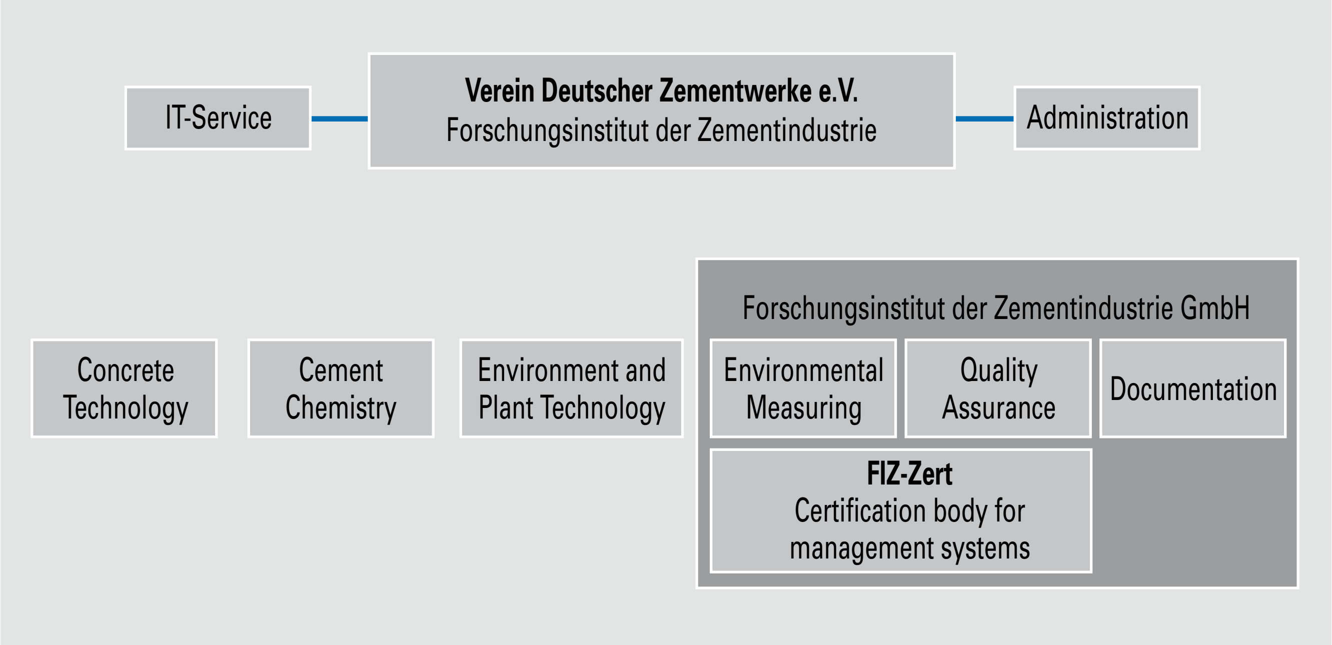
The many results of the work of the committees, working groups and commissions and from the research activities of the institute are provided to the members and to a wider specialist audience in numerous publications, colloquia, seminars, lectures and conferences. Most of these publications are provided in electronic form on VDZ's website. They can also be ordered from VDZ's website or from the online Beton-Shop that VDZ operates jointly with BDZ and BetonMarketing Deutschland GmbH at www.bdz-vdz.betonshop.de

Publications

The latest edition of “Environmental data of the German cement industry” was published in 2007, providing comprehensive, continuously updated documentation of environmentally-relevant data from the German cement industry. The CO_2 Monitoring Report was also updated.

VDZ-Mitteilungen (VDZ Newsletters), published three times a year, continue to provide the latest news about the activities of VDZ and its Research Institute. During the period under review, numerous articles dealt with developments in the area of CO_2 emissions trading, REACH, ASR and interpretations regarding the best available techniques (BAT) in cement production. As usual, these were complemented with news about current research work being carried out in the Research Institute and results of work carried out in other research facilities.

In addition to the VDZ Newsletters, many safety codes of practice and checklists dealing with important workplace safety topics and discussing options for preventing risks were published.



Again, during the period under review many different research topics were dealt with and published. A number of these were used as a basis for successful dissertations that were supervised in the Research Institute. For instance, Christian Schneider and Vera Tigges examined the properties and characterisation of blast furnace slags from different aspects. Stefan Seemann summarised the results of his study of the effects of the grinding atmosphere on the properties of cements containing blast furnace slag. In a concrete engineering study Eberhard Eickschen produced comprehensive results on the mechanisms of action of air-entraining admixtures. Besides these papers, the Research Institute was also able to offer opportunities for a large number of degree theses and student research projects dealing with a wide range of cement manufacturing and application topics.

Training and advanced training

Training, advanced training and knowledge transfer are among the most important tasks performed by VDZ. With its advanced training system it offers training courses for the technical fundamentals of cement production, in-depth training of special technical subjects and long-term advanced training courses for management staff. These include training courses for industrial foremen and production controllers as well as seminars on quality assurance, environmental protection and cement applications.

The industrial foreman training course "Lime/Cement" has been offered for almost fifty years in collaboration with the Federal Association of the German Lime Industry. The training courses, which are split into theoretical and practical segments, take 18 months and conclude with an examination before the Düsseldorf Chamber of Industry and Commerce. The first residential segment of the 23rd industrial foreman training course started in October 2007. In the following 18 months the participants from the lime and cement industries were prepared for the final examination, which took place in Düsseldorf on 11 March 2009. The course was held in the new training facility in Hilden for the first time. The very good underlying conditions offered by the new training facility certainly helped make this course a success.

Apart from the training and advanced training courses for foremen, control room operators are also trained specifically in VDZ's training facility. The advanced training involves a seven-week theoretical segment at VDZ and a practical part in the respective works. During the course, participants are trained in the fundamentals of operation, burning, preparation, measuring and control technologies and environmental engineering.

Science Foundations

Founded on 2 June 1995, the "Gerd Wischers Foundation" fosters the training and development of junior scientific staff. The foundation has assets of € 1 533 875. The interest income accruing on this amount allows four or five scholarships to be awarded at a time. During the period under review, two dissertations dealing with "Generation and Control of the Workability Characteristics of Self-Compacting Concrete" and "Alkalinity of the Pore Solution" were successfully completed. A current research project in the field of concrete engineering deals with the mode of action of shrinkage reducing admixtures. In addition, various short-term scholarships for degree theses in the fields of concrete engineering and research projects on emission recording were awarded. The Foundation promoted in the reference period for example papers about characteristics of fly ash in cement as well as research projects about modelling in cement hydration.

Research Institute of the Cement Industry ■

VDZ maintains the Research Institute of the Cement Industry to carry out its many functions. These functions are defined by its management in consultation with the Technical and Scientific Advisory Board and with the approval of the Board of Directors. With its Research Institute, VDZ boasts a renowned and internationally acknowledged scientific institution that covers the entire range of cement manufacture and application. The institute possesses a pool of modern instruments and is optimally equipped for carrying out demanding fundamental investigations. The Research Institute can also act on behalf of third parties, such as by performing tasks under public law as an officially notified emissions monitoring body or as an officially accredited testing laboratory. Moreover, the Research Institute increasingly offers expert advisory and consultancy services on technical matters, in line with the purpose of the association. The Institute is comprised of five departments.

The Cement Chemistry department of the Research Institute deals with the entire lifecycle of cement, from production through to the use and recycling of cement-based construction materials. Characterisation of raw materials and fuels and reactions occurring during the burning of cement clinker as well as setting and hardening processes are also focuses of the department's work. The department also closely examines the interactions between various main constituents of cement with each other and with admixtures/additions and reactions that can damage concrete. Apart from traditional application-related research, over the last years the Institute has been increasingly involved in the provision of services in this wide field of work.

The manufacture of cement starts with mining the raw material in the quarry and the subsequent clinker burning and grinding processes in the cement works. This is where the work and research focus of the Environment and Plant Technology department lies. To take account of the complexity and variety of the environmental and plant technology aspects that have to be considered in the environmentally friendly, energy-efficient and, also, economical manufacture of cement, the Environment and Plant Technology department employs scientists from various disciplines, supported by technicians and laboratory technicians with many years of theoretical and practical experience. The department has environmental and process engineering laboratories and modern measuring equipment for investigations and improvements in cement works, allowing it to carry out extensive experiments. The department also offers a wide range of services in the field of expert environmental assessments, environmental consulting and advanced training.

The Environmental Measuring department is notified as an independent measuring body. Because of this it can also carry out work in the legally controlled area. The department is also authorised to carry out legally stipulated acceptance measurements. Against the background of increasing internationalisation in the cement industry, there has also recently been growing demand for the services of the environmental measuring body from outside Germany. The environmental measuring body comprises an interdisciplinary team of engineers, scientists, technicians and laboratory technicians with many years of experience. On this basis, the department offers services in all environmentally relevant areas. This especially includes all emission measurements demanded in the respective regulations.

The Quality Assurance department provides testing, inspection and certification services. It mainly works as an accredited body in the legally regulated area. Quality monitoring and quality assurance of cement and cement-based binders by the quality surveillance organisation are among the traditional key competencies of the German Cement Works Association. In this regard the department handles the tasks of the quality surveillance organisation as a statutory accredited testing, inspection and certification body for construction products.

The Concrete Technology department deals with current issues in the areas of concrete constituents as well as concrete technology and applications. Based on extensive findings from various research projects it increasingly carries out special developments and improvements on concrete and mortar mixtures for the customers' particular areas of application. A rather more traditional service in the field of concrete technology is building condition analyses and subsequent assessment. If this shows that repairs are necessary, the department can also offer the required consulting services. Due to the Research Institute's leading role in issues relating to alkali-silica reactions, it prepares many expert opinion reports and carries out numerous assessments of aggregates. Assessments of chemical attacks on concrete are requested by the concrete and reinforced concrete industries while the department also prepares expert opinion reports for sewage systems and sewage treatment plants.

The general services offered by the Research Institute include administration, providing information and data processing with its data centre, library, documentation and publishing work and the mechanical and electronics workshops. The laboratories of the Research Institute are accredited and the Institute also has a certified quality and environmental management system in place. The organisational chart on page 15 shows the structure of the Institute with its individual departments and FIZ-Zert, the certification body for management systems.

At the time of reporting, the Research Institute employs roughly 160 staff. At present, the institute offers 7 training positions in various areas. In the period under review, 2 trainees successfully completed their chemical laboratory technician apprenticeships at the institute.

Data processing/IT

Consolidation of the IT systems was largely completed in 2007 and 2008. The connections to the Berlin (BDZ) and Erkrath (BMD) locations were optimised with additional DSL technology.

With regard to software on the client side, the operating system Microsoft Windows XP is used in combination with Office 2003. On the server side, Windows Server 2003 is used. The spectrum is rounded off with special software, which is used mainly to record measurement data and in the general scientific area. Several individual systems are also used, for laboratory management and laboratory controlling for example. We have no plans to change the client operating system at present (to Windows Vista for instance).

A total of 16 servers and 170 workstations are supported at three locations. The main projects during the period under review were the introduction of a new storage system, replacing local workplace printers with central printing systems and extending backup capacities with LTO3 tape storage units and online hard disk storage systems.

Installation of the in-house access points was extended, so that all meeting rooms and the entrance area now have wireless LAN access.

We plan to introduce a document management system with workflow components. The system is currently being tested; a pilot project is planned for the second quarter of 2009. Use of thin clients is also being examined in another pilot project.

Information centre – Library

The information centre provides the employees of the Research Institute with a comprehensive collection of literature, which, upon approval, can also be used by people other than Institute employees. The library currently has a stock of about 40000 volumes (as at the end of March 2009). These include about 14000 monographs, 21000 journals, 5000 standards and numerous research reports, annual reports and special prints. The centre subscribes to roughly 160 current periodicals to provide up-to-date information. The scientific staff assess these periodicals and draw attention to relevant articles. Any articles that are deemed to be important are transferred to the literature database. The literature database currently holds about 63 000 data records. The data records contain bibliographic information and references to the content and are indexed by means of controlled vocabulary descriptors (thesaurus). Over the next few years, the literature database will experience a significant increase in data as the subsequent recording of the card index, which contains literature references from before 1985, continues. The ZKG system, which allows allocation of monographs to certain subjects, thus grouping them together for certain subject areas, continues to be used for classifying and structuring the information centre's stock. The library is also involved in producing, issuing and dispatching VDZ's publications. In addition to handling sales via the Internet Beton-Shop (http://www.bdz-vdz.betonshop.de) that is operated jointly with BDZ and BetonMarketing Deutschland GmbH, it maintains a efficient and extensive exchange of literature with many research organisations at home and abroad. In this way the library also acquires literature that is not readily available for its collection on concrete technology, cement chemistry, process engineering and environmental protection.

The key function of the information centre is to provide extensive information to staff and VDZ members in a timely manner. In this respect the availability of information and documents in electronic format is becoming increasingly important. For example, since 2009 the literature database has been enhanced with scanned tables of contents of books and periodicals. This allows direct access to additional information about specific sections in the literature and an additional means of research through a full text search in the tables of contents. Conventional and electronic document delivery services make an important contribution to the provision of information in the centre by procuring literature that the library does not have on hand.

Since 2006, FAUST has been used as a data base and retrieval system in the information centre. Because of this system's high degree of flexibility, in future it will enable a high level of integration of the individual database applications and the development of new database applications as additional services.

Accreditation/Certification

The focus of the Research Institute's responsibilities has shifted further over the past years. For instance, in the period under review, in addition to research activities the extensive service portfolio covering the entire range of cement and concrete production was extended further. Special emphasis was placed on a high level of efficiency in the Institute and also as regards the various local activities that were carried out. The workflows are largely regulated by an integrated quality and environmental management system based on standards DIN EN ISO 9001 and DIN EN ISO 14001. In 2008, both management systems were certified successfully for the second time by independent experts. The Research Institute of the Cement Industry is also accredited on the basis of international standard DIN EN ISO/IEC 17025. This accreditation of the laboratories covered about 300 test features. Moreover, the requirements for independent measuring and test institutions for recording emissions and immissions were satisfied in all respects. VDZ's quality surveillance organisation also has the competency to certify products pursuant to DIN EN 45011. This proof of competency has also been accredited. Thus, all requirements demanded by national and international customers for a qualified measuring and testing institution are fulfilled. Against this background, the logical consequence was that the various units and laboratories provided more services at an international level last year. This applied especially to activities in the statutory building and pollution control areas. For these areas accreditation is a valuable qualification criterion which continues to find a high level of acceptance on the market.

Services ■

The Research Institute can also provide services for third parties by rendering expert advisory or consultancy services on specialist matters in line with the purpose of the association. This also includes assignments under public and private law, such as via the surveillance organisation's activities as a testing laboratory, inspection and certification body, as an environmental monitoring body, or as a certification body for management systems (environment and quality). The services are rendered separately from the nonmaterial activities of VDZ's joint research. The individual projects are invoiced separately and are subject to stringent confidentiality requirements that apply both in-house and towards third parties. Consultancy services are offered and billed on the basis of fixed daily rates. Fixed prices are charged if the services rendered are standardised activities.

Mortar and concrete

Research work and services provided in the areas of mortar and concrete include current and important issues in the fields of concrete constituents, concrete engineering and concrete applications. The services offered include optimisation and use of blast furnace and Portland-composite cements. Projects to improve resistance to acids, frost and de-icing salt were also carried out. Work was also carried out in the areas of damaging alkali-silica reactions and sulphate resistance. The services offered include the following contract investigations:

- Development of optimised concrete and mortar mixes for the respective clients' area of application
- Testing unset and set concrete and unset and set mortar
- Investigating durability:
  - Frost and de-icing salt resistance according to the CF, CIF, CDF, cube, slab and bar test methods
  - Alkali-silica reaction in the 40°C fog chamber and with the 60°C test (performance method)
  - Chloride migration test
  - Penetration behaviour of water-endangering substances
  - Abrasive wear
  - Determination of the air pore parameters in hardened concrete
- Investigation of the pore structure using methods such as mercury intrusion measurement, permeability measurement and water absorption measurement (15 MPa)
- Rheological investigations with the Viskomat
- Hydration heat determination (isothermal and semi-adiabatic)
- Extraction of pore solution from concrete to determine pH and conductivity
- Determination of the zeta potential using the electro-acoustic measuring method
- Testing admixtures
- Initial testing according to DIN EN 934-2
- Electro-chemical corrosion testing according to DIN V 18998
- Investigation of aggregates
- Testing grouts

VDZ Management (f. l.): Klaus Meyer, Stefan Schäfer, Silvan Baetzner, Christoph Müller, Martin Schneider, Martin Oerter, Volker Hoenig, Jörg Rickert

Chemistry and mineralogy

An understanding of the chemical-mineralogical processes of cement manufacture and applications is an important requirement for optimising the clinker burning process and the product properties. Cement chemistry activities are aligned to current issues and include assessment and optimisation of the main constituents of cement as well as development of testing and measuring methods. For this purpose, the Institute has a highly efficient analytical laboratory with a wide range of equipment. The laboratory is accredited according to ISO/IEC 17025. Due to the many years of cooperation with cement producers and concrete users, the Research Institute has gained ample experience in the analysis, development of methods and provision of expert advice in the field of chemical-mineralogical testing of raw materials and the cements and products produced from them. The service portfolio includes the following contract investigations:

- Characterisation of Portland cement clinkers
- Quantitative phase analysis with Rietveld refinement
- Reference investigations on cements and concrete constituents based on the applicable standards
- Determination of hydration heat
- Sulphate optimisation of cements
- Determination of thermal and calorific values
- Structural analysis of cementitious systems
- Environmental analyses, such as trace analysis of metals and semi-metals
- Determination of water-soluble chromate according to TRGS 613 and EN 196-10
- Emission forecasts when different raw materials and fuels are used

Environmental expertise

The high significance which the cement industry attaches to environmental protection is mirrored in the numerous activities of the Research Institute. Due to its extensive experience in the area of plant evaluation and permit management, useful synergies arise especially for environmental impact audits since even for complex projects all necessary services can be obtained from one source. Our staff are offered continuous training. Their involvement in current research projects always enables them to draw on the latest findings in the preparation of their expert reports. The service portfolio includes the following contract investigations:

- Emission and environmental impact forecasts
- Discharge conditions for emissions/calculation of stack height
- Recommendations to improve the emission and environmental impact situation
- Environmental compatibility studies
- Plant technology investigations
- State-of-the-art/best available technique
- Complex dispersion calculations
- Soil investigations
- Noise assessments

Plant technology investigations

The Institute's clients benefit from its many years of experience in the field of thermal and mechanical process engineering, which the staff have gained both nationally and internationally while providing consultancy services for plant optimisation. Together with the clients, the Institute's employees develop innovative processes that enable emission reduction in cement works at reasonable costs. To this end, the Institute has an expert team with cutting-edge measuring equipment at its disposal to handle the complete planning and organisation of all process engineering investigations in cement works. The tests are developed and assessed by the one source. The Institute's expertise covers thermal and mechanical process engineering, including complex environmental engineering issues. Its service portfolio includes the following contract investigations:

- Technical consulting services
- Material balances, energy balances, measures to reduce energy consumption
- Process measurements of kiln and grinding systems and secondary measures to reduce emissions
- Optimising the operation of kiln and grinding systems
- Investigation and limitation of material recirculation systems
- Process engineering modelling of the clinker burning process
- Parameter studies and development of
- optimisation measures

Environmental measurement

The Research Institute of the Cement Industry operates the Environmental monitoring body which is both accredited according to the international ISO/IEC 17025 standard and recognised as an independent monitoring institute by the German environmental authorities. A multi-disciplinary team of engineers, scientists and laboratory technicians with many years of experience provides services covering all areas that are relevant to the environment. This particularly includes any kind of emission measurement ensuing from the related national and international regulations. Besides dust and gas emissions, the environmental measuring body also assesses the environmental impact in the areas surrounding cement works. The profile of services is rounded off by measurements and forecasts of noise and vibration. The service portfolio includes the following contract investigations:

- Planning and professional implementation of emission measurements at industrial plants
- Development of measuring schedules with consideration of the relevant guidelines
- Emission measurements and sampling of airborne pollutants (e.g. nitrogen oxides, trace elements, dust, organic hydrocarbons, PCDD/F, etc.)
- Determination of noise emissions and noise levels
- Development of noise-reduction concepts and plant-specific noise charts

- Determination of emissions and environmental impacts of blasting vibration
- Checking that continuously operating measuring equipment has been installed and functions correctly and also calibration of the equipment
- Assessment of measuring points
- Environmental impact measurements

Product certification

Quality monitoring and quality assurance of cement and cement-based binders by the quality surveillance organisation are among the traditional key competencies of the German Cement Works Association. 560 cements from 60 works are tested and inspected according to national and European statutory specifications. Based on agreements with foreign bodies, inspections can also be carried out according to private law regulations. National and European recognition as a testing, inspection and certification body by the responsible building supervisory authorities covers the following:

- Cement and cement-type binders
- Concrete additions
- Concrete admixtures
- Mortar and concrete
- Cement-based mixtures

VDZ's quality surveillance organisation and the associated laboratories are also accredited under private law according to EN 45011 and ISO/IEC 17025.

Systems certification

The FIZ-Zert certification body certifies and inspects management systems (quality, environment). FIZ-Zert is accredited according to ISO 17021 for this area. The body especially certifies industrial minerals companies and companies in similar industries that are involved in the manufacture and use of construction materials (especially cement, binders, concrete products and pre-fabricated concrete parts). Certification is based on standards ISO 9001 and ISO 14001. Certification can also be carried out in combination with legally regulated and obligatory product certification (e.g. pursuant to EN 197).

Verification of CO_2 emissions

Over the last years FIZ-Zert has verified recurring CO_2 emissions in connection with the European emissions trading system. Customers can benefit from the high technical competency and also from the extensive legal knowledge of our experts. These experts, who work exclusively for FIZ-Zert, are either certified experts or notified EMAS verifiers. This guarantees that the evaluation of monitoring concepts as well as the examination of emission reports carried out by FIZ-Zert satisfy even the highest demands.

I

Process technology of cement manufacture

Control of a ball mills’ outlet

Plant operation ■

Influence of the primary air feed on rotary kiln flames

The use of alternative fuels in rotary kiln firing systems rules out low-NO_x burners because of their extremely low primary air flows and requires burners that have been specially modified for the use of high quantities of alternative fuels. Nitrogen oxides emissions are then reduced as required, for example in a downstream selective non-catalytic reduction (SNCR) system. These days, with a variety of ring gap configurations, tubes and lances, modern rotary kiln burners are able to incinerate many different alternative fuels with various combustion characteristics. Because of their different combustion characteristics compared to regular fuels, alternative fuels change the heat release in the flame, which reduces the maximum flame temperature, makes the temperature profile in the rotary kiln flatter and increases the kiln inlet temperature. When the primary air feed is adapted to suit the alternative fuel, this can counteract the negative effects that the fuel has on the flame and the clinker burning.

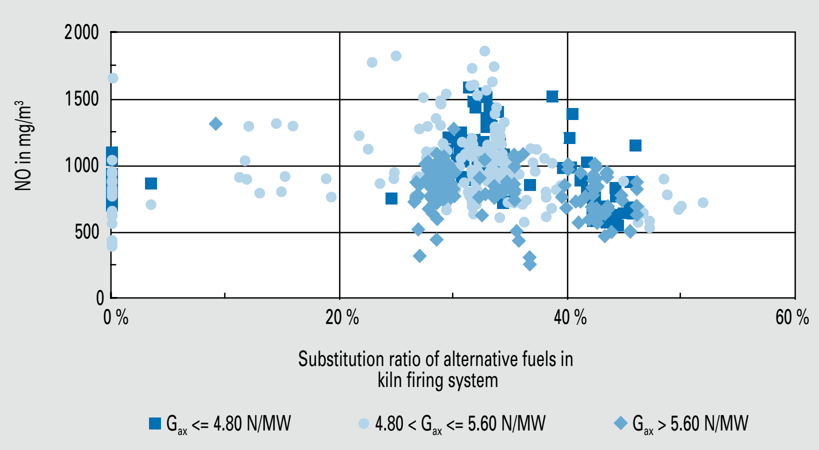


Fig. 1-1: Nitrogen oxide concentration in the kiln inlet gas versus the substitution ratio of alternative fuels in the kiln firing system, classified to different overall axial momentum flows G_{ax}

During the period under review, in a project funded by a consortium of industrial research groups, the Research Institute of the Cement Industry investigated the possibility of shaping the flame and influencing the combustion process with the help of the primary air supply. The flame shaping was investigated in two kiln lines and the kiln inlet gas was measured to record the development of pollutants. In one burner the finely conditioned fuel was fed between the axial air and the swirl air. Due to the concentric arrangement of the tubes and the compact design of the burner it was possible to effectively mix the hot secondary air into the fuel flow. With a moderate alternative fuel contribution to the rotary kiln's heat capacity of just 36 %, it was seen that the development of nitrogen oxide pollutants was similar to other burner types but that there was much less flame swirling. As **Fig. I-1** indicates nitrogen oxide formation decreases slightly with increasing substitution ratio beyond 40 %. In comparison to low momentum flows, with higher overall axial momentum flows both the level of nitrogen oxides is lower and the spread is narrower. In the experiments, the free lime content of the produced cement clinker was between 0.8 and 1.2 wt.-% and thus within the normal range. In the clinker burning, no dependency on the burner setting or the level of substitution was identified. The clinker phase composition was subject to the usual fluctuations according to the composition of the kiln feed.

During the period under review, another kiln test was carried out at the end of the year. This cement kiln was fitted with a new burner during winter maintenance. An older low-pressure burner was replaced by a new high-pressure burner. After commissioning a new kiln trial is planned so that a comparison can be made between two burners from the older and newer generations in one kiln line.

The results were presented in speeches at the 2007 VDI specialist conference "German Flame Day" in Berlin, Germany, and at the international scientific conference on "Energy and Environment in Construction, Ceramic, Glass and Refractory Technologies" in Karpacz, Poland, in 2008.

In 2008, the Environment and Process Engineering Committee assigned a rotary kiln burner working group to examine the industrial use of new burner generations:

- Exchange and discussion of operating experience with new or modified rotary kiln burners
- Effects of the rotary kiln burner on the clinker quality, use of alternative fuel, protection against wear, burn-out/carbon monoxide formation, nitrogen oxide emissions and kiln operation
- Discussion with burner suppliers about "optimum" burner design and operation
- Development of general rules for the optimum use of alternative fuels in the kiln firing system
- Support for the research project "Optimising the main firing system with maximum use of alternative fuels"

The working group is currently drawing up a picture of the current burner generation in German cement works and is looking at the present state of technological development. To do this, the group is working together with burner suppliers. The working group has compiled specifications for rotary kiln burners for a workshop with burner suppliers. Operating experiences are to be discussed with burner operators based on an exemplary design for rotary kiln burners from the burner suppliers. The results of the working group's activities will be presented in a process engineering code of practice with recommendations for the operation of rotary kiln burners with the use of alternative fuels.

Modelling the flow relationships in the calciner

The possibility of using largely reliable numerical CFD (computational fluid dynamics) to simulate the processes taking place in the calciner simplifies specific optimisation of the kiln operation and can also reduce the number of expensive, time-consuming experiments that have to be conducted on operating kilns. Moreover, it becomes easier to make sound statements about the technical implementation of staged combustion in precalciner kilns to reduce pollutants. Other areas for numerical simulation in this connection are investigation of damage and concept studies for dimensioning, for energy optimisation and for the flexible use of alternative fuels.

In collaboration with the Department of Energy Plant Technology (LEAT) at Bochum University in Germany and the Chair of Environmental Process Engineering and Plant Design at the University of Essen/Duisburg (Germany), the Research Institute of the Cement Industry performed a simulation project funded by the German Federation of Industrial Research Associations (AiF). The aim of this project was to use numerical simulation in order to optimise the technical operation of precalciners in terms of the formation of pollutants and to discover ways of reducing NO_x.

The specific processes of fuel combustion, formation and reduction of NO_x, decarbonation and calcining, turbulence modulation and effects on radiation were modelled successfully with sole consideration of coal as a fuel and were validated by measurements performed by the Research Institute at real cement plants. Taking into account the complexity of the cement manufacturing process and the difficulty of measuring and recording local variables in the calciner, it was possible in many cases to achieve a very good correlation between the calculated values and the values obtained in the experiments (**Fig. I-2** and **Fig. I-3**). On the whole, it was possible to simulate the process behaviour accurately and also to illustrate the effects of the different boundary conditions on operation.

On the basis of the results from this AiF project, the substitution of coal with alternative fuels in different precalciner systems is being investigated with CFD methods in a follow-up project. The objective is to expand the possibilities of using alternative fuels in precalciners and thus make a significant contribution towards maintaining the competitiveness of the German cement industry. In addition, operators of precalciners should be able to use alternative fuels specifically to reduce NO_x with, for example, staged combustion and thus reduce costs for secondary reduction measures. **Fig. I-4** shows the NO_x profile in the calciner and its system limits from the reference experiment V. 1 using only lignite as a fuel and from the two experiments V. 3.1 and V. 3.2 with high fluff substitution rates of about 80 % in relation to the thermal output in the calciner. The measuring point in the kiln inlet is the system limit and also the boundary condition with the starting parameter for the simulation of the processes in the calciner. The NO_x profile from experiment V. 1 serves as a reference for the two experiments V. 3.1 and V. 3.2 with high substitution rates. In addition, this reference experiment can be used in a first CFD simulation with coal as a fuel to provide an adequately reliable qualitative assessment in the validation of the model results. Overall, in these two experiments higher NO_x levels were measured from the measuring level middle calciner to cyclone 6A/B. This effect can be attributed to a shift in the burn-out zone due to the higher use of fluff and to its rougher particle distribution. This assumption is confirmed by higher temperatures in the calciner itself and at the measuring points on the outer wall of the calciner. The results as presented in Fig. 1.4 shall be used to validate the CFD simulations.

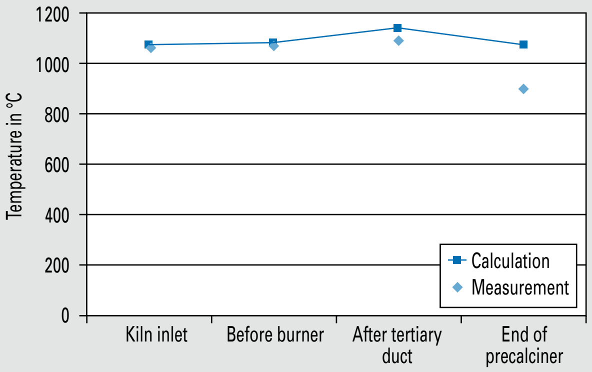


Fig. I-2: Comparison of measured and calculated temperatures

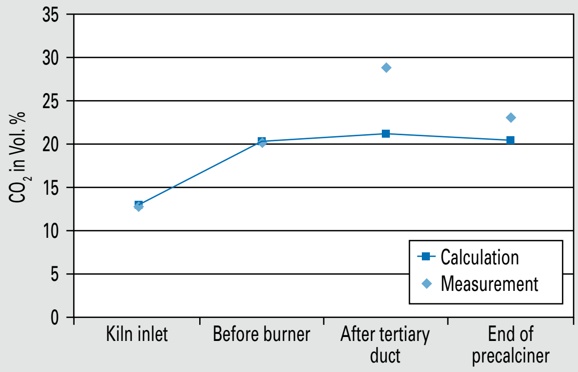
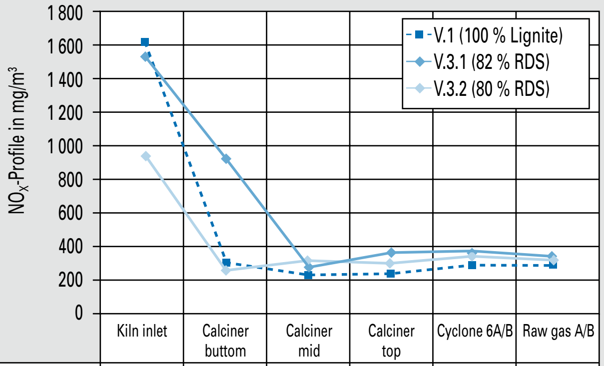


Fig. I-3: Comparison of measured and calculated CO_2 concentration



	Kiln inlet	Calciner buttom	Calciner mid	Calciner top	Cyclone 6A/B	Raw gas A/B
V.1 (100 % Lignite)	1 616	294	220	231	277	288
V.3.1 (82 % RDS)	936	254	303	288	334	303
V.3.2 (80 % RDS)	1 535	915	258	360	356	330

Fig. I-4: NO_x concentrations in profile

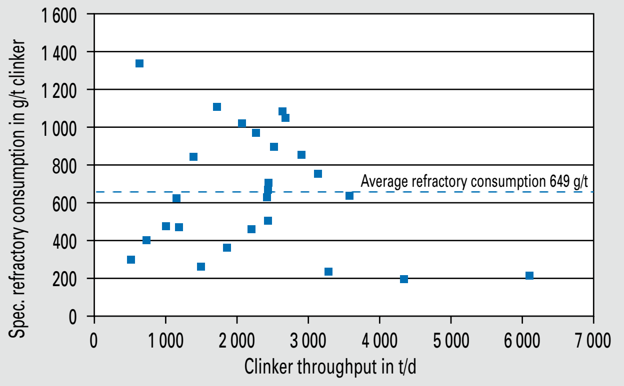


Fig. I-5: Average refractory consumption

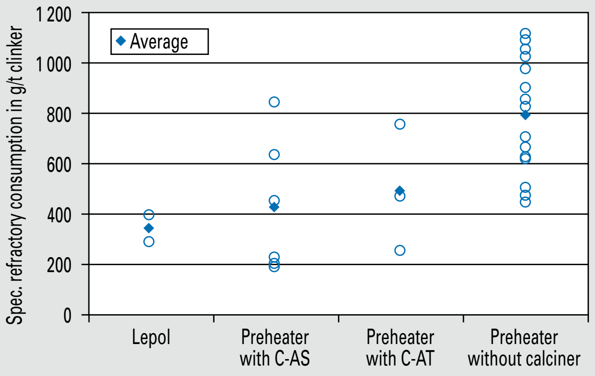


Fig. I-6: Refractory consumption by type of plant

Refractory materials

Over the past years the expertise available in cement works regarding the use of refractory materials has gradually declined. Therefore, the "Refractory Materials" working group was established to summarise the current level of knowledge in this field in a code of practice.

Since the start of the 1990s there has been a massive change in the conditions for using refractory materials in rotary kilns in the cement industry. The main reasons for this are the changes that have been made in kiln operation with rates of substitution increasing every year through the use of alternative fuels. These days, alternative fuels replace about 54 % of conventional fossil fuels in German rotary kilns. Under these operating conditions, with high rates of alternative fuels much longer sintering zones of up to 9 times the kiln diameter are observed. Apart from this, these zones often have frequently changing coatings. Ten years ago, the length of the sintering zone was about 5 to 6 times the diameter of the kiln. These days, this changed mode of operation is replaced by the use of highly refractory magnesite bricks over an extended area of the sintering zone.

A number of alternative fuels contain more sulphur or chlorine than the substituted standard fuels. Sulphur and chlorine react with alkalis to form alkali sulphates or chlorides, which tend to form recirculation systems at the kiln inlet and the calciner and thus cause an accumulation of vaporous alkali compounds in the kiln atmosphere. In this atmosphere the refractory materials are damaged mainly by infiltration of these alkali compounds. Because of this, these zones are fitted with acid bricks that were developed from special high alumina grades and which are more resistant against alkali bursting. By using a chlorine bypass near the kiln inlet, it is possible to reduce this accumulation and thus indirectly prolong the service life of the lining. The chlorine bypass relieves the kiln system by removing some of the kiln exhaust gas that is enriched with alkali chlorides and sulphates from the inner circulation system.

By a questionnaire the working group gathered and assessed the experiences of operators regarding the use of refractory materials in rotary kilns with consideration of different plant and operating parameters. The evaluation of this survey showed that the average consumption of refractories in German rotary kilns is about 650 g/t clinker, see **Fig. I-5**. This value refers to consumption of refractory bricks and masses averaged over 3 to 5 years. There was a relatively wide range of consumption depending on the type of kiln used. The lowest consumption of refractory materials is 200 g/t clinker, although consumption in several works was exceeding 1000 g/t clinker. No dependency between consumption of refractory materials and clinker throughput of the kiln plant was identified.

As regards the kiln-related impacting variables, the type of pre-heater used is decisive (**Fig. I-6**). Refractory consumption in kilns with a precalciner tertiary air duct is relatively low – on average about 420 g/t clinker. Conventional plants with cyclone pre-heaters consume approx. 800 g/t clinker, which is almost twice the amount of precalciner plants. The low refractory consumption of precalciner plants can be attributed to the fact that combustion in the precalciner at temperatures of 800 to 1 100 °C relieves the rotary kiln from a thermal aspect and thus results in reduced consumption of refractory material. On the other hand, the smaller dimensions of the rotary kilns, which are generally used in combination with precalciners, appear to have a favourable effect on the consumption of refractory materials. More thermal relief is given inside the rotary kiln if the combustion air for the calciner firing is fed through tertiary air ducts.

Possibilities and limitations of using sewage sludge as an alternative fuel in the cement industry

In times of rising fuel prices and increasingly stringent demands regarding the prevention of climate-damaging CO_2 emissions, the use of biogenic fuels is becoming increasingly attractive in the cement industry from both ecological and economic points of view. Sewage sludge is an especially interesting alternative to normal fossil fuels because it is classified as a biogenic fuel (CO_2-neutral). By using sludge as a fuel, the cement industry is also making a significant contribution towards the safe disposal of waste. In a research project funded by the AiF (German Federation of Industrial Research Associations), the Research Institute conducted operating and product investigations as well as a feasibility study which confirmed that sewage sludge can be utilised economically and in a manner that is harmless to the environment and the product.

Fig. I-7: Dried sewage sludge pellets (TS 90)

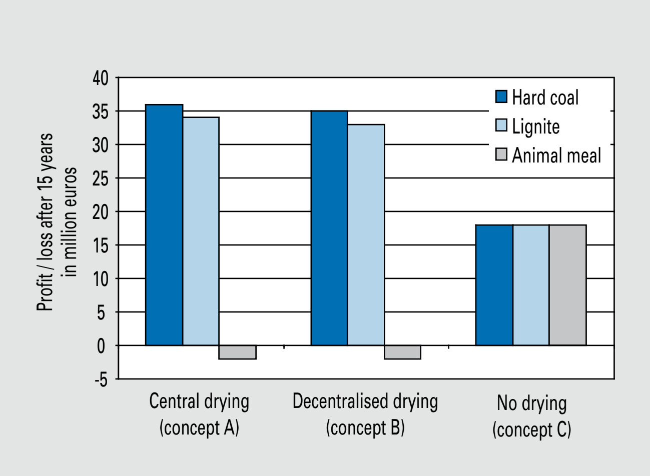


Fig. I-8: Comparison of the concepts

Operating and product investigations

Systematic tests were carried out on three kiln lines in order to obtain information about the effects of sewage sludge on kiln operation, mercury emissions and the quality of the product. Possibilities of optimising the burners were also considered. The use of mechanically dewatered sewage sludge (MDSS) and ground and pelletized dry sewage sludge (DSS) (**Fig. I-7**) compared to operation without sewage sludge were investigated. The sewage sludge made up between 5 and 11 % of the heat output of the firing system.

When DSS was used, the energy balances showed a clinker-specific fuel energy use of approx. 3 600 kJ/kg clinker. In contrast, use of MDSS led to a higher thermal energy consumption of approximately 250 kJ/kg clinker, which was especially attributed to the increased water content. The mercury balances compiled during the kiln tests showed slightly higher mercury input for the outer and inner balance area; however, the limit value for mercury emissions of 0.03 mg/m^3 (daily average) was not exceeded. The mercury cycles were effectively relieved by the manner in which the kilns were operated. No effects on the emission of nitrogen oxides or carbon monoxide were identified either.

On all balance days on which sewage sludge was used, the investigations of the produced cement clinker showed a slightly reduced concentration of alite and a slightly higher belite concentration. The resulting cements show slightly reduced compressive strengths after 28 days, although these were largely balanced out again after 90 days. Only slightly higher phosphate inputs were found in the clinker.

During the optimisation of the burner settings, when co-firing pelletized sewage sludge, it was found that there was slight possibility of influencing the rotary kiln firing by means of the burner. The primary air quantity was tested at different settings, but did not allow the intensification of the firing. As regards slow-igniting fuels that prolong the heating and ignition segments, expectations that increasing the quantity of primary air would bring the flash point and thus also the flame closer to the burner mouth again were not confirmed under the given conditions. In addition, with sewage sludge used in the range of 10 % of the thermal output of the firing system, there was no significant effect on the temperature profile in the sintering zone.

To summarise, in all the kiln tests with DSS no significant effects on kiln operation, emissions or the products were determined due to the use of sewage sludge. With different grades and possibilities, sewage sludge is highly suitable as an alternative fuel and can be justifiably classified as an environmentally compatible utilisation option.

Cost effectiveness

The aim of considering the cost effectiveness was to compare and assess the conditions for using dry sewage sludge which is dried with waste heat in the cement works and also sludge that is dried locally in the sewage treatment plant. Three concepts were examined (**Fig. I-8**), in which the energy sources hard coal, lignite and animal meal were substituted with sewage sludge.

The investigation shows that the use of sewage sludge in the cement industry differs mainly in terms of investments and in the method of transport required for delivery. Ultimately, the form of drying, the fuel that is to be substituted and the amount of sewage sludge that can be purchased and its price will be decisive for the economic effectiveness in the use of sewage sludge. Sensitivity analyses showed that the biggest risk factors are the available volume of sewage sludge, the capacity utilisation of the systems that would have to be constructed and the price of the sewage sludge.

Modelling the motion of the grinding media in ball mills

On average, the electrical energy required to produce cement in Germany is approx. 100 kWh/t cement, 30 % of which is used alone to grind clinker and interground additives. Generally, ball mills are used to grind cement. In spite of their relatively low levels of efficiency, they are very reliable to operate and are especially able to produce a broader particle size distribution in the ground cement. For this reason, in cement grinding we should not expect to see ball mills being completely replaced by other milling processes for at least some time to come. It is practicable to make full use of all the existing optimisation potential. However, it is difficult to estimate the interaction of the different operating parameters and their effects on the content of the mills, as the inside of the mills in particular are not accessible for technical measurements. Direct particle simulation is a promising tool for optimising the energy consumption of cement grinding in ball mills.

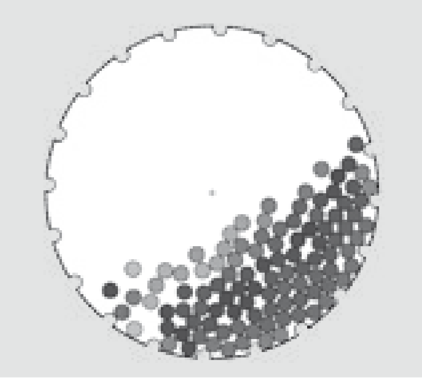


Fig. I-9: Snapshot of the simulated motion of the grinding media at 28 rpm. A typical cascade movement is identifiable.

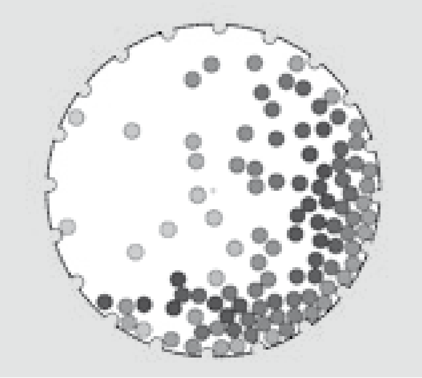


Fig. I-10: Snapshot of the simulated motion of the grinding media at 69 rpm. A typical cataract movement is identifiable.

Efficient methods for calculating and visualising bulk materials have been available since the end of the 1990s. In addition, the current level of technological development now also allows particle-mechanical simulation of these materials – and not only of individual particles but also over relevant time intervals. These simulations are used extensively in conveying technology for bulk materials. Most of these methods are aggregated under the generic term "Discrete Element Method" (DEM). Basically, the motion equations of all particles contained in a system are solved over the time that is being considered. If the particles collide, the resulting forces are approximated with suitable contact models and are considered in the motion equations. The structure and parameterisation of these models must be carefully adapted to the respective application case. In this way, it is possible to effectively simulate complex fillings, such as the charge of a ball mill.

To examine the processes inside ball mills in detail, the Research Institute of the Cement Industry uses a two-dimensional model developed in theoretical physics. It is described as "molecular dynamics" and enables the simulation of particle systems in the manner described above. The grinding media and the surrounding grinding chamber are approximated by disks. The simulation allows data to be determined that cannot be recorded by technical measuring methods in reality. Of particular interest are speed and pressure distributions, which allow subsequent conclusions to be drawn about the comminution process.

While simulations theoretically allow access to systems that cannot be recorded by technical measuring methods, they always represent a simplification of reality. Therefore, the prediction quality depends significantly on the exact validation of the models that are used. Consequently, the simulation calculations (numerical experiments) are always carried out in combination with extensive experiments in the Research Centre's semi-technical closed-circuit grinding plant. **Fig. 9** and **Fig. 10** show snapshots of the simulated ball charge of the grinding system at different speeds. Recognisable in Fig. 9 is the cascade movement typical for low speeds, while Fig. 10 shows the cataract movement that is typical for high speeds. Using complex algorithms for evaluation, it is also possible to create animations of the motion of the grinding media that can provide important findings beyond a purely mathematical level. The results of the simulation were validated by comparative performance measurements.

On the basis of these technical simulation requirements, in future it will be possible to more effectively optimise cement grinding in ball mills. Of particular interest is the composition of the charge make-up, which is currently determined according to purely empirical rules. If this was optimised, significant energy savings could be expected. The biggest problem is guaranteeing the operating reliability of the mills through suitable boundary conditions. Only by considering actual operating conditions appropriately will it be possible to ensure that the results of mathematical optimisation can also be successfully transferred to existing cement mills. For this reason, more extensive efforts are being made to link molecular dynamics with existing process technology models to provide a holistic description of the comminution process.

Energy consumption ■

Kilns

In the period under review, the licensed kiln capacity of the German cement industry increased slightly from 110 720 t/d (2006) to 111 400 t/d in 2008. The operating permits of three kiln plants expired. As a consequence, the total number of kilns with operating permits decreased from 60 to 57. The kiln systems operated in Germany today are almost exclusively plants that use the dry or semi-dry processes. In addition, there are permits for eight shaft kilns. The average kiln throughput rose from 2 106 t/d in 2006 to 2 249 t/d in 2008. **Table I-1** gives an overview of the status of the available kilns. Plants with cyclone or grate preheaters account for 98.9 % of the total licensed capacity. In 2008, the percentage of cyclone preheaters rose again to 93.1 % (in relation to capacity). The number of precalcining plants increased by one to twelve. Of these, nine plants are equipped with a tertiary air duct. Since their kiln throughput is higher by comparison, precalcining systems represent more than a quarter of the installed, licensed clinker capacity of the German cement works.

The capacity utilisation of the kiln plants rose from 70 % in 2006 to 77 % in 2008, which can mainly be attributed to increased cement exports and increased clinker stocks as a result of CO_2 emissions trading. In 2008, capacity utilisation fell to 71 %, almost reaching the previous year's level. The capacity utilisation data is based on an assumed kiln plant availability of 320 days per annum.

Fuel energy consumption

The main use for fuel energy in cement manufacture is for burning the cement clinker. To a lesser extent, thermal energy is used to dry other main components of cement, such as blast furnace slag. To manufacture cement clinker with its characteristic properties, the raw materials, principally limestone marl and clay, are burned at temperatures of 1 400 to 1 450 °C. Because of the product specifications and the high temperature process which they require, the cement industry is one of Germany's energy-intensive industries. For this reason, the cement industry has always tried to reduce its energy consumption and hence fuel energy costs. **Fig. I-11** shows the trend of the specific thermal energy consumption of the cement industry from 1950 to 2005. From 1987 onwards, the new federal states are included in the figures. As the diagram illustrates, the burning process in the German cement works is now optimised to such an extent that no significant further reductions can be expected from process technology measures.

First voluntary commitment towards climate protection fulfilled

In 1995, the German cement industry and other energy-intensive industrial sectors undertook to contribute to the reduction of CO_2 emissions in Germany. The cement industry's voluntary commitment involved lowering its specific energy consumption by 20 % in the period from 1987 to 2005. At 2 825 kJ/kg cement, the cement industry reached its target in 2005.

The Research Institute has surveyed the output and energy consumption data of the German cement industry since 1995. After being summarised and made anonymous, this data will be submitted to the Rheinisch-Westfälisches Institut für Wirtschaftsforschung (RWI) for plausibility checking.

The German cement industry continually lowered its specific fuel energy consumption over the past decades by modernising its kiln and grinding systems. In the wake of German reunification, this drive gained particular momentum as the plants of the East German cement industry underwent revamps providing them with state-of-the-art technology within a few years. In the old federal states, a number of older plants were also replaced by new ones. The increased production of cements with several main constituents represents a further important measure towards reducing fuel energy consumption per tonne of cement.

Due to the significant drop in cement production during the period under review, the absolute fuel energy consumption of the German cement industry declined by about a fifth from 1987 to 2008. This considerable decrease was also attributable to the fact that the specific thermal energy consumption per tonne was reduced by roughly 20 % over the period reviewed (**Fig. I-12**). While the specific thermal energy consumption of rotary kilns still topped 3500 kJ/kg cement in 1987, last year it was just 2 764 kJ/kg cement. This was mainly attributable to the reduction of the clinker/cement factor. In 1987, this was 86 % but had been reduced to 73 % by 2008. The German cement industry thus honoured its first pledge on climate protection.

Fuel mix

The composition of the fuels utilised in the German cement industry has changed continually over the past years. Between 1987 and 2008, total fuel usage fell from 119.9 to

Table I-1: Number and capacity of licensed kilns in Germany from 2006 to 2008

		Status: 01/01/2007			Status: 01/01/2008			Status: 01/01/2009		
		Number	Capacity		Number	Capacity		Number	Capacity	
			t/d	%		t/d	%		t/d	%
Kilns with cyclone preheater		41	100 550	90.8	41	101 000	92	41	103 700	93.1
Kilns with grate preheater		11	8 970	8.1	9	7 500	6,8	8	6 500	5.8
Shaft kilns		8	1 200	1.1	8	1 200	1.1	8	1 200	1.1
Total		60	110 720	100	58	109 700	100	57	111 400	100
Average kiln capacity in t/d	rotary kilns		2 106			2 170			2 249	
	shaft kilns		150			150			150	
Clinker production [1)](year)			(2006)			(2007)			(2008)	
in million t/a			24.9			27.0			25.4	
Utilisation [2)]in %			70			77			71	

[1)] After CO_2 monitoring
[2)] Assumed availability 320 d/a

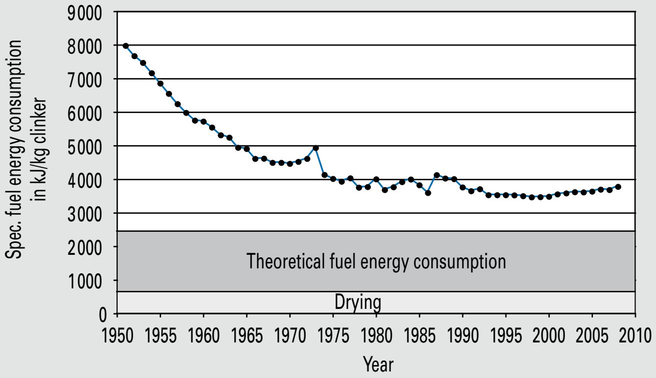


Fig. I-11: Specific fuel energy consumption of German cement works (old federal states until 1987, entire federal republic from 1987 onwards)

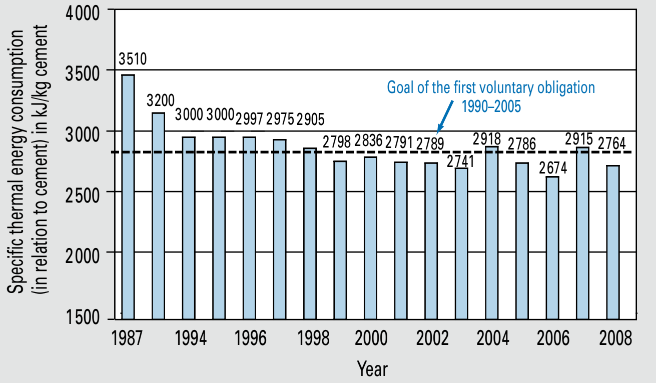


Fig. I-12: Specific thermal energy consumption according to the voluntary climate protection commitment

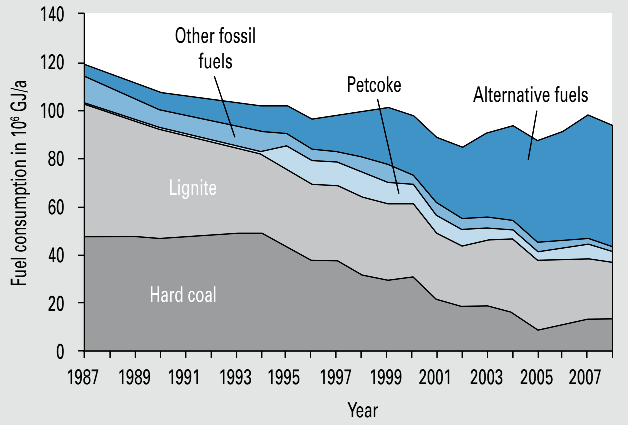


Fig. I-13: Fuel consumption in the German cement industry since 1987

Table I-2: Use of alternative fuels in the German cement industry

Alternative fuel	2006 1 000 t/a	2008 1 000 t/a
Tyres	265	266
Waste oil	69	80
Fractions from industrial and commercial waste, thereof:	1 370	1 548
Wood pulp, paper and cardboard	244	150
Plastics	363	460
Packaging materials	0	0
Textile industry waste	9	2
Other	754	936
Meat and bone meal, animal fat	317	231
Reprocessed fractions from municipal waste	212	220
Scrap wood	14	12
Solvents	93	102
Fuller‘s earth	4	0
Sewage sludge	238	267
Other such as: Oil sludge Organic distillation residues	32	175

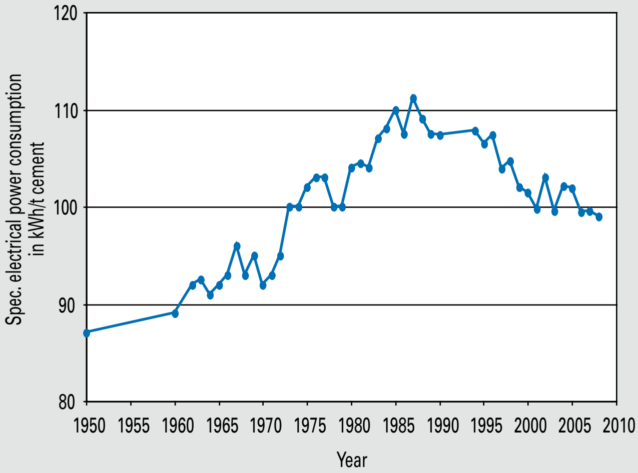


Fig. I-14: Specific electrical power consumption of German cement works (old federal states until 1987, then the entire federal republic)

95.8 million GJ/a, which was attributable to the slump in production, among other factors. In absolute terms, this corresponds to a reduction of 20.1 %. As can be seen from **Fig. I-13**, the proportion of alternative fuels continued to rise in the period under review, totalling 54.4 % in 2008 as opposed to 23.0 % in 1999. The increasing use of alternative fuels primarily entailed the substitution of lignite during the period under review. The consumption of light distillate and heavy fuel oil as well as natural gas remained at a very low level. These fuels are chiefly utilised for kiln start-up.

The break-down of alternative fuels for the years 2003 and 2008 demonstrates that traditional alternative fuels, such as used tyres and waste oil, continued losing in importance in comparison with other alternative fuels. **Table I-2** shows that the input of used tyres was just under 270 000 t/a, whereas the quantity of waste oil utilised increased slightly from 69 000 t/a in 2006 to 80 000 t/a in 2008. The use of fractions from industrial and commercial wastes increased substantially from 1 370 000 t/a in 2006 to 1 547 000 t/a in 2008. Utilisation of processed fractions from municipal waste remained at a similar level of more than 210 000 t/a. The use of meat and bone meal and animal fat began in 2000 in the wake of the BSE crisis and was initially increased to 452 000 t/a by the year 2003. However, since these materials have also been increasingly utilised in other co-incineration plants such as power stations, their use in the cement industry has declined to 231 000 t (2008).

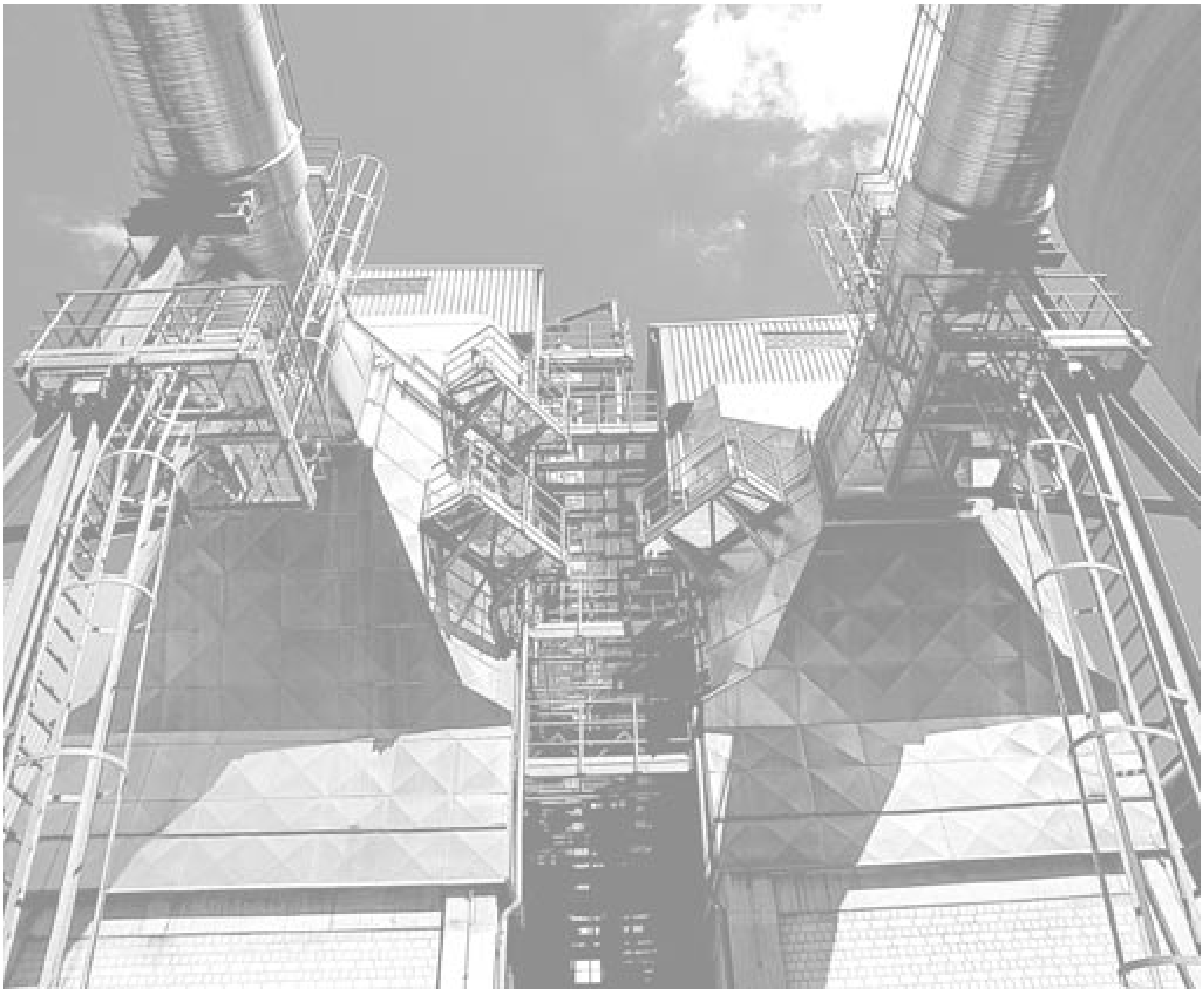
Electrical power consumption

Electrical energy is primarily consumed in cement manufacture for raw material processing (about 35 %), for burning and cooling the clinker (approx. 22 %) and for cement grinding (approx. 38 %). **Fig. I-14** shows the trend of electrical power consumption by German cement works in the period from 1950 to 2005. The long-term rise in electrical power consumption was stopped after German reunification. Over the following years, it stabilised at a range between 100 and 102 kWh/t cement and is now just below 100 kWh/t cement.

Cements with other main constituents in addition to clinker, such as blast furnace slag or limestone, consume more grinding energy since they need to be ground more finely to achieve the same quality. On the other hand, the corresponding electrical power required for the manufacture of substituted clinker (raw material preparation, burning process) is saved. The use of energy-efficient mill types, such as high-pressure twin-roll mills, has gained acceptance in the cement industry. However, since the workability of the cement produced in these mills does not correspond to those of cement ground in conventional ball mills, subsequent grinding in a ball mill is usually still necessary. Therefore, it is still impossible to realise the full energy saving potential. Even separating the grinding processes of the different main constituents and subsequently mixing them in mixing systems apparently does not allow for significant reductions under regular operating conditions.

II

Environmental protection in cement manufacture



Flue gas treatment devices of a cement kiln

Legislation ■

Revision of the BAT paper for the cement and lime industries

The European Integrated Pollution Protection and Control Directive (IPPC Directive) is an important document in connection with the operation of industrial installations in Europe. On the basis of this European directive the technological status of certain industries must be defined and described throughout Europe at regular intervals. This takes place via BAT reference documents (BREF documents) whose compilation is coordinated centrally by a European Commission office in Seville, Spain. The BAT paper dating from 2001 that currently applies to the cement and lime industries is one of the first of these documents that was subjected to a revision process. This process has taken almost three years and was finalised in April 2009 with a concluding meeting of the Information Exchange Forum (IEF) in Brussels, Belgium. The final draft has succeeded in achieving mutual agreement between the EU Commission, the participating countries and the industry on all points. The split views between the authorities and industry representatives were completely avoided this time. Together with the technical aspects of the cement and lime industries, the revised document now also includes suitable descriptions for the production of magnesium oxide. This was at the request of the industry concerned.

From the cement industry's point of view, the following points in the revised BREF document should be especially highlighted:

1. Specific energy consumption for modern cyclone preheaters (with/without calciner): for the specific energy consumption of these modern kilns a range of between 2 900 and 3 300 MJ/t clinker is specified. In addition, the BREF document contains the information that this value may be higher by 160 to 320 MJ/t on an annual average due to normal fluctuations, such as start-ups and shutdowns. This definition takes account of the potential fluctuations in kiln operation.

2. Use of waste: the use of suitable waste in the clinker and cement production processes is expressly acknowledged to be a best available technique (BAT). One of the main reasons why this result could be achieved was that over the last years the European cement industry has been able to provide evidence that waste utilisation in their works is environmentally safe and sound.

Table II-1: BAT associated emission levels (BAT-AEL) for NO$_X$ from the flue gases of kiln firing and/or preheating/precalcining processes in the cement industry

Kiln Type	Unit	BAT-AEL (daily average value)
Preheater kilns	mg/Nm^3	< 200–450 1)2)
Lepol and long rotary kilns	mg/Nm^3	400–800 3)

1) BAT-AEL is 500 mg/Nm^3, where after primary measures/techniques the initial NO$_x$ level is > 1 000 mg/Nm^3

2) Existing kiln system design, fuel mix properties including waste, raw material burnability can influence the ability to be in the range. Levels below 350 mg/Nm^3 are achieved at kiln with favourable conditions. The lower value of 200 mg/Nm^3 has only been reported as monthly average for three plants (easy burning mix used)

3) Depending on initial levels and ammonia slip

3. Dust emissions: for dust emissions a BAT level of < 10 to 20 mg/Nm^3 is defined. Electric and fabric filters are both counted equally as best available techniques. If fabric filters or new or regenerated filters are used, the lower BAT emission level must be strived for.

4. Nitrogen oxide emissions: the definition of the current best available techniques in connection with reducing nitrogen oxide emissions was discussed intensively during the revision process. For preheater kilns a BAT emission level of < 200 to 450 mg/Nm^3 is specified. If the initial NO$_x$ level is above 1 000 mg/Nm^3, the associated BAT emission level extends by up to 500 mg/Nm^3. **Table II-1** shows the exact agreements in connection with the definition of a BAT emission level for NO$_x$. In this connection it should also be mentioned that selective catalytic reduction (SCR) can only be regarded as BAT when process development in the cement industry is more advanced and when suitable catalysts are available. As opposed to this, selective non-catalytic reduction (SNCR) is defined as BAT. When the SNCR method is used, the additional ammonia slip may be up to 50 mg/Nm^3.

On the whole, the revised BREF document sets demanding specifications for further development of environmental protection in the cement industry. This is regardless of the fact that the BAT emission levels defined in the document are expressly not emission limit values. Rather, they are concentration ranges that could be achieved with consideration of the specific border conditions in the individual plants if a certain technology was used. Naturally, emission limit values must be above this associated BAT emission level.

The final draft of the revised BAT reference document can be viewed on the website of the European Commission office in Seville. It is expected that the finished document will be finally released in the second half of 2009.

Use of alternative fuels in the German cement industry

German cement manufacturers have many years of experience in the appropriate and safe use of suitable waste in the clinker burning process. Based on these experiences, in 2008 the rate of substitution in terms of fuel energy consumption was increased to more than 54 % through the use of suitable alternative fuels (**Fig. II-1**). This is all the more remarkable when we consider that this figure is an average value. In 2008, some rotary cement kilns operating in Germany achieved actual substitution rates of more than 80 % in terms of fuel energy consumption.

Most of this utilised waste continues to come from the areas of processed industrial and commercial waste (**Fig. II-2**). Most of the energetically recycled waste used in German cement works has come from these material groups for many years now. Since 2002, there has also been an increase in the amount of municipal sewage sludge utilised in German cement works. Prior to this, many politicians had been against this ecologically sensible way of utilising sewage sludge. Because of this, in the past it was extremely difficult to obtain the corresponding approvals.

By using suitable alternative fuels, the German cement industry has been able to save more than 1.7 million metric tonnes [t] of coal equivalents in primary energy. This represents a considerable contribution towards conserving natural resources and also reduces fuel-related fossil CO$_2$ emissions in the clinker burning process considerably. On top of this, the material group of processed industrial and commercial waste can contain a large proportion of biogenic carbon. Recent investigations have shown that this biomass proportion can contribute between 20 % and 50 % of the carbon contained in the fuel. Consequently, the use of alternative fuels in German cement works has a considerable potential to reduce fuel-related CO_2 emissions in the clinker production process.

Start of PRTR reporting

The previous European EPER system for environmental reporting was replaced by the European Pollutant Release and Transfer Register (E-PRTR). For the first time in 2008 operators of the relevant plants reported the release and transfer of pollutants to the responsible authorities for the new pollutant register. In summer or autumn 2009, the data will be provided on the internet and thus made available to the general public.

The basis for this pollutant register is the European PRTR regulation which was implemented in Germany with the PRTR Act (SchadRegProtAG). Reportable activities are listed in the annex to the PRTR regulation. Within the mineral industry installations for the production of cement clinker from a capacity of > 500 t/d are affected; all kiln systems operating in Germany exceed this capacity threshold. However, a report only has to be submitted if the amount of pollutants emitted exceeds certain thresholds.

A new feature compared to the previous EPER system is that opencast mines and quarries also have to submit a report if the “active area” exceeds 25 hectares. Primarily, the relevant pollutant is fine dust (PM10) if the corresponding threshold of 50 000 kg/a is exceeded. Basically, there are problems in determining these generally widely distributed fine dust emissions, since many different operational and meteorological factors have an influence on the amount of emissions. By using simple emission factors at best it would be possible to roughly estimate the emitted loads. For the next report the environmental authorities must provide more precise specifications as to how the fine dust emissions of opencast mines and quarries are to be determined.

These and other questions regarding cement works reporting were discussed in a VDZ working group. The available PRTR guidelines (e.g. from the European Commission, UBA, VGB, BBS) were discussed and contact was established to the bodies commissioned by the German Federal Environment Agency.

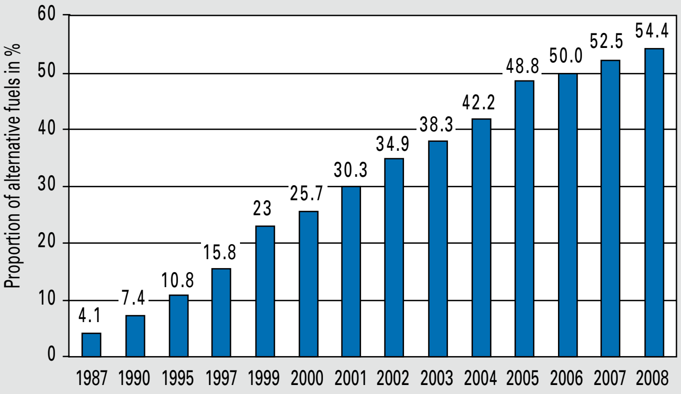


Fig. II-1: Trends in the use of alternative fuels in the German cement industry

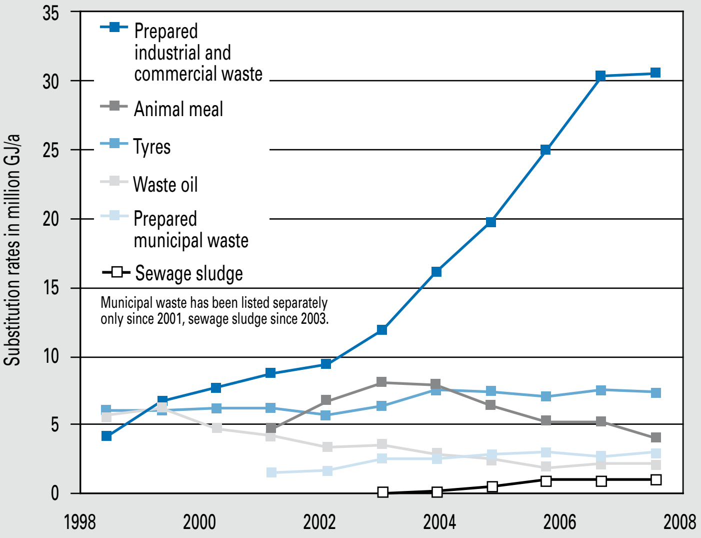


Fig. II-2: Trends in substitution rates for selected materials

For reporting in Germany a standard national input software product was developed (BUBE-Online) with which the PRTR data and also the data for the 11th Federal Immission Control Ordinance can be gathered via the internet. After a plausibility check by the responsible state authorities or the Federal Environment Agency, the data will be entered in the national pollutant register and will then be passed on to the European Commission where it will be transferred to the European register.

As opposed to the EPER report which had to be submitted every three years, the PRTR system requires an annual report. In the course of the legislative changes resulting from the introduction of the PRTR, the rhythm for submitting an emission declaration according to the 11th Federal Immission Control Ordinance (BImSchV) was extended to four years.

Table II-2: CO_2 emissions in the German cement industry from 2005 to 2008

	Absolute CO_2 emissions in 10^6 t/a				Specific CO_2 emissions in t CO_2/t cement			
	2005	2006	2007	2008	2005	2006	2007	2008
Fuel-related [1)]	4.18	4.25	4.38	4.05	0.132	0.123	0.128	0.117
Electricity-related	2.17	2.29	2.28	2.30	0.068	0.067	0.067	0.066
Raw materials-related	12.92	13.21	14.31	13.44	0.406	0.383	0.419	0.388
Energy-related	6.35	6.54	6.65	6.35	0.200	0.189	0.195	0.183
Total	19.27	19.75	20.97	19.79	0.606	0.573	0.614	0.571

[1)] without alternative fuels

Table II-3: Specific CO_2 emissions in the German cement industry (in t CO_2/t cement)

Year	From thermal energy consumption [1)]	From electrical energy consumption	From limestone decarbonation	Total
1990 [2)]	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

[1)] Without alternative fuels

[2)] Basis year of voluntary commitment from 2000

Climate protection ■

Development of CO_2 emissions

Fuel-related CO_2 emissions

The greenhouse potential of emissions from the cement industry is almost exclusively attributable to carbon dioxide. The quantity of other greenhouse gases, such as the ones cited in the Kyoto Protocol, occurring in cement manufacture is either extremely small or zero. During the clinker burning process, CO_2 emissions are produced by the conversion of fuel energy required to generate process heat. Additionally, fuel energy is consumed for the processes involved in drying other main cement constituents, such as blast furnace slag. In the period from 2005 to 2008, specific fuel-related CO_2 emissions from the German cement industry ranged from 0.132 to 0.117 t CO_2/t cement. In absolute figures this represents a reduction from 4.18 to 4.05 million metric tonnes CO_2 per annum. This does not include CO_2 emissions from the use of alternative fuels – based on the voluntary commitment system – because they completely replace fossil fuels. Since the waste would otherwise release its carbon content to form CO_2 or other greenhouse gases somewhere else, the utilisation of alternative fuels leads to an overall reduction in CO_2 emissions.

This consideration of alternative fuels constitutes a substantial difference in comparison to reporting under the terms of emissions trading. Emissions trading includes all fossil fuels and the fossil proportions of waste-derived fuels. Only the biogenic proportions of the fuels are assigned an emission factor of 0. The replacement of the traditional fossil fuels – lignite and hard coal – by other fuels with lower specific CO_2 emissions, such as natural gas, is impossible because of the costs involved. As fuel costs have a decisive influence on the cost of cement production, the cement industry will continue its endeavours to increasingly substitute fossil fuels with waste-derived fuels. In this context, the utilisation of biogenic waste-derived fuels and fuels containing biogenic portions, respectively, will play a more important role in the future.

The emission factors agreed upon and applied under the terms of the voluntary commitment also differ from the values specified for EU emissions trading. Although the values deviate only slightly in terms of quantity, the differentiation in emissions trading is much more marked. Electrical power consumption accounts for some 10 % of the total energy consumed by the cement works. If, however, electrical power consumption is regarded as primary energy, its share – and thus that of the CO_2 emissions resulting from its use – is higher. Between 2005 and 2008, CO_2 emissions from electricity consumption was between 0.066 and 0.068 t CO_2/t cement. In absolute figures they remain virtually constant at about 2.2 million metric tonnes. The scale on which the German cement industry generates its own electricity is very low.

Raw material-related CO_2 emissions

CO_2 is released during the calcination of limestone (CaO_3), which is the most important raw material. Raw material-related CO_2 emissions for each metric tonne of clinker produced depend on the raw material formulation, although they vary only to a low degree. In Germany, it is about 0.53 t CO_2/t clinker or in the 2005–2008 period, between 0.383 and 0.419 t CO_2/t cement. As a result of increased exports, total raw material-related CO_2 emissions in the German cement industry increased from 12.9 (2005) to 14.3 million metric tonnes CO_2 per annum in 2007, only to fall again to 13.4 million metric tonnes CO_2 per annum in 2008. **Table II-2** shows the specific and absolute CO_2 emissions for the period under review. A reduction in raw material-related CO_2 emissions – in relation to a metric tonne of cement – is only possible to a limited extent through the increased production of cements with several main constituents. In relation to a met-

Fig. II-3: Use of selective dissolution on a sugar cube.

ric tonne of clinker a reduction is practically impossible.

In conclusion, the CO_2 emissions for the German cement industry in the period from 1990 to 2008 are summarised in **Table II-3**. The basis year for the cement industry's voluntary commitment to specific energy-related CO_2 emissions is 1990.

Determining biogenic carbon in alternative fuels

As a result of CO_2 emissions trading the determination of the biogenic carbon content of alternative fuels has taken on a new significance. At present, different determination methods can be used depending on the origin and composition of the samples.

Since there has been a lack of suitable alternatives, over the last few years the selective dissolution method has been widely used in Germany and Europe. This is based on the technical specification CEN/TS 15440, which was developed under the overall control of a European standardisation group, CEN/TC 343. Annex E of this technical specification describes the method relevant for the cement industry to determine the biogenic carbon content of a fuel sample. It is important that the biogenic carbon content is in relation to the total carbon (TC) content of the sample. In this wet-chemistry process the sample must first be treated with concentrated sulphuric acid. This acid can displace the water from the organic constituents with biogenic origins. In a second step, the remaining biogenic carbon is treated with a strong oxidising agent and is extracted from the sample in a gaseous form. Ideally, only the inert proportion and the corresponding inorganic carbon remain, which can be determined by drying and subsequent weighing. Via an additional determination of the total carbon content in the untreated sample and in the non-biogenic part it is then possible to calculate the biomass content. **Fig. II-3** shows selective dissolution of a biogenic material using a sugar cube as an example. Extraction of the water changes the colour of the sugar cube to black because of the remaining carbon. When the oxidising agent, hydrogen peroxide, is added, this causes a lot of gas formation due to the expulsion of the carbon.

One advantage of selective dissolution is that qualified laboratories can carry out this method without the need for complicated equipment. A disadvantage is that many individual analyses are needed, all of which must be included in the corresponding calculations. Precise determination of the total carbon content remains a critical aspect. With the commonly used analysers only a few milligrams of sample can be weighed. Because of inhomogeneities even this step can cause considerable errors. However, if the laboratory staff works carefully and if the analyses are repeated sufficiently often, it is possible to compensate for these errors. Thus, for many alternative fuels used in the cement industry selective dissolution can be used as a relatively inexpensive method for determining the biogenic proportion.

However, there are also materials that are not suitable for selective dissolution due to their substance properties. These include, for example, all fuel mixtures that are already impinged with fossil carbon (e.g. lignite dust). In these cases selective dissolution delivers values that are too high for the biogenic proportion. Technical specification CEN/TS 15440 contains the corresponding exclusion criteria.

These materials can be analysed with the ^{14}C method. Currently, a draft technical specification (prCEN/TS 15747) also exists for the use of this method. This process, which has been known for many years in archaeometry, makes use of the fact that a small part of the carbon that occurs naturally in the atmosphere consists of the radioactive isotope with the atomic weight 14. This carbon isotope has a half-life of approximately 5 500 years. Accordingly, fossil fuels that are several hundred thousand years old have no ^{14}C isotopes. In contrast, their content in biogenic fuels virtually corresponds to the concentration in the natural atmosphere. On this basis and with the help of known analysis methods (liquid scintillation counter, beta counter tube or high-resolution mass spectrometer) it is possible to determine the biogenic carbon content in a sample. One advantage of this method is that it can be used for all samples. The disadvantage is the comparatively high costs resulting from the complicated measuring technology.

Analysis based on the ^{14}C method also allows investigations to be carried out directly on flue gas samples. The Research Institute of the Cement Industry has been working together with ECRA in this field for many years continuously developing the corresponding process. In two large-scale field trials it has been shown that the method can be used for rotary kilns in the cement industry. Current development work is focusing on identifying suitable sampling equipment and a suitable medium that is able to store an adequate amount of CO_2.

European climate policy

On 17 December 2008, the European Parliament passed a package of measures defining European climate policy for the period after 2012. Apart from the modified emissions trading directive, the climate package also contains three more directives on effort sharing, geological storage of carbon dioxide and promotion of renewable energies. The parliamentary resolutions will have considerable effects on energy consumption and CO_2 emissions in the EU member states and especially

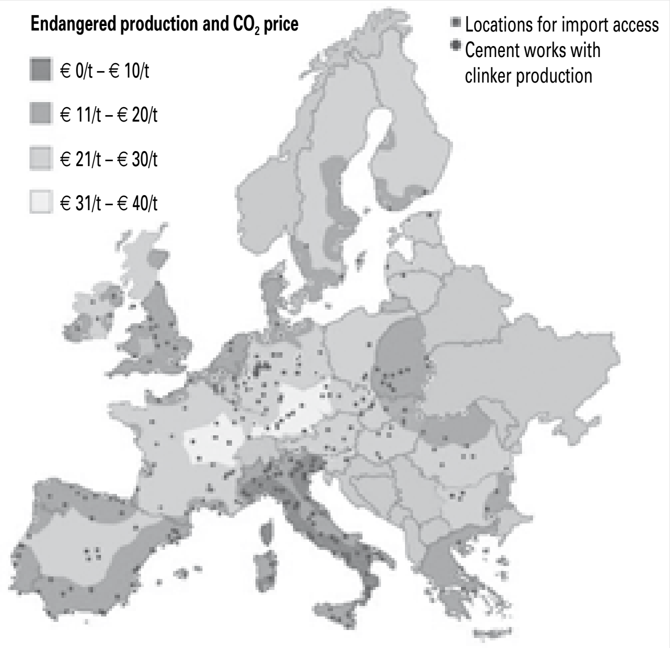


Fig. II-4: Risks for clinker production in Europe as a result of added costs of emissions trading (Source: BCG Study, Assessment of the impact of the 2013-2020 ETS proposal on the European cement industry)

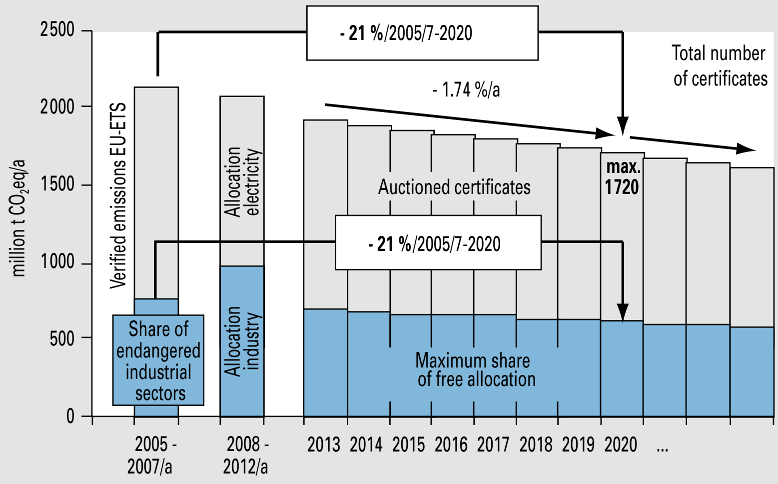


Fig. II-5: Targets for the EU emissions trading sector and additional pro-rata reduction defined by the maximum free allocation share

for energy-intensive industries. The main instrument for industry remains CO_2 emissions trading, but the other directives will also have direct or indirect consequences for industry.

Emissions trading

After intensive negotiations between the European Council and Parliament, in addition to ecological aspects the changes to the Emissions Trading Directive (EU ETS Directive) accepted by the EU Parliament now also take economic needs more greatly into account. Accordingly, sectors at serious risk of relocating production now include those in which the additional CO_2 costs of full auctions and certificate prices of 30 €/t CO_2 exceed 30 % of gross value added. For the cement industry this value is well exceeded at more than 60 %. The sectors at risk are excluded from full auctions and are to continue receiving a free allocation on the basis of product-specific benchmarks.

Before the negotiations in Brussels, the effects that the originally planned auction system would have had on the cement industry were impressively underlined by a study completed by McKinsey last autumn which was commissioned by VDZ and BDZ. Boston Consulting Group (BCG) carried out a similar study at an European level for CEMBUREAU. Both came to the conclusion that the added costs of auctioning emissions certificates would pose a major threat to the cement industry as a result of relocating production facilities. In the case of full auctioning, it could be expected that in 2020 more than 80 % of clinker production would be relocated outside Europe (**Fig. II-4**). As a result of the enormous transport distances this would increase global CO_2 emissions by 7 to 38 million metric tonnes each year.

Production-specific benchmarks now have to be developed for free allocation to the threatened sectors. At the start of 2009, the EU Commission and the EU member states established the corresponding working groups. In the Emissions Trading System Directive the starting point for determining benchmarks is defined as the average specific emissions of the 10 % most efficient plants in the sector. In addition, in the EU ETS Directive free allocation is restricted on a pro rata basis. Because of this, the affected sectors have the same reduction obligation for 2020 of -21 % compared to 2005 (**Fig. II-5**). Therefore, in the allocation it is likely that in addition to the production volume and the respective benchmark, a pro rata reduction will be applied to comply with the overall reduction target.

The EU ETS Directive also envisages arrangements for financial compensation for the indirect cost burdens in sectors at risk by imposing higher electricity prices. The precise structure of this instrument is under the responsibility of the individual member states and is the subject of consultation between the German federal government and the EU Commission with the involvement of the industry associations.

Other directives in the climate package

In the “Effort Sharing” Directive reduction targets are set for social areas in the EU member states that are not subject to CO_2 emissions trading. Essentially, these include traffic, households and parts of trade and industry. The EU has set itself the target of reducing its greenhouse gas emissions by at least 20 % between 1990 and 2020. If a new Kyoto agreement is made, which includes similar reduction obligations for the most important industrial and developing countries, the EU would raise this target to 30 %. This reduction target was distributed among the EU member states in the December 2008 resolutions. Germany has an obligation to reduce emissions by a further 14 % between 2005 and 2020. The reduction targets for Germany are of a similar magnitude to those for other larger EU member states, such as France (14 %), Italy (13 %) and the UK (16 %).

A cap is defined for each member state, which declines in a linear manner from 2013 to 2020. To allow some flexibility, banking and borrowing emission certificates (borrowing emission certificates before they are due and banking them for future use) is allowed to a certain degree. Apart from this, countries that are better than their cap can transfer emission certificates to other member states.

The EU has also set itself the target of increasing the share of energy consumption from renewable energies throughout Europe to 20 % by 2020. This obligation is also distributed among the member states with the directive to promote renewable energies. In 2005, in Germany the share of renewables in energy consumption was 5.8 % – this has to increase to 18 % by 2020. The comparative figures for other member countries are: France (23 %), Italy (17 %), UK (15 %). Countries that already use a high proportion of renewable energies in energy conversion have correspondingly higher targets. In addition to this, the share of renewable energies in traffic is to be increased to 10 % in all member states by 2020.

In future, bio-fuels may be counted only when they fulfil defined sustainability criteria. It can be expected that demand for biomass and waste with biogenic fractions will increase considerably in other sectors, especially electricity generation.

With the directive on geological storage of CO_2 the EU Commission defined harmonised requirements for the selection, approval, operation, monitoring and decommissioning of CO_2 storage facilities. In large industrial plants carbon capture and storage (CCS) is regarded as a very important technology that will drastically reduce anthropogenic CO_2 emissions in the atmosphere over a period of 30 to 50 years. The directive also defines responsibilities and competencies for CO_2 storage facilities. It also regulates free and fair access to transport networks and storage facilities for all interested parties. The directive defines guidelines on precautions for liability cases.

The member states decide where the CO_2 storage facilities will be located. As captured CO_2 is not deemed to be waste, it is not subject to waste laws and can be transported across national borders without any problem. While storage in water columns – in other words, in deep marine environments – is not allowed, storage in former gas and oil caverns below the North Sea is considered to be the most promising option. These storage facilities offer a combination of CO_2 storage and the technology of increased gas and oil production in which the CO_2 is used to press residual gas and oil out of the storage facility that would otherwise be virtually impossible.

CO_2 storage facilities must be monitored with technical measuring equipment before they are commissioned, during operation and for at least 30 years after they are decommissioned so that any leaks can be detected. The operator is responsible for the storage facility. When the storage facility is decommissioned, the operator remains responsible for at least 20 years before this responsibility passes over to the government.

When the directive comes into force, no more fossil fuel-fired power plants may be approved unless they include plans for CO_2 capture systems. Similar specifications for industrial plants are not planned at present.

CO_2 Capture and Storage

The topic of climate protection has become increasingly important over the last years and is now being discussed by a wider public. These days, politicians agree that a portfolio of measures is necessary to limit the temperature rise in the atmosphere to a maximum of 2 °C in the coming years. One of these measures is to capture CO_2 at power stations and other large firing systems and then to store this in underground storage facilities. This is referred to as carbon capture and storage, often abbreviated in literature to CCS. With our current level of knowledge the technologies are extremely expensive and require a lot of energy. Also needed is a network of CO_2 pipelines to transport the CO_2 to the storage facilities. In addition, the long-term safety of storage is extremely important. For these reasons the use of CCS technologies still remains controversial.

The Research Institute of the Cement Industry is investigating the potential use of CCS in the clinker burning process in an ECRA project. This research project is split into several phases. In phase I, a literature study was carried out which investigated all the possible capture measures. It was shown that in particular the oxyfuel process and chemical absorption processes (amine scrubbing) could potentially be suitable for use in cement kiln systems. In phase II of the project, detailed analyses of rotary kiln systems in the cement industry were carried out for this reduction method.

The use of the oxyfuel method, in other words combustion with pure oxygen, would require extensive process engineering changes in the clinker burning process. On the other hand, downstream chemical absorption processes could probably be installed with no major effects on the process engineering of the cement kiln systems, as this emission reduction measure would be installed at the tail end of the waste gas system and would thus have little effect on the burning process. However, there is a particular need for investigation into solvent degradation and the provision of energy for regenerating the exhausted absorption agent. The cost issue naturally also has to be assessed.

Oxyfuel technology

One of the methods being discussed for capturing CO_2 from flue gases is the oxyfuel technology with flue gas recirculation. In oxyfuel technology, combustion is not carried out with air but with oxygen. This considerably increases the CO_2 concentration in the flue gas because the flue gas volumetric flow is not diluted by atmospheric nitrogen. However, since combustion with pure oxygen would result in excessively high combustion temperatures in the sintering zone, some of the flue gas has to be recirculated to the combustion process to adjust the combustion temperature (**Fig. II-6**). With this method CO_2 is enriched in the flue gas and can then be liquefied directly or captured with another

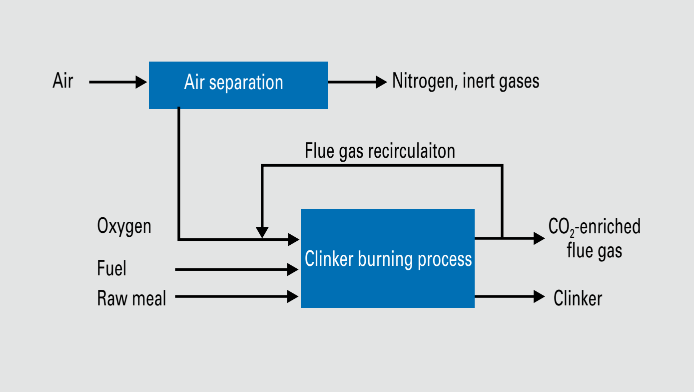


Fig. II-6: Application of oxyfuel technology in the cement clinker burning process

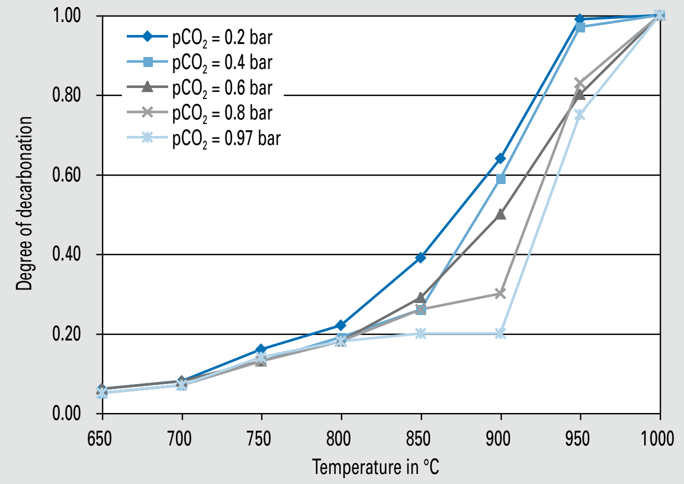


Fig. II-7: Shift in equilibrium in the calcining reaction of a raw meal to higher temperatures as the CO_2 partial pressure increases

technology before being transported to the storage facility. This technology thus has a considerable effect on the burning process and requires some changes in the plant engineering.

For instance, additional units have to be installed on the works site, such as an air separation plant and a CO_2 cleaning and compression facility. The provision of oxygen from an air separation unit (ASU) is also an extremely energy-intensive process step. Apart from that, the oxygen content in the combustion gas – the optimum is probably above 21 % by volume – represents another degree of freedom. The energy consumption of the ASU depends directly on the purity of the oxygen, which co-determines the composition of the flue gas and, consequently, the expenditure for cleaning before the CO_2 is transported to the storage facility. Another major impacting factor on the CO_2 concentration of the flue gas is the proportion of false air. However, sealing the clinker burning process more than is currently the practice would be difficult because of the transitions between static and moving parts, such as the kiln hood or the kiln inlet.

Moderate oxygen enrichment in the combustion air has been used for many years in the power plant, steel, glass and cement industries. For example, in some cement works, especially in the USA, experience has been acquired with oxygen enrichment to improve production output and energy efficiency. While the power plant industry is already operating pilot plants to capture CO_2 emissions using oxyfuel technology, there is no knowledge of the technology being used in the cement industry to date.

Oxyfuel technology has a considerable effect on the clinker burning process because of the changes in the gas phase composition ($CO_2/N_2/O_2$). This includes effects in terms of plant operation and also effects on the chemical-mineralogical kiln feed reactions. This means that the burning process would have to be modified extensively. Therefore, within the scope of a research project laboratory investigations and simulation calculations with a process engineering model developed at the Research Institute are being conducted.

In the laboratory investigations it was seen that the CO_2 partial pressure induces varying shifts in equilibrium in the calcining reaction depending on the tested materials. This, in turn, increases fuel energy consumption (**Fig. II-7**). In addition to this, in various analyses of the kiln meals it was also determined that the varying temperature shifts in the respective calcining processes are essentially influenced by the closure-level of the silicon and calcium oxide components, which has a strong effect on the exothermal diffusion-controlled consecutive reaction to the clinker phases.

For the simulation calculations a reference condition was first defined in order to assess changes in system operation. This is a kiln system with a capacity of 3 000 t/d and a five-stage preheater, calciner and tertiary air duct. Based on this condition the nitrogen was removed from the primary air. This alone caused a marked increase in the temperature profiles in the kiln. In the simulated modification of the kiln atmosphere from air to oxyfuel operation it was seen that the temperature profiles of the system fall as the CO_2 concentration increases because of the higher specific heat capacity of CO_2 compared to N_2 (**Fig. II-8**). This results in an overall shift in the temperature profile. Formation of the clinker phase shifts throughout the length of the kiln because of changes in the heat transfer behaviour; however, there are only a few deviations in the final product, the clinker (**Fig. II-9**).

Based on the results obtained so far, the project envisages more simulation studies with the model and laboratory investigation into the behaviour of clinker burning and cooling in a CO_2 atmosphere.

Post-combustion Capture

The term post-combustion CO_2 capture covers various technologies used to capture carbon dioxide from the flue gas after combustion. This is done by absorption, adsorption or CO_2-selective membranes.

Absorption capture of CO_2 from the flue gas is done in a gas scrubber. The flue gas is fed through a counter-flow column where the scrubbing fluid selectively captures the carbon dioxide from the flue gas. In this way up to 99 % of the carbon dioxide can be captured from the flue gas. As the rate of capture increases this also increases energy consumption, which would suggest that capture of between 85 % and 95 % is the most practical range worth considering at present.

If CO_2 capture is to become relevant for the cement industry, absorption gas scrubbing would be the most promising method in the medium term. First of all it is already state of the art in other industrial processes and secondly it is especially suitable for medium and low CO_2 partial pressures, as found in flue gases under normal pressure. Furthermore, existing rotary kilns could be retrofitted with this end-of-pipe measure with no effects on the clinker burning process.

Adsorption methods would be unsuitable for kiln systems, as they can only be used effectively with much higher CO_2 partial pressure. Membrane processes could work more energy efficiently. However, they are still at a basic research stage and will not be available for large-scale technical use in the foreseeable future.

CO_2 capture by absorption

Absorption gas scrubbing is an established method for capturing CO_2; to date it has been used, among other things, to treat natural gas. Amines or carbonates that react reversibly with CO_2 are used as absorbing agents. The process consists of an absorption and a desorption column. In the latter, the CO_2 is separated from the absorbing agent. This takes place by the amine solution being heated in a boiling vessel. Because of the higher temperature, the solubility of CO_2 in the absorbing agent shifts so that the CO_2 is released from the liquid.

Significant for absorption gas scrubbing are the very high energy consumption and a high purity of the captured CO_2 – generally in excess of 99 %.

Requirements for the clean gas

The composition of the clean gas is important for efficient CO_2 capture. Oxygen and acidic gases such as SO_2 attack the absorbing agent and degrade it. Consequently, narrow concentration values have to be maintained so that losses of absorbing agents remain within a reasonable level.

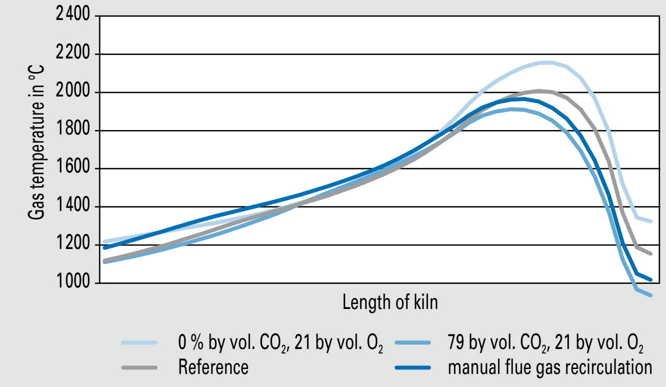


Fig. II-8: Temperature profiles of the kiln gas in relation to the proportion of CO_2 in the combustion atmosphere

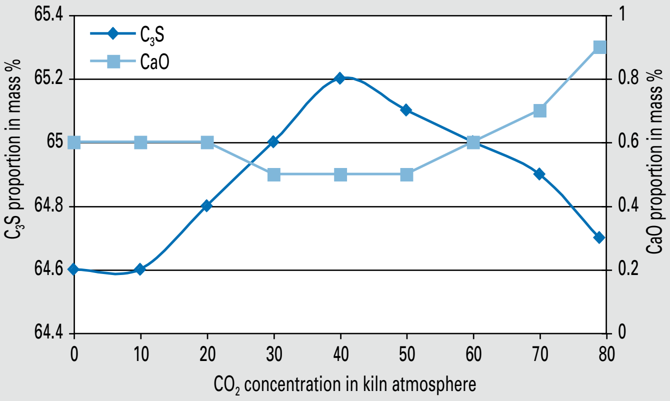


Fig. II-9: Effect of the burning conditions on alite formation and the free lime content under increasing CO_2 concentrations

Annual averages for German cement works show that the NO_x concentrations comply with the requirements; as regards the concentration of sulphur dioxide, this is the case in about half the plants. Dust concentrations in the flue gas largely meet the requirements. However, further research must be carried out especially in this area. This also applies to the concentration of CO, trace gases and heavy metals.

The proportion of false air and the resulting oxygen concentration is another problem. The influence of oxygen on the absorbing agent can be effectively prevented using inhibitory substances. However, the false air also increases the volume of flue gas that has to pass through the scrubber. Consequently, compressors and columns have to be dimensioned larger.

Energy consumption

Consumption of thermal and electrical energy is the biggest challenge for retrofitting a CO_2 capture system that is economically feasible. According to current estimates, specific energy consumption per metric tonne of clinker would more than double in a system with carbon capture. With the current technology, about 2 500 MJ thermal energy per metric tonne of clinker would be needed alone for the boiling vessel to capture the released CO_2 in an efficient rotary kiln system.

As the rotary kiln process is already very efficient, it would only be possible to use small amounts of energy from the existing system. Even with systems with high fuel energy consumption, only about 10 - 20 % of the boiling vessel heat could be covered by using waste heat. **Fig. II-10** shows the most important material and energy flows in CO_2 capture; this example assumes that energy is supplied from a power plant. Pumps and compressors are supplied with electrical energy (W_{el}) from the power plant, the boiling vessel is heated by hot

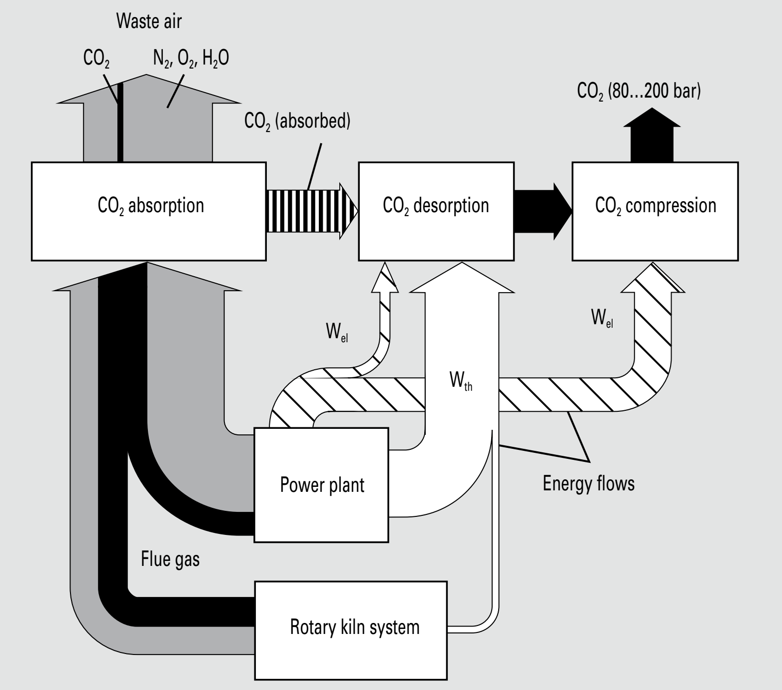


Fig. II-10: Cement works with CO_2 capture and power plant for energy supply: estimates of the main mass and energy flows

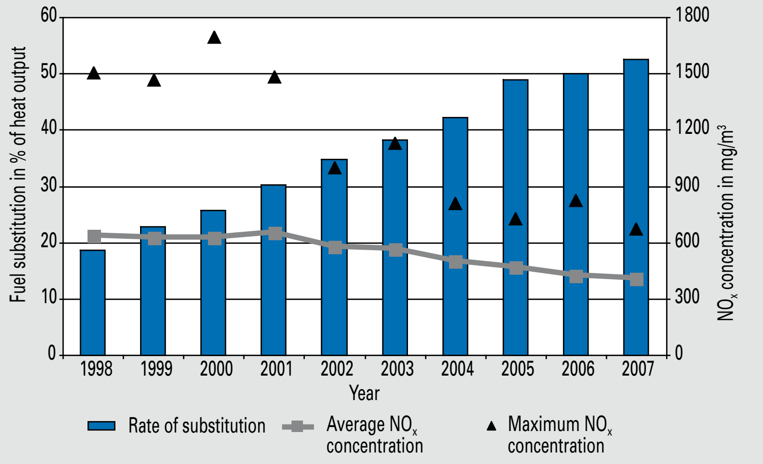


Fig. II-11: Development of NO_x emissions from 1998 to 2007 with information about fuel substitution

steam (W_{th}) from the power plant and from the rotary kiln system.

Outlook

With the current technological status, retrofitting an absorption CO_2 capture system would require too much energy for it to be used in flue gas scrubbing in an economically feasible fashion. However, continuing developments, especially in the area of absorbing agent regeneration and increasing prices for CO_2 emission rights within the scope of European emissions trading could change this situation in the medium term. Should CO_2 capture become necessary and economically viable, post-combustion technology is very probably the first available solution.

Environmental data ■

Each year since 1998 VDZ has published the "Environmental Data of the German Cement Industry" which is based on a survey conducted among almost all German cement manufacturers. The current issue can be downloaded as a pdf file from the literature/environment and resources/environmental data section at www.vdz-online.de. Printed copies can also be obtained from the Research Institute publications office.

The brochure documents the use of raw materials and fuels in clinker and cement manufacture. The quantities of alternative fuels used are shown in detail. Accordingly, the proportion of total fuel energy consumption that alternative fuels accounted for was more than 54 % in 2008. The content focuses on emissions from the kiln flue gases of cement plants that can be regarded as being representative for the German cement industry.

In addition to dust, the flue gas components NO_x (**Fig. II-11**) and SO_2, as well as all relevant trace elements and organic constituents of the flue gas are considered. Their concentrations in the clean gas and the associated substance loads, in other words the quantities emitted in kg/year, are illustrated in graphs for all clinker kilns operated in Germany. If a component could be determined by measurement, it is possible to provide clear data about the concentration and the annual load; the accuracies of these can be described by the measuring uncertainty. However, this is not possible for measured values or measurements below the detection limit. In these cases no emission concentrations are shown in the figures; only a theoretical upper limit can be given for the emission. This is calculated under the assumption that the concentration of the substance in the clean gas reached the detection limit.

At present, these estimates with upper limits are often unavoidable in the determination of trace element emissions from rotary kiln systems in the cement industry. Because of the way they behave in the clinker burning process and the high retention capacity of the dedusting systems, the concentrations of trace elements are often below the detection limit of the measuring method. **Fig. II-12** presents emission concentrations in mg/m³ of the trace element chromium as an example. For example, in 2007, 108 values for chromium concentrations in clean gas were determined through measurements in 42 kiln systems. How-

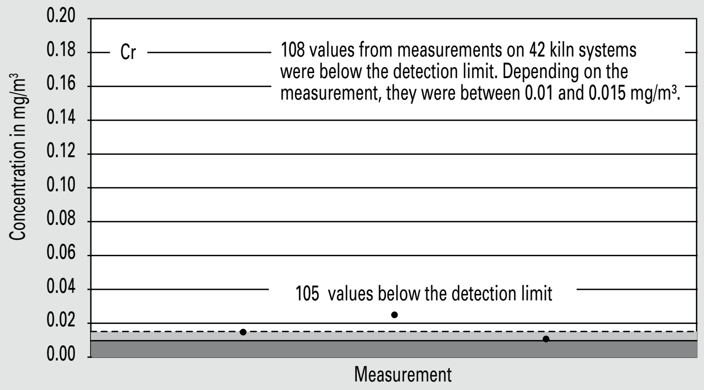


Fig. II-12: Measured values (2007) of the chromium concentration in the clean gas of 42 rotary kiln systems

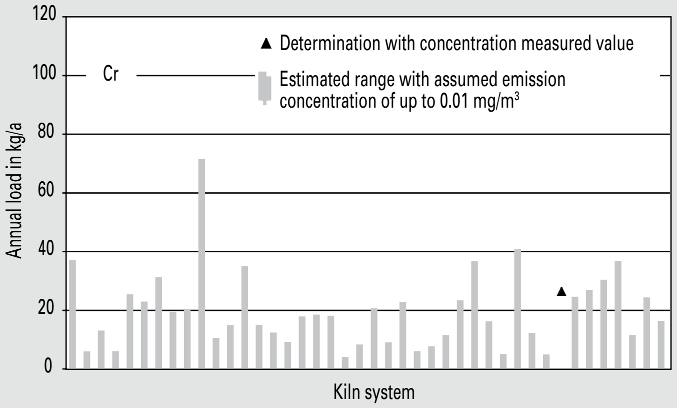


Fig. II-13: Chromium emissions (annual loads in 2007) of 42 rotary kiln systems

ever, only the three values shown (points) are greater than or equal to the detection limit, which is between 0.01 and 0.015 mg/m³ depending on the measurement and analysis method (cross bar).

Consequently, in **Fig. II-13** it is only possible to show the chromium load via the concentration values and the clean gas volumetric flow (m³/year) clearly for one plant (triangle). For 41 plants the emissions have to be estimated via an assumed concentration value of 0.01 mg/m³ (horizontal line). It is only in the most unfavourable case that the actual emitted loads correspond to the illustrated upper limit, which has to be especially considered in an environmental policy assessment of the data.

Reducing gas and dust emissions ■

Status of NO_x reduction

Reducing NO_x emissions is a subject that has concerned the cement industry for more than 20 years. As emission limits have been lowered steadily over the years, higher demands have been placed on processes to reduce NO_x emissions.

To comply with the current emission limit values in most cases SNCR (selective non-catalytic reduction) is the most suitable method. In the German cement industry 35 of these systems are currently installed, in Europe more than 100 SNCR units are also now often installed as a secondary reduction measure in pre-calciner systems. Because of the favourable boundary conditions for effective NO decomposition, namely a relatively low initial NO_x level and a long retention time in a suitable temperature window, kiln systems with a calciner can achieve a low NO_x level with low NH_3 slip.

Based on the National Emission Ceilings Directive (NEC Directive) for various air pollutants there is increasing pressure on companies to initiate measures to reduce NH_3 emissions. Although the cement industry makes only a very small contribution to NH_3 emissions, this subject is increasingly being raised by the approval authorities, many of whom are now demanding monitoring of NH_3 emissions in addition to ensuring a low NO_x limit value. In the latest revision of the BREF document an upper limit of 50 mg/m³ is proposed for additional NH_3 slip when an SNCR system is used. As regards NH_3 emissions, it must be remembered that total emissions consists of a basic raw material-derived level and the NH_3 slip (caused by injecting ammonia to reduce NO_x). Consequently, limits should relate only to the NH_3 slip.

Development of the SCR process

While the SNCR method can be regarded as state of the art for NO_x reduction in the clinker burning process, this applies only with restrictions to the SCR method (selective catalytic reduction). To further develop the SCR process in the European cement industry SCR trials are planned or already being carried out in pilot and demonstration plants. With these developments it should be possible to comply with low NO_x limits with only little NH_3 slip and in some cases also to reduce raw material-related NH_3 emissions.

In Italy, two SCR systems have already been installed in cement works and a third is in the planning stage. In Austria, various pilot investigations have already been started. If these are successful, they will be followed by the construction of demonstration plants. As a result of the contact between the German and Austrian cement industry associations, VDZ and VÖZ, it is ensured that the experiences from the Austrian SCR projects can also be used by the German cement industry.

Two SCR demonstration projects are also planned for Germany. The first system in the raw gas arrangement is scheduled to commence operation in early 2010. The second system in the clean gas arrange-

Table II-4: Maintenance specifications for mercury analysers currently installed in German cement works

Measuring facility	Manufacturer	Version	Weekly	Monthly	Half-yearly	Yearly
MERCEM	SICK MAIHAK GmbH, Meersburg	Oct. 2008	Visual checks of measured values, system cabinet, liquid output, rinsing bottle	Checks of pressures, flow, reactor every 3 months: replace $SnCl_2$ solution, top up Hg test gas	Replace reagents and consumables	Replace consumables, service recommended
HM 1400 TR	(VEREWA) Durag GmbH, Hamburg	N/A	Check zero point, measuring gas flow, system pressure	N/A	Replace reactor material, Tygon hose	Replace consumables, top up Hg test gas
SM-3	Mercury Instruments GmbH, Karlsfeld	Oct. 2008	Check hose, measuring gas flow; drain condensate	Check cooler, settings of hose pump every 3 months, top up Hg test gas	Check hot filter, replace hoses, top up Hg test gas	Replace consumables, top up Hg test gas

ment (tail end with waste heat utilisation) is planned for 2011.

VDZ is supporting both works in both the planning and start-up phases and also in an extensive measuring programme over several years, during which the many unanswered questions can be investigated. Among other things, in one works a combination of SCR and SNCR technologies is to be tested. This may allow costs to be reduced as a result of a leaner catalyst design. Also planned are investigations into the catalytic oxidation of organic pollutants and into the behaviour of mercury on the SCR catalysts.

Continuous measurement of mercury emissions – regular internal maintenance by the operator

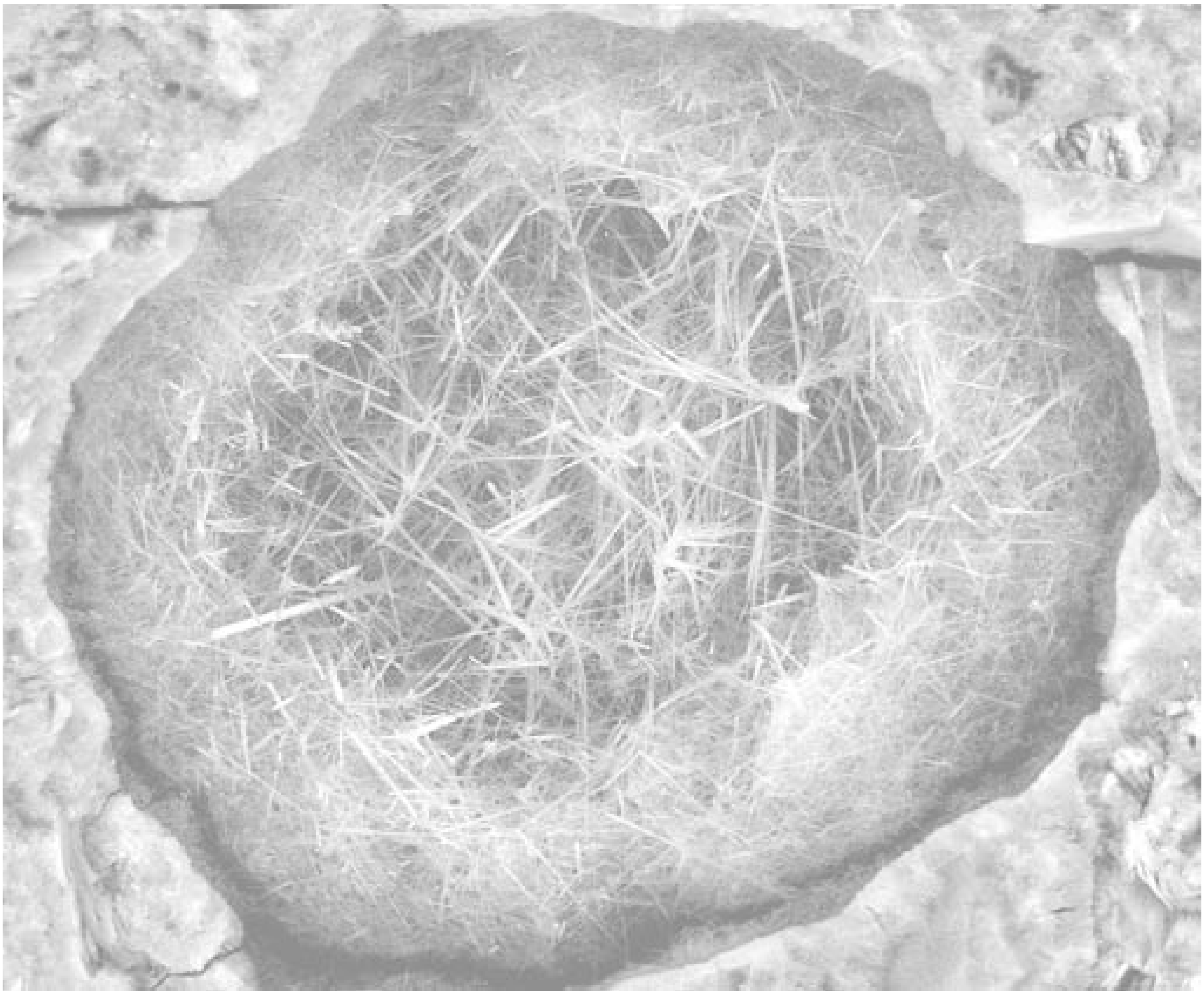
Mercury emissions from rotary kiln systems in the cement industry where waste is utilised energetically must be measured continuously due to statutory guidelines in Germany. There are some commercially available measuring devices on the market that are approved by the respective authorities. However, in spite of these suitability tests there have been difficulties right from the outset as regards stable operation of the analysers in practice. At present in the German cement industry 34 continuously operating mercury emission analysers are installed in the stacks. Although in the past the industry, in collaboration with the Research Institute of the Cement Industry, has put a lot of time and effort into research and development to ensure long-term reliable functioning of the analysers, problems continue to occur in practice. These problems relate to the basic calibration capability of the devices under different process conditions. It is also still practically impossible for the operators to conduct the regular internal quality controls demanded in the European standard (DIN EN 14181) themselves.

The German Federal Environment Agency continues to attribute the continuing problems to inadequate maintenance of the devices. Because of this, the Federal Environment Agency has asked all the manufacturers of the devices to revise the maintenance manuals specifically for the individual devices. **Table II-4** shows the maintenance plans from the manuals for the mercury analysers currently installed in German cement works.

On the basis of the standard DIN EN 14884 (specific implementation of the general standard DIN EN 14181 for mercury analysers) device operators must carry out regular internal quality assurance measures (QAL 3). In the course of this, the operator must regularly record the zero and reference points and any drift. Since no stable test gases and/or reference standards are commercially available, as a general rule the respective measurements to prove internal quality assurance have to be carried out by a qualified measuring institute or even by the device manufacturer. In any case, operators of continuously operating mercury emission measuring devices are advised to obtain the revised maintenance manuals from the manufacturers and to initiate the required measures for the respective device type. Because of the continuing problems in practical operation of the mercury emission analysers in some cases – in particular regarding long-term stability – the continuous measurement of mercury emissions is also not yet described as best available techniques in the latest revised BAT reference paper. Rather, agreement has been reached to continue monitoring how development progresses in Germany and Austria and then in the next revision of the BAT reference document to decide whether continuous measurement of mercury emissions can actually be regarded as best available techniques for the cement industry. However, this definition will change nothing in terms of the statutory regulations in Germany and, consequently, the cement industry's obligation to continue debating this issue.

III

Performance of cement



Crystals of ettringite in a concrete air void

Chemico-mineralogical composition ■

The chemical composition of the cements manufactured by the VDZ's member works is regularly analysed by X-ray fluorescence analysis. **Table III-1** summarises the mean, maximum and minimum values of the Portland cements in the different strength classes according to EN 197. A presentation of CEM I 32,5 of ordinary early strength (N cements) can be dispensed with, as this cement type is now only produced with the special "LH/ SR" property (low heat of hydration, high sulphate resistance) at a small number of sites.

Market shares have continued to shift in favour of Portland-composite cements, especially in strength class 32,5. So-called M cements (with several main constituents) are now being produced in particulary increased volumes. In addition to CEM II/ B-M (S-LL) cements, which contain both blastfurnace slag and limestone as main cement constituents, there is also an increase in the production of M cements containing fly ash and limestone (V-LL). The chemical compositions of the most important Portland-composite cements are listed in **Table III-2**. At individual production sites, oil shale, fly ash or silica fume are also used as main constituents for Portland-composite cements.

Table III-3 summarises the chemical composition of the blastfurnace cements (CEM III/A and CEM III/B) currently produced. The cement types CEM III/C, CEM IV and CEM V, which are produced only occasionally, are of lesser importance in Germany. It remains to be seen whether fields of application that go beyond the current scope of ap-

Table III-1: Chemical composition of Portland cements in different strength classes according to EN 197-1

	CEM I														
Strength class	32,5 R			42,5 N			42,5 R			52,5 N			52,5 R		
	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean	max
SiO_2	18.92	20.61	22.65	18.67	21.14	23.39	18.67	20.73	23.29	19.25	20.64	22.50	19.38	20.78	22.96
Al_2O_3	3.52	5.21	6.10	3.47	4.52	5.83	3.17	4.82	5.97	3.03	4.68	5.57	3.05	4.75	5.78
TiO_2	0.18	0.27	0.34	0.17	0.22	0.29	0.18	0.24	0.32	0.17	0.24	0.30	0.14	0.24	0.30
Fe_2O_3	1.12	2.66	4.50	1.10	2.71	6.67	1.17	2.87	6.49	0.03	2.63	5.29	0.06	2.25	5.30
Mn_2O_3	0.04	0.10	0.67	0.03	0.11	0.59	0.03	0.09	0.68	0.02	0.07	0.20	0.01	0.05	0.11
P_2O_5	0.01	0.23	0.53	0.04	0.17	0.46	0.02	0.22	0.54	0.04	0.22	0.33	0.01	0.22	0.55
CaO	61.31	62.69	66.53	61.47	64.12	66.62	60.52	63.33	66.38	61.40	63.99	66.76	61.51	64.14	66.64
MgO	0.82	1.90	3.33	0.68	1.22	2.41	0.67	1.60	3.49	0.61	1.48	3.55	0.63	1.40	2.82
SO_3	2.41	2.97	3.57	2.38	2.85	3.21	2.16	3.14	3.84	2.25	3.12	4.03	2.19	3.51	4.05
K_2O	0.61	1.00	1.44	0.37	0.71	1.00	0.38	0.89	1.53	0.34	0.72	1.35	0.33	0.82	1.39
Na_2O	0.13	0.21	0.32	0.10	0.18	0.26	0.08	0.20	0.28	0.07	0.20	0.28	0.10	0.21	0.28
Na_2O_{eq}	0.61	0.86	1.12	0.43	0.64	0.81	0.44	0.80	1.20	0.45	0.68	1.11	0.45	0.77	1.31
LOI	1.06	2.15	3.48	0.52	2.05	2.81	0.50	1.86	3.04	0.30	2.01	3.28	0.58	1.61	3.55

Table III-2: Chemical composition of Portland-composite cements according to EN 197-1

	CEM II														
Cement type	CEM II/A-S			CEM II/B-S			CEM II/A-LL			CEM II/B-P			CEM II/B-M (S-LL)		
	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean	max
SiO_2	20.51	22.26	24.61	22.72	24.48	26.17	17.14	18.64	20.98	28.20	29.78	33.10	19.21	20.71	23.52
Al_2O_3	4.51	5.77	6.84	5.55	6.63	7.47	2.97	4.52	5.45	7.22	8.18	8.65	4.33	5.42	6.20
TiO_2	0.25	0.47	4.03	0.31	0.43	0.65	0.13	0.22	0.29	0.39	0.42	0.46	0.18	0.30	0.45
Fe_2O_3	0.94	2.22	3.84	0.80	1.85	3.48	0.05	2.28	4.15	2.99	3.34	3.87	0.08	1.94	2.90
Mn_2O_3	0.05	0.13	0.65	0.06	0.15	0.63	0.01	0.08	0.65	0.07	0.12	0.23	0.04	0.10	0.32
P_2O_5	0.02	0.21	0.50	0.03	0.15	0.31	0.08	0.20	0.47	0.07	0.21	0.41	0.01	0.13	0.48
CaO	56.82	60.22	63.11	54.87	57.03	59.57	59.24	62.03	64.62	43.75	47.17	51.85	56.08	59.00	61.67
MgO	1.31	2.41	4.41	2.01	3.27	4.73	0.67	1.53	2.85	1.07	1.67	2.24	1.46	2.46	3.94
SO_3	2.17	3.06	3.81	1.75	2.77	3.53	1.98	2.93	3.61	1.91	2.60	3.32	2.17	2.85	3.50
K_2O	0.46	0.88	1.26	0.43	0.78	1.17	0.37	0.76	1.50	1.00	1.65	2.16	0.38	0.89	1.40
Na_2O	0.11	0.23	0.34	0.14	0.28	0.45	0.10	0.18	0.30	0.53	0.83	0.94	0.17	0.23	0.35
Na_2O_{eq}	0.58	0.83	1.11	0.60	0.79	1.22	0.35	0.69	1.11	1.24	1.92	2.29	0.51	0.86	1.73
S^{2-}	0.06	0.19	0.38	0.15	0.33	0.57	–	0.05	0.09	–	–	–	0.12	0.19	0.36
LOI	0.73	2.03	3.36	0.63	2.02	3.61	4.32	6.60	8.56	3.52	4.06	4.80	3.09	5.82	9.13

proval according to DIN 1045-2 can be tapped for these cements.

Additives to improve early strength of blastfurnace cements ■

Over the last years, the Research Institute of the Cement Industry has developed a hypothesis to explain the often low early strength of blastfurnace cements that differs entirely from the previous ideas about this phenomenon. In the past, this was attributed to a moderate participation of the granulated blastfurnace slag in the hydration process. However, fundamental chemical-mechanical work in the Research Institute of the Cement Industry has produced an entirely different picture.

Granulated blastfurnace slags that contribute to low early strength in building materials bonded with blastfurnace cement tend, in fact, to exhibit a high chemical reactivity. The high reactivity of these blastfurnace slags is expressed in their strong corrosion in an aqueous medium. For strength-promoting hydration of the blastfurnace slag in blastfurnace cements it is not only the extent of the chemical reaction with water that is important, but also the properties of the hydration products that are formed in terms of the mechanical structural stability of the resulting hardened cement paste.

Complex reactions produce different compounds

Some of the different blastfurnace slags used in cement have completely different chemical compositions. During hydration of blastfurnace cement, water penetrates the glass structure of the granulated blastfurnace slag and allows its chemical conversion.

The new compounds that are formed affect the further progress of hydration. For example, aluminosilicates can form, which lie on the blastfurnace slag particles like a protective layer and slow down any further corrosion. If the blastfurnace slag contains only a little aluminium, after various reaction products containing aluminium are formed (such as hydrotalcit-like phases) there may be too little aluminium left to create such a protective film. The result is increased corrosion.

Initially, low-calcium silicate hydrogels form. The amount is determined by the degree of corrosion and the excess silicon that cannot be bound to other constituents of the blastfurnace slag, such as aluminium and calcium.

Table III-3: Chemical composition of blastfurnace cements in different strength classes according to EN 197-1

	CEM III					
Cement type	CEM III/A			CEM III/B		
	min	mean	max	min	mean	max
SiO_2	25.09	27.15	30.04	29.14	30.48	32.44
Al_2O_3	6.68	7.80	9.70	8.58	9.36	10.21
TiO_2	0.35	0.60	1.16	0.45	0.81	1.13
Fe_2O_3	0.69	1.47	2.86	0.44	0.96	1.66
Mn_2O_3	0.07	0.21	0.79	0.12	0.21	0.49
P_2O_5	0.01	0.13	0.35	0.01	0.07	0.21
CaO	47.55	52.48	56.81	42.62	47.45	49.65
MgO	3.04	4.45	7.20	4.33	5.76	9.05
SO_3	1.29	2.67	3.72	0.94	2.23	3.68
K_2O	0.46	0.77	1.10	0.51	0.70	1.25
Na_2O	0.18	0.29	0.54	0.21	0.30	0.38
Na_2O_{eq}	0.52	0.80	1.13	0.55	0.77	1.11
S^{2-}	0.29	0.57	0.97	0.53	0.83	1.06
LOI	0.50	1.70	3.39	0.42	1.19	3.14

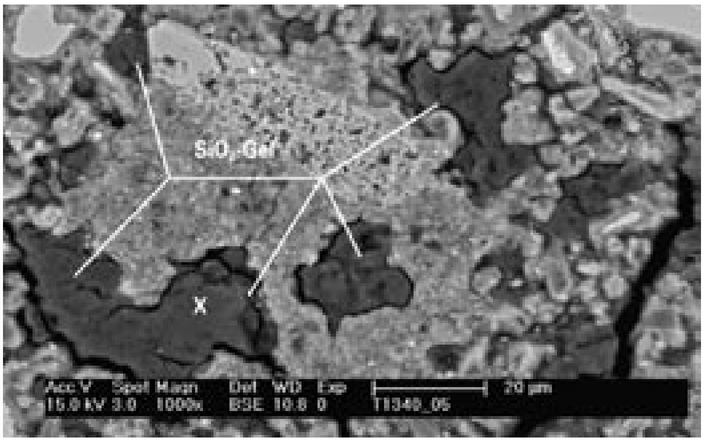


Fig. III-1: REM image of the polished section of a hardened blastfurnace cement paste after 7 days of hydration

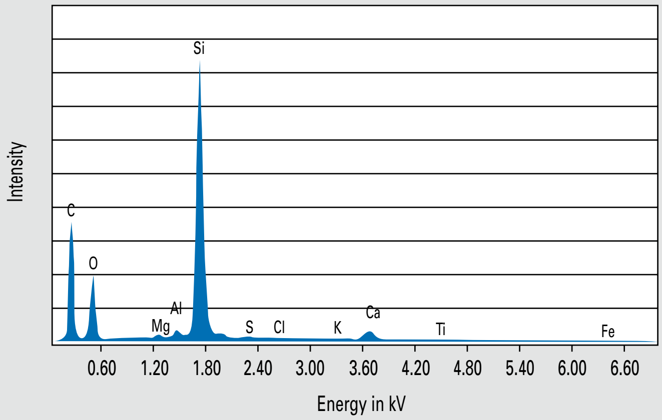


Fig. III-2: Result of the EDX point analysis at the position in Figure III-1 marked with an "X".

Fig. III-1 shows a polished section of a blastfurnace cement that has hydrated for seven days, which exhibited a very low standard mortar compressive strength. In actual fact, on the surface of the section, phases of very pure silicate hydrogel can be seen (**Fig. III-2**), which carry on in-

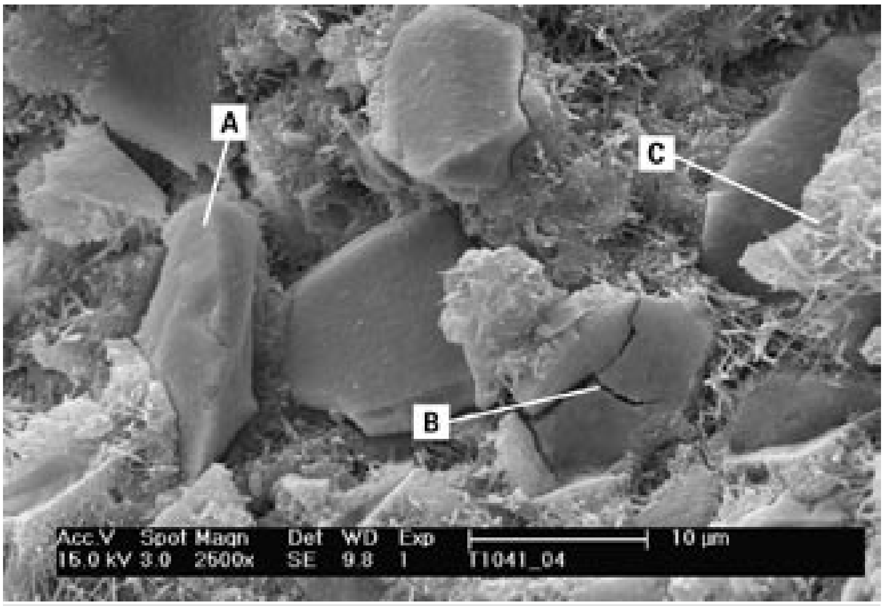


Fig. III-3: REM image of the hardened cement paste fracture of a blastfurnace cement with a weak-performance granulated blastfurnace slag after 7 days of hydration.
A: Non-corroded core of a blastfurnace slag particle with an almost completely detached layer of corrosion products
B: Shell of corrosion products, blastfurnace slag particles completely removed
C: Part of the layer of corrosion products still adhering to the particle core

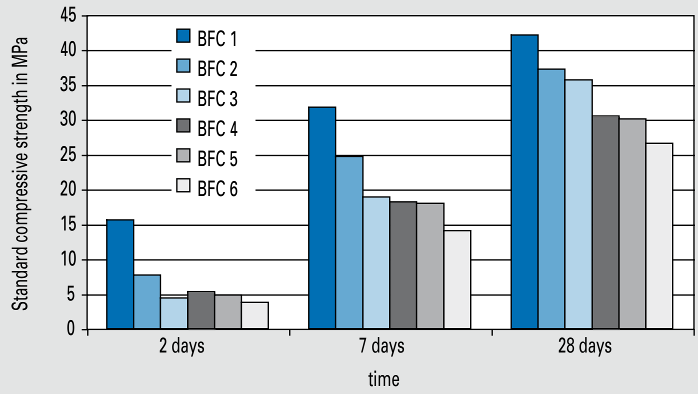


Fig. III-4: Standard mortar compressive strength according to EN 196-10 of blastfurnace cements (BFC) 1, 2, 3, 4, 5 and 6 after 2, 7 and 28 days of hydration

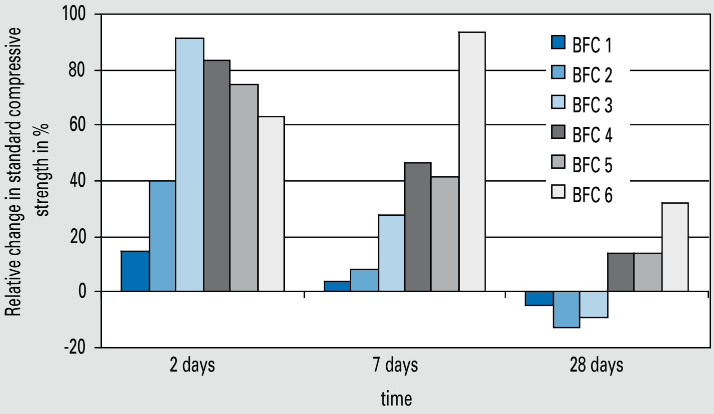


Fig. III-5: Percentage change in standard mortar compressive strength according to EN 196-1 of blastfurnace cements (BFC) 1, 2, 3, 4, 5 and 6 when metakaolin (MK) is added in relation to the standard mortar compressive strengths of blastfurnace cements without the addition of metakaolin after 2, 7 and 28 days of hydration

to the depth of the hardened cement paste microstructure. This silicate hydrogel has also penetrated into the drying cracks of the polished section. It appears to be (at least to start with) a very low viscosity hydrogel that moves and distributes itself readily in the microstructure of the hardened cement paste. However, it is very difficult to prepare sections of hardened blastfurnace cement paste while maintaining the hydrogels that are rich in water for scanning electron microscopic investigations.

Silicate hydrogels are weak structural constituents

According to the latest findings, the silicate hydrogels are plastic formable amorphous masses. The contact zone between the hydrogel and the other products of the earlier hydration reactions and the not yet corroded blastfurnace slag particles is a weak point in the bonding of the microstructure of the hardened cement paste (**Fig. III-3**).

The subsequent mechanical instability is expressed in lower tensile loading strength and inevitably leads to a reduction in the compressive strength of blastfurnace cements. During hydration, the silicate hydrogels are converted into mechanically more stable phases, such as calcium silicate hydrates or simply into gels with less water. This increases the structural stability and the compressive strength. The stability-reducing effect of the high silicate hydrogels is thus limited to early strength. In contrast, the final strength of building materials containing blastfurnace cements often exceeds that of corresponding building materials containing Portland cement.

Reactive aluminates double early strength

Blastfurnace slag particles with a high aluminium content can reduce their corrosion in an aqueous medium by forming protective aluminosilicate layers on the surface. The formation of high silicate hydrogels and their strength-reducing effect is also reduced to the same extent. Therefore, the Research Institute of the Cement Industry examined whether in low aluminium blastfurnace slags early strength could be improved by adding additives rich in aluminium to the respective blastfurnace cements. This was tested on six blastfurnace cements each with 65 mass % blastfurnace slag and different standard mortar compressive strengths. Metakaolin (5 mass %) is the most reactive additive containing aluminium.

Fig. III-4 and **Fig. III-5** illustrate the standard mortar compressive strength of blastfurnace cements with and without additive (metakaolin). It can be seen that the blastfurnace cements without additive, which have a lower early strength, react especially to the addition of the additive (see BFC 2-4). If the granulated blastfurnace slag already contains a high level of aluminium, as expected, the corresponding blastfurnace cement exhibits no efficiently increased early strength when aluminate is added (see BFC 1).

What is noticeable is the relative strength increase in the standard compressive strength of the blastfurnace cement BFC 6 when metakaolin is added after seven and 28 days of hydration respectively (Fig. III-5). The reason for this phenomenon could be the especially strong corrosion tendency of the granulated blastfurnace slag.

Fast corroding blastfurnace slags do not exploit their potential performance in blastfurnace cements in terms of early strength. A transformation of the silicate hydrogel that is formed into bad-bearing, non-plastic phases and thus the development of a higher standard mortar compressive strength takes a relatively long time without the addition of an additive. Calcium dissolved in the pore space can diffuse into the silicate hydrogels and transform them into calcium silicate. However, adding metakaolin can reduce the degree of blastfurnace slag glass corrosion right at the start of hydration. Because of this, fewer hydrogels form. The silicate hydrogels in less plastic, and thus more mechanically stable phases can become coated quicker. Under these conditions the quantity of strength-reducing hydrogels after seven days hydration would be lower than in blastfurnace cement containing no metakaolin. With this mechanistic interpretation approach it is possible to explain the relatively large improvement in standard mortar compressive strength.

Two other aluminates and an inert additive (limestone meal) were tested in blastfurnace cement BFC 3. However, in the series of additive substances that were investigated an increase in early strength was achieved only with the reactive, thermally activated aluminates, such as metakaolin and calcium aluminate cement (**Fig. III- 6**).

The hydrogel hypothesis is based on a reduction in strength that could also be caused by the quantity of hydrogel that forms. In this respect, the silicate excess in blastfurnace slag is especially important.

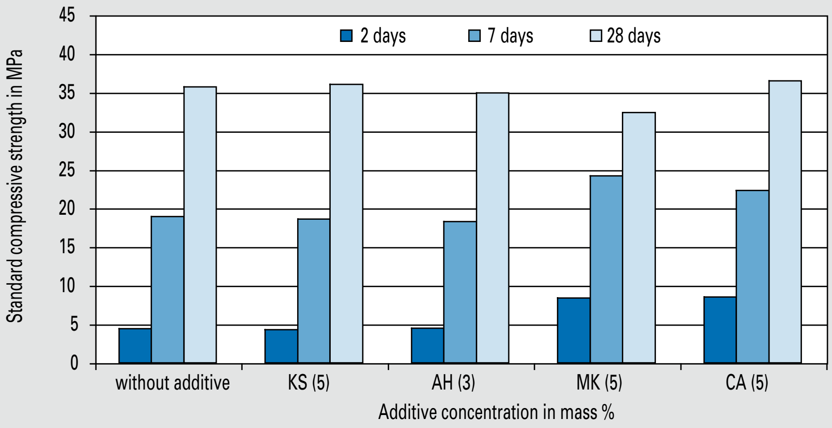


Fig. III-6: Standard mortar compressive strength according to EN 196-1 of blastfurnace cement 3 with and without the addition of the additives limestone meal (KS), aluminium hydroxide (AH), metakaolin (MK), calcium aluminate cement (CA) (figures in brackets refer to the dosing of the additive as a % in relation to the mass of the blastfurnace cement/additive mixture)

However, it appears that the quality or structure of the silicate hydrogels that form are decisive for the standard mortar compressive strength. It seems that the extent of reduction in early strength of blastfurnace cements can also be increased depending on the composition and consistency of the gels.

The chemical composition of granulated blastfurnace slags can at least be used as orientation in the evaluation of blastfurnace slag properties as long as the other impacting parameters (such as glass content and structure, particle size) are also considered.

Using clinker microscopy to solve operational issues ■

Production control in clinker manufacture is usually carried out with the help of chemical analyses and the parameters calculated from these analyses. Since in the industrial production process there are deviations to the thermodynamic equilibriums that are postulated for this, the results of these calculations often do not match the actual composition of the clinker. Because of this, X-ray diffractometric characterisation with Rietveld refinement is carried out to determine the actual phase composition of clinker. However, in many cases even this can also deliver only limited explanations for the deviations from the “target” condition that are observed. For more detailed information a microstructure analysis of the clinker nodules with the help of reflected-light microscopy is necessary.

Possible applications

Clinker microscopy is especially useful in investigations into the effects caused by the use of new raw materials and fuels. Potential effects of changes in the process engineering (e.g. calciner, burner, clinker cooler) or operating parameters (e.g. flame management, material throughput) on the clinker can also be observed well under the microscope. In all cases, comparisons of microstructures before and after the respective changes in production conditions are particularly indicative. Clinker microscopy can also be very useful for clarifying acute problems in the manufacturing process.

Case studies

A number of case studies from a series of clinker investigations conducted throughout the world are presented below, where relatively low alite concentrations were found in the clinker despite raw meal compositions with high lime saturation factors. In some cases the early strength of the cements was much lower than expected. With the help of clinker microscopy it was possible to determine the causes and develop proposals to improve the clinker quality.

Grinding fineness and homogeneity

Inadequate fineness of the raw meal is a common cause of reduced clinker quality. Under normal conditions the chemical components of the raw meal can no longer be adequately converted and this results in

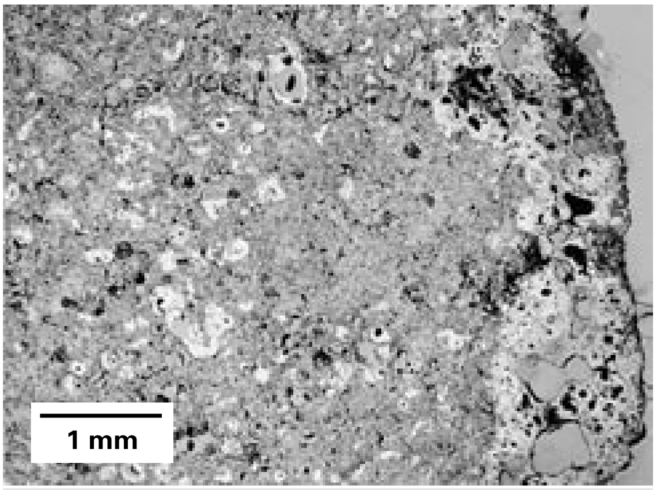


Fig. III-7: Belite crust of a clinker nodule due to accumulated, silicon-rich fuel ash

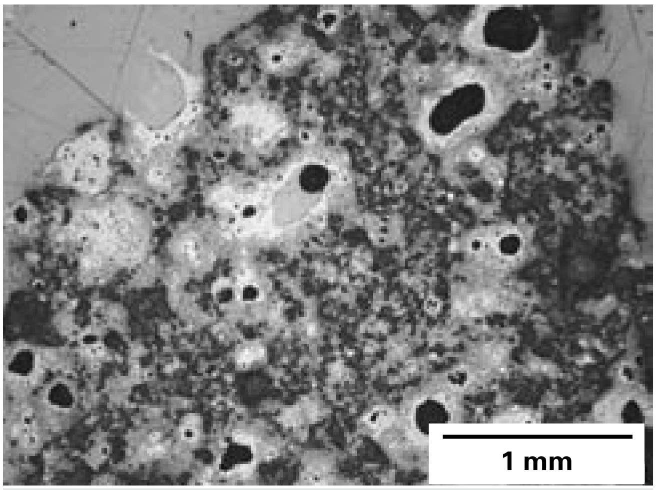


Fig. III-8: Belite clusters (light) and high free lime content (dark) in a clinker nodule caused by insufficient sintering

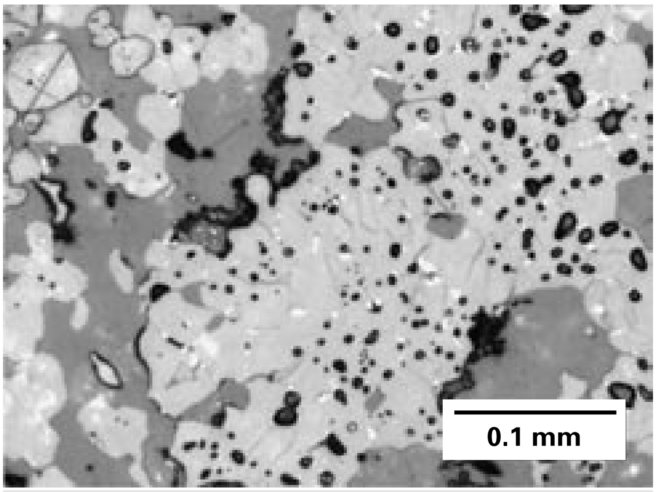


Fig. III-9: Phosphate-rich belite (light grey), interspersed with fine-grained free lime particles (dark)

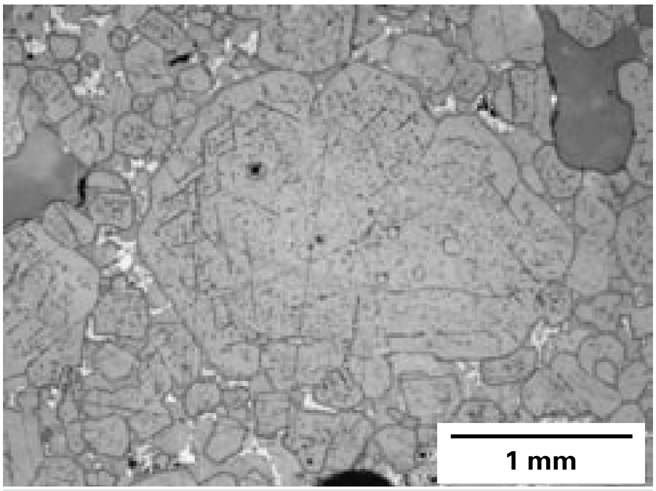


Fig. III-10: Alite crystals with belite/free lime exsolutions along crystallographically preferred orientations as an indication of reducing burning conditions

considerable local deviations from the lime saturation factor. For example, large quartz particles cause the formation of belite clusters, since there is no more CaO in the direct vicinity to convert them into alite. On the other hand, because of the low mobility of CaO under sintering conditions, free lime clusters form from coarse limestone particles. Another potential cause for inhomogeneities are large ash particles that can especially occur with fuels that are difficult to comminute. Like quartz grains, ash grains rich in silica can also cause the formation of belite clusters. If belite clusters are concentrated in the core of the clinker nodules, the cause can generally be found in the raw meal or ash input in the calciner. If the ash particles are input via the main firing system, the clusters are generally to be found in concentric streaks or crusts on the rim of the nodules (**Fig. III-7**).

Residence time at sintering temperature

Reduced formation of alite can also occur when the burning conditions do not allow sufficient sintering of the clinker phases. The causes for such a "poorly burned" clinker should especially be sought in irregularities in flame management. Low sintering temperatures or shortened sintering zones in combination with high kiln throughput can cause the residence time of the kiln charge to be too short, so that the raw materials can no longer react completely. The signs of "poorly burned" clinker are very porous clinker granules in which accumulations of belite and free lime occur directly next to each other (**Fig. III-8**).

Effect of phosphate

When inhomogenously distributed fuels rich in phosphate are used, characteristic belite accumulations containing finely distributed free lime particles can be found (**Fig. III-9**). These are solid solutions of belite containing phosphate that remain stable and do not convert to alite under normal sintering conditions. With coarse grained phosphate carriers, it is even possible that calcium phosphate clusters will form that contain no reactive clinker phases. Effects such as this can also be relevant if the total phosphate content of the clinker is in the uncritical range below 1 mass %.

Reducing burning conditions

Reducing burning conditions – such as due to an insufficient supply of oxygen or smouldering fuel particles in the kiln charge – can cause alite to degrade during the clinker cooling. This effect can be proven clearly with a microscope and in practice can lead to high concentrations of free lime and a marked reduction in cement strength. Even weak reducing conditions can be detected by the first warning signs of fine exsolutions of belite and free lime in alite crystals (**Fig. III-10**). These exsolutions often occur in chains along crystallographically preferred orientations in the alite crystals. Another problem can be that when alite degrades, γ-belite is formed, which has no hydraulic properties.

Formation of coarse nodules

The formation of a large number of coarse clinker nodules, for example because of high chloride or sulphate inputs in the area around the kiln inlet, can cause an overlapping of several disadvantageous effects. For example, poorly burned domains can occur inside the nodules, even if the burning conditions are actually adequate for complete sintering and the nodules appear hard burned on the surface. A dense sinter layer on the surface can enclose alkali chlorides in the core of the nodules. The cooling conditions also differ considerably across the cross-section of the nodules. With clinker microscopy it is possible to investigate such zonary structured clinker nodules very accurately.

Practical benefits

Although as a test procedure the analysis of the microstructure of clinker with optical microscopy is time consuming, it can provide a lot of information that would not otherwise be obtainable alone from integral test methods on representatively prepared samples. The effects of changes of material or process engineering conditions can be described especially well in a before-and-after analysis, which can also provide information about potentially necessaryly corrections. Therefore, if changes are planned in the clinker burning process, at least reference samples of uncomminuted clinker from all relevant operating conditions should be kept so that if changes are noticed in the product it is possible to conduct a proper analysis of the causes.

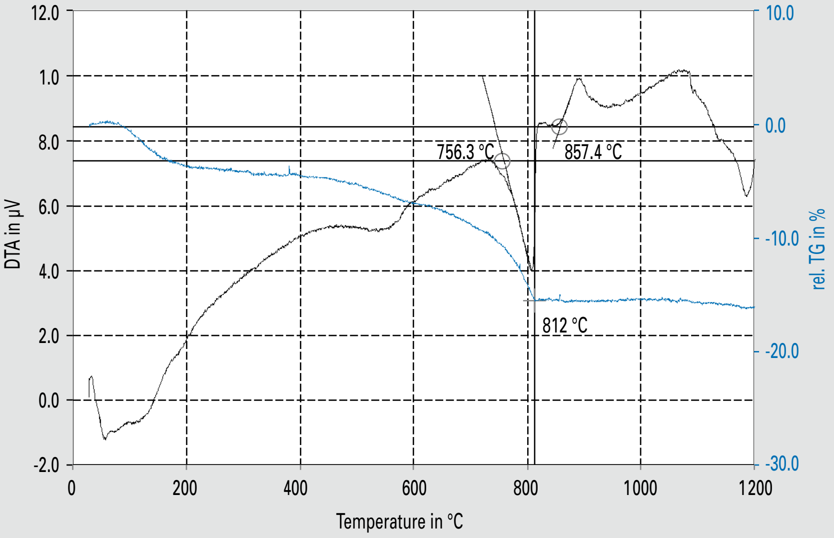


Fig. III-11: STA measurement of the untreated clay sample

Clay as a pozzolanic main constituent of cement ■

These days, clays are used especially as a raw material in the ceramics industry to produce clay bricks and as raw meal components in the cement industry. However, calcined clay may also be used as a main constituent of cement according to DIN EN 197-1 if the content of reactive silicon dioxide is at least 25 mass %. Although suitable raw material deposits are available, calcined clays are used relatively seldom in the manufacture of cement. There are several reasons for this, including:

- Use of other pozzolanic cement main constituents
- Lack of plant technology to handle clays that could be used
- Expenditure to characterise the deposits

Cement manufacturers are trying to reduce the usage of clinker in cement production. Because of this, the use of new main cement constituents is becoming increasingly interesting. In Europe, clays are available in useable quantities and suitable qualities, which makes them perfectly suitable as a natural calcined pozzolana. The quality of suitable clay deposits is in the range between the clays that are used in the ceramics industry and those required for cement raw meals. Therefore, the use of clays as a naturally calcined pozzolana would not collide with other uses.

The pozzolanic activity of calcined clays depends on the type of clay minerals that are available. In this regard, the main factors are their chemical composition and degree of crystallisation. During calcination water is expelled from the clay minerals; this causes them to lose their crystalline structure and they convert to amorphous aluminosilicate phases. As the amorphous character of the dehydrated phases increases, their pozzolanic activity also increases. At high temperatures crystalline phases occur that generally exhibit less pozzolanic reactivity. The optimum firing temperature of a clay is thus between the dehydration temperature of the clay minerals and the start of recrystallisation. Apart from the calcination temperature, the period of calcination is also decisive for the subsequent reactivity of the calcined clays. If the period is too long, this reduces the specific surface area of the calcined particles due to the start of sintering processes. This also reduces their pozzolanic activity.

Description of the project, method and results

In the following example, the firing conditions at which a calcined clay achieves the required 25 mass % of reactive silicon dioxide are to be determined. To do this, a simultaneous thermal analysis (STA)

Table III-4: Firing conditions and results of the determination of the content of reactive silicon dioxide according to DIN EN 197-1

Sample	Firing temperature in °C	Firing time in min.	Reactive silicon dioxide acc. to DIN EN 197-1 in %
1	750	60	21.9
2	810	60	22.6
3	850	60	24.3
4	750	180	20.0
5	810	5	21.2
6	810	30	23.3
7	850	30	24.6
8	1 000	30	29.0
9	600	30	18.3

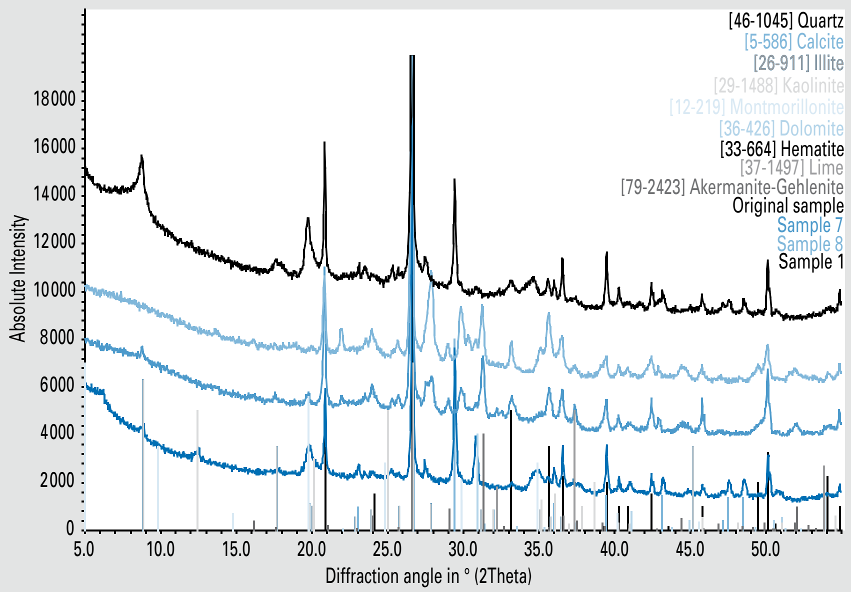


Fig. III-12: X-ray diffractograms of the clay sample in its original condition and of samples 1, 7 and 8

was carried out on the starting material (**Fig. III-11**). The DTA and TG signals show endothermic mass loss at temperatures around 550 °C and 800 °C. These are the dehydration reactions of various clay minerals. Around 900 °C an exothermic signal marks the start of the recrystallisation of new phases. After the STA had been evaluated, the firing temperatures and times for handling the clay samples were defined. The clays were fired accordingly and the reactive silicon dioxide was determined according to DIN EN 197-1. The results are listed in **Table III-4**.

The clays were calcined using about 100 g of the sample; which were tempered in corundum crucibles in a Nabertherm kiln under the defined firing conditions. The samples were then ground finely so that they were suitable for analysis and their phases were investigated by X-ray diffractometry (XRD). **Fig. III-12** shows the results of the X-ray diffractometry investigations on three selected samples compared to the original sample.

The clay sample to be investigated consists of the clay minerals montmorillonite, kaolinite and illite. There are also other mineral phases, such as microcline, quartz and calcite in different quantities. After a one-hour temperature treatment at 750 °C (Sample 1), the start of degradation of the carbonatic phases calcite and dolomite can be recognised in the X-ray diffractogram. The clay minerals also start to degrade. This can be seen by the reduced kaolinite signal. Montmorillonite and illite, on the other hand, are still present after the treatment at 750 °C.

During the investigations it was seen that when the temperature treatment was kept to just thirty minutes this had a positive effect on the reactivity of the sample. Therefore, the other samples were tempered for only 30 minutes. When the temperature was increased from 750 °C to 850 °C, the amorphous content of the samples increased considerably (Sample 7). In addition, as can be seen in the X-ray diffractogram, at this temperature new mineral phases form, such as anorthite, wollastonite, melilite and hematite.

At a temperature of 1 000 °C (Sample 8) the clay minerals completely dehydrated and also formed new phases. However, with 29 mass %, this was the sample with the highest content of reactive silicon dioxide (see Table III-1). Hence, complete dehydration of the clay minerals is decisive for their pozzolanic reactivity. The negative effect of the formation of non-reactive phases seems to be less important here. On the whole, a relatively short treatment (30 minutes) at high temperatures is important for the creation of a high content of reactive silicon dioxide in the sample.

Calcined clays can be used as pozzolanic main cement constituents according to the specifications of DIN EN 197-1. However, the standard demands a content of at least 25 mass % of reactive silicon dioxide in calcined clay. In individual cases, firing conditions (temperature and time) must be coordinated to suit the respective deposit. In this case, after a firing time of 30 minutes at 1 000 °C, the treated product contained 29 mass % of reactive silicon dioxide. To create reactive silicon dioxide it is important that the existing clay minerals are completely destroyed.

Possibilities and limits of Rietveld analysis of cements ■

Quantitative phase analysis of clinker and cement samples using X-ray diffractometry (XRD) and Rietveld refinement is no longer purely a scientific issue; rather, it is commonly used in the works laboratories of the cement industry. The use of modern, increasingly convenient evaluation programs also provides users who are not familiar with the theoretical mineralogical and metrological background with reproducible results. As a general rule, this type of application is fully adequate for use in production control, where the aim is to confirm a constant product property.

Risks of black box systems

However, there are certain risks associated with the use of evaluation programs as black box systems to determine absolute phase proportions. Rietveld refinement is based on the comparison between the measured results and the diffraction diagram calculated from the specified phases. To make this calculation it is necessary to know all the minerals that are contained in the sample. In addition, a large number of metrological parameters and structural parameters of the phases are mathematically included in the refinement. Depending on the choice of these variable parameters, their permitted variation bandwidth and their starting values, it is possible to obtain results that deviate considerably from each other although the quality of the refinement seems to be the same. Careful pre-adjustment of the starting parameters attuned to the measurement task and critical evaluation of the results are just as vital as identifying all the mineral phases in the sample. This is the only way to obtain a satisfactory analysis of the phase composition of a complex mixture, such as clinker or cement.

Series of experiments with defined mixtures

In a series of experiments carried out at the Research Institute of the Cement Industry, the effects that pre-adjusting the structural parameters of cement phases have on their quantitative determination using Rietveld refinement were analysed. For this purpose four laboratory cements were produced as mixtures of separtly burned clinker phases with sulphate agents. The purity of all the raw materials was determined with XRD; this was reproducible due to the mainly mono-mineral samples.

Table III-5 presents a comparison of the evaluation results with the actual mixture ratios. One particular problem was the use of precipitated calcium sulphate as the sulphate agent phase “gypsum” or in a partially dehydrated form as “hemihydrate”. It seems that the extreme fine granularity of these components causes preparation-related accumulation on the surface of the sample, so that with practical physico-mineralogical structural parameters there is always an over-determination of gypsum and hemihydrate. Therefore, the comparative values in Table III-5 are calculated regarding the actual values for gypsum and hemihydrate.

Table III-5: Comparison of the actual phase content of four laboratory cements and the phase content determined with XRD and Rietveld refinement (figures in mass %)

Phase	Cement 1		Cement 2		Cement 3		Cement 4	
	Target	XRD	Target	XRD	Target	XRD	Target	XRD
Alite	59.3	59.1	57.4	57.5	60.5	58.4	61.8	60.1
Belite 1)	18.1	18.6	17.5	16.1	9.1	7.8	9.3	9.2
Aluminate	9.0	8.1	8.7	9.2	2.8	2.3	2.8	2.3
C_3A_{cub}	8.2	7.6	8.0	8.5	2.6	2.3	2.6	2.3
C_3A_{orth}	0.8	0.5	0.7	0.7	0.2	0	0.2	0
Ferrite	5.2	6.5	5.1	5.7	15.5	17.4	15.9	17.5
Free lime	0.5	0.4	0.5	0.4	0.2	0.3	0.2	0.2
Periclase	1.2	1.0	1.1	0.8	1.2	1.1	1.2	1.5
Anhydrite	3.0	3.9	2.4	3.3	6.0	7.4	2.7	3.1
Hemihydrate 2)	2.0		4.0		4.0		2.7	
Gypsum 2)	–		1.6		–		2.7	

1) Including bredigite

2) Over-determination, thus target values used for evaluation

The results show that the contents of alite, belite and, in clinkers rich in iron, ferrite can be determined with an accuracy of approximately ± 2 mass % and aluminate and anhydrite with about ± 1 mass % accuracy. Minor constituents, such as free lime and periclase, exhibit deviations of maximum 0.5 mass %, which could, however, signify a high relative error due to the low contents of the minerals.

Selective dissolution of the silicate phases using methanol-salicylic acid is a suitable method for a better differentiation of the C_3A modifications and to determine the trace constituents. The aluminates, ferrite and, for example, sulphate phases accumulate in the insoluble residue; there are also no peak overlaps with alite and belite. In this case the quantity ratio of the two aluminate modifications was specified and the periclase content was confirmed.

Recommendations

From the results of the investigations it is possible to derive a number of recommendations for adjusting the structural parameters for Rietveld refinement:

- The lattice parameters of all minor constituents, including the sulphate agent phases, should be fixed.
- The lattice parameters of the orthorhombic C_3A should be fixed; the ratio of the aluminate modifications should be compared with the MS decomposition.
- The crystallite size of the minor phases should not be too small nor should the half-widths be too big, as otherwise the peaks overlap with the background and over-determinations can occur. The starting value should be in the top half of the permitted variation bandwidth.
- In the case of gypsum the (010) texture must always be considered; values below 0.7 are not uncommon. With synthetically produced gypsum other textures can occur, for example as a result of a needle-like crystal habit.
- Texture effects are also possible with calcite (104), anhydrite (100 or 010), alite (10-1), in which case the starting value should be set to 1 („no texture“).

While the consideration of these rules of thumb without a critical inspection of the results of the refinement will not guarantee error free analysis, it will considerably limit the bandwidth of possible results. The results for the phase content often output by the evaluation software with several decimal points imply an accuracy that actually is not achieved. Even if the result is specified to just one decimal point, this does not necessarily reflect the actual phase composition.

Round robin test for radiographic quantification of blastfurnace slag in cement

X-ray powder diffractometry is not only suitable for the identification and quantitative determination of crystalline phases. Amorphous constituents, such as blastfurnace slag in cement, can also be quantified under certain conditions. This provides an alternative method to the current procedures for determining blastfurnace slag. To investigate the capability of X-ray diffractometry in this area, VDZ organised a comparative test for X-ray diffractometric determination of the content of blastfurnace slag.

In the works' own production control departments, calculation of the blastfurnace slag content in cements based on an analysis of lead compounds in the raw materials and in the cement sample is widespread. In third-party inspections, the selective dissolution process is mainly used as the reference method. The microscopical counting method with chemical correction calculations is another option.

But interest in X-ray diffractometry to quantify the proportion of blastfurnace slag is also attracting more and more attention because reliable results are provided with relatively little expenditure. Basically, two X-ray diffractometry methods can be considered; these were used within the comparative test.

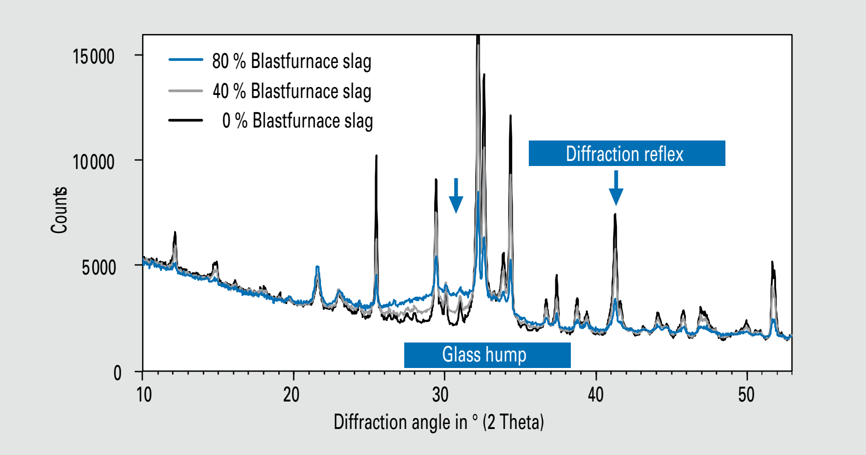


Fig. III-13: X-ray diffraction diagram of cements with different contents of blastfurnace slag and the associated form of the glass hump

Determining the background

Blastfurnace slag has a glass-like, mainly X-ray amorphous structure. In the X-ray diffraction diagram it causes a hump-like increase in the background pattern in the angle range between 22 and 38° (2 theta). The height of this glass hump corresponds to the content of blastfurnace slag (**Fig. III-13**). To determine this, it is possible to calibrate and evaluate either the absolute X-ray intensity at a reflection-free diffraction angle or the integral background intensity across the entire hump-like area. The latter method depends very much on the definition of the device-related background line in this diffraction range which is independent of the glass content. Therefore, in the comparative test the method chosen to quantify the blastfurnace slag content was the absolute X-ray intensity at the diffraction angle 30.5° (2 theta).

Rietveld analysis with spike

The second method of radiographic quantification of the blastfurnace slag content is based on the use of a crystalline inner standard (spike). The subsequent Rietveld evaluation of the measurement determines the content of all crystalline phases in the sample and normalises these to a value of 100 mass %. The non-crystalline content of the sample can then be calculated from the ratio between the spiked and the determined contents of the inner standard.

The 14 participants in the round robin test were provided with two industrially manufactured blastfurnace cements and a Port-

Table III-6: Results of the round robin test for X-ray diffractometric determination of the content of blastfurnace slag (figures in mass %)

Material	Investigated feature	Average	Comparison standard deviation	Repeatability standard deviation	Reference method or mixed value
Portland-slag cement	X-ray diffraction/ background	24.61	1.91	1.49	25.15/25.00
	X-ray diffraction/ spike	23.84	1.13	1.9	
	Other	24.49	2.18	0.22	
Blastfurnace cement 1	X-ray diffraction/ background	69.24	2.35	1.06	67.01
	X-ray diffraction/ spike	67.21	1.4	1.26	
	Other	69.33	2.13	0.19	
Blastfurnace cement 2	X-ray diffraction/ background	74.26	4.15	0.99	72.03
	X-ray diffraction/ spike	72.32	1.01	0.74	
	Other	72.28	1.71	0.49	

Table III-7: Chemical composition (including loss on ignition) of the starting constituents Portland cements (Z) and blastfurnace slags (BFS) including phase calculation according to Bogue (loss-on-ignition-free), all figures in mass %

	Z1	Z2	BFS A	BFS B	BFS C	BFS D	BFS E	BFS F
LOI	2.96	0.70	0.94	0.41	1.31	0.36	0.64	1.51
SiO_2	18.97	21.51	30.25	36.02	34.69	36.10	38.91	35.12
Al_2O_3	5.36	4.68	15.96	11.36	11.70	12.97	9.54	11.94
TiO_2	0.27	0.25	1.13	0.47	0.89	0.63	0.96	0.73
P_2O_5	0.22	0.07	0.07	0.01	0.01	0.01	0.06	0.01
Fe_2O_3	3.87	2.52	0.66	0.35	0.42	0.25	0.54	0.91
Mn_2O_3	0.10	0.03	0.39	0.48	0.33	0.31	1.18	0.34
MgO	1.80	1.83	10.00	9.36	6.80	10.30	8.45	6.98
CaO	61.80	63.93	38.68	40.28	42.30	37.54	37.57	41.28
Sulphate as SO_3	2.92	3.30	0.65	0.15	0.25	0.02	0.04	0.01
K_2O	1.59	0.97	0.39	0.38	0.47	0.71	1.24	0.38
Na_2O	0.19	0.21	0.39	0.27	0.27	0.26	0.36	0.27
Na_2O_{eq}	1.24	0.85	0.65	0.52	0.57	0.73	1.18	0.52
O_{2eq}	0.00	0.00	-0.48	-0.47	-0.59	-0.53	-0.50	-0.51
S^{2-}	–	–	0.96	0.94	1.18	1.07	1.00	1.02
C_3S	67.88	62.17	–	–	–	–	–	–
C_2S	4.84	15.20	–	–	–	–	–	–
C_3A	7.89	8.20	–	–	–	–	–	–
C_4AF	12.14	7.72	–	–	–	–	–	–

land-slag cement mixed in the laboratory for analysis. Apart from X-ray diffractometry, in individual cases the selective dissolution method and other alternative solutions were used for comparison.

The results of the round robin test are listed in **Table III-6**. Both reproducibility within any one laboratory and the comparability between different laboratories are in no way inferior to the precision of previously established methods. They are within standard specifications.

However, the individual results also confirmed that adequate reliability of the different X-ray diffractometric approaches depends on specific conditions. For instance, to evaluate the background intensity it is necessary to have calibration samples whose components must correspond to those in the sample to be investigated. This requires works-specific calibration. Thus, the method is especially suitable for the works' own production control. When the Rietveld method with the inner standard is used, it became clear that an additional calibration step was necessary to describe the effect of the substance that is used as a spike. In principle the evaluations from this method could also be used for different works.

Sulphate resistance of cements containing blastfurnace slag ■

According to the respective standard, blastfurnace cements with at least 66 mass % of blastfurnace slag are regarded as cements with a high sulphate resistance. However, the fact that lower contents of blastfurnace slag are also suitable for a high sulphate resistance has also been seen in the first building supervisory authority approvals of CEM III/A cements as SR cement in Germany. The regulations in several other European countries also include CEM III/A and even CEM II/B-S as cements with a high sulphate resistance. The relevant literature contains various descriptions of the mechanism that leads to increased sulphate resistance of concrete or mortar based on blastfurnace cement. In some cases, chemical aspects and in others physical aspects are said to be primarily responsible. In general, however, the increase in the physical diffusion resistance of the hardened cement paste is deemed to be the main cause of higher sulphate resistance.

The chemical-mineralogical effect of the composition of blastfurnace slag on sulphate resistance was investigated in a research project funded from the German Federal Ministry's budget via the German Federation of Industrial Research Associations (AiF) "Otto von Guericke". The aim was to determine the importance of the chemical composition of blastfurnace slag on sulphate resistance through systematic investigations of various blastfurnace slags with consideration of different physical parameters and influences. Also investigated was whether and under which conditions cements containing blastfurnace slag of less than 66 mass % could fulfil the criteria for high sulphate resistance.

Cements containing blastfurnace slag with 30, 50 and 70 mass % were manufactured on the basis of two different Portland cement clinkers and five blastfurnace slags (A, B, D, E, F). The sulphate content of the cements was adjusted uniformly to 3 mass % with a sulphate agent mixture of 50 mass % hemidydrate and 50 mass % anhydrite. The two Portland cement clinkers (Z1 and Z2) both had a C_3A content of about 8 mass % and differed mainly as regards their alkali content, with 1.24 and 0.85 mass % Na_2O equivalent. The five blastfurnace slags represent the quality bandwidth of blastfurnace slags generally manufactured in Germany and essentially differed in terms of the content of aluminium oxide and magnesium oxide (**Table III-7**).

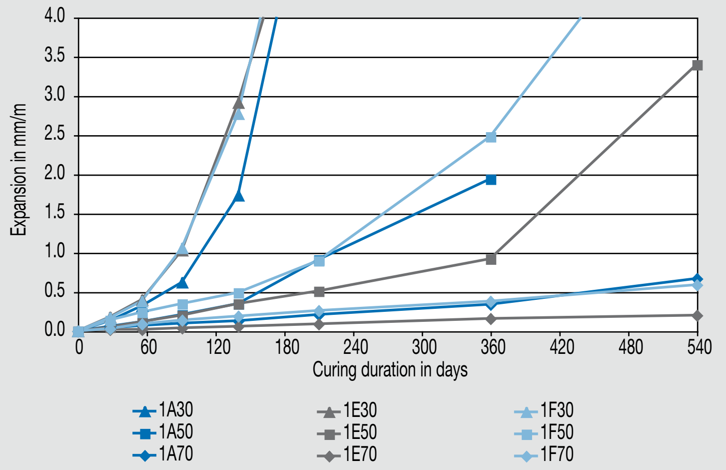


Fig. III-14: Relative length changes of mortar flat prisms when cured in sodium sulphate solution (29800 mg sulphate/l) at 8 °C

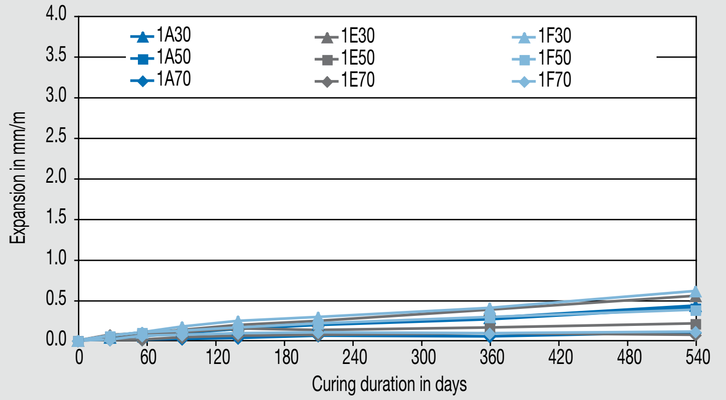


Fig. III-15: Relative length changes of mortar flat prisms when cured in sodium sulphate solution (3000 mg sulphate/l) at 8 °C

Table III-8: Compressive strength after 14 days pre-curing (before the start of sulphate curing)

Blastfurnace slag	A	F	E
70 mass % BFS	44.4 MPa	35.0 MPa	27.3 MPa
50 mass % BFS	48.5 MPa	41.2 MPa	32.0 MPa
30 mass % BFS	48.5 MPa	45.6 MPa	40.3 MPa

To test the sulphate resistance in accordance with the SVA rapid test methods, flat mortar prisms with the dimensions 1 x 4 x 16 cm³ and a water/cement ratio of 0.50 were produced. The method was developed by the committee of experts (SVA) for the approval of cements with high sulphate resistance. In this case, flat prisms with a water/cement ratio of 0.70 were also included in the programme to take account of higher capillary porosity and lower diffusion resistance. The mortar prisms were kept for two days in a wet room in their moulds before being pre-cured for another twelve days at 20 °C in a saturated calcium hydroxide solution. Parallel to this, standard prisms with the dimensions 4 x 4 x 16 cm³ were produced and pre-cured in the same manner.

The test samples were cured in a sodium sulphate solution (test solution) and also in a calcium hydroxide solution (reference solution). Concretes in foundations are usually subjected to similar soil temperatures. The formation of thaumasite is also thermodynamically facilitated in the presence of carbonate/CO_2. Supplementary experiments were carried out at 20 °C. Two test solutions were used, a 4.4 % sodium sulphate solution (29800 mg sulphate/l) according to the established test procedures of the SVA and the previously used test method according to Wittekindt, and a practice-related 0.44 % sodium sulphate solution (3000 mg sulphate/l, maximum concentration in exposure class XA2).

Results

According to the SVA method, for a cement with high sulphate resistance the expansion of the flat prisms must not exceed 0.5 mm/m within 91 days. As expected, this criterion was fulfilled by the cements containing 70 mass % blastfurnace slag. However, even in the cements with 50 mass % blastfurnace slag expansion still remained below this limit value. In this project only the cements with 30 and 40 mass % blastfurnace slag failed the criterion, as expected. When the test period was extended, the number of cements whose test samples exhibited greater expansion than 0.5 mm/m increased. After 360 days, only cements with 70 mass % blastfurnace slag remained below the expansion limit value (**Fig. III-14**).

Besides this expected mass dependency it was also discovered that there was a dependency on the blastfurnace slag itself. When blastfurnace slags A and F were used, the test mortars not only expanded more, they also disintegrated. On the other hand, with blastfurnace slag E, it was only the sample with 30 mass % blastfurnace slag that expanded more (26 mm/m after 540 days); but it did not disintegrate. In the test with a practice-related sulphate concentration, none of the test samples expanded strongly. Even the flat prisms based on cements with just 30 mass % blastfurnace slag expanded by about 0.5 mm/m after 540 days (**Fig. III-15**).

According to the development in compressive strength (**Table III-8**), blastfurnace slag A is the most reactive blastfurnace slag. It also exhibited the lowest sulphate resistance potential. According to common knowledge, the hardened cement paste structure containing blastfurnace slag A should have exhibited a lower diffusion resistance to sulphate than the structure with blastfurnace slag F and, in turn, this should have had a lower resistance than the structure with blastfurnace slag E. But the results of the porosity tests do not confirm this behaviour. More porosity was linked to a higher blastfurnace slag content and blastfurnace slag E had a larger pore volume than blastfurnace slags F and A, particularly in the capillary pore area (**Fig. III-16**). This is surprising since capillary porosity is especially important for transport and diffusion processes. A more diffusion resistant structure should exhibit lower capillary and higher gel porosity and thus have a higher resistance to sulphate. But this connection could not be determined. This was also seen in scanning electron microscopic analyses of the structures. The penetration depth of sulphate in the samples measured by EDS was very similar for all blastfurnace slags.

Conclusions

In line with practical building experience, all cements with a blastfurnace slag content of 70 mass % (CEM III/B) exhibited a high sulphate resistance, with no indication that the composition of the blastfurnace slags had any noticeable influence. In contrast to this, in some cases the chemical composition of the blastfurnace slag had quite a considerable effect on sulphate resistance in cements with 50 mass % blastfurnace slag (CEM III/A) and 30 mass % (CEM II/B-S). For “less suitable” blastfurnace slags such a low blastfurnace slag content is not sufficient to obtain a sulphate resistant mortar under all test conditions. However, the mortar samples based on “the most suitable” blastfurnace slag exhibited a high sulphate resistance under all test conditions. Accordingly, sulphate resistance highly depends on the “silicon excess” (in relation to aluminium and calcium) of the blastfurnace slag. Cements with low aluminium and silicon-rich blastfurnace slags seem to be most suitable for producing cements with SR properties (**Fig. III-17**). In contrast, the opposite composition appears to be best for strength development.

Damage in the form of expansion phenomena and loss of structural cohesion were observed only when test solutions with a high sulphate concentration of about 30g/l were used; however, this is not used in practice. Secondary gypsum forms in the structure of the samples, which causes damage. Based on the tests with lower sulphate concentrations in the test solutions, however, it was not possible to differentiate between the blastfurnace slags. The samples of all test cements remained intact and exhibited only low expansion. Therefore, the importance of the test conditions for the results and the conclusion must still be clarified.

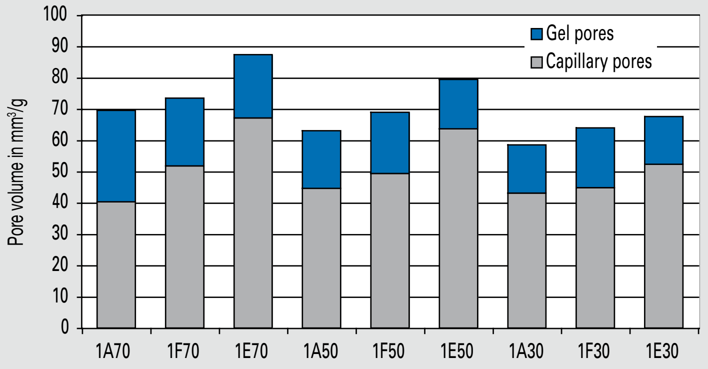


Fig. III-16: Porosity after 14 days pre-curing at 20 °C

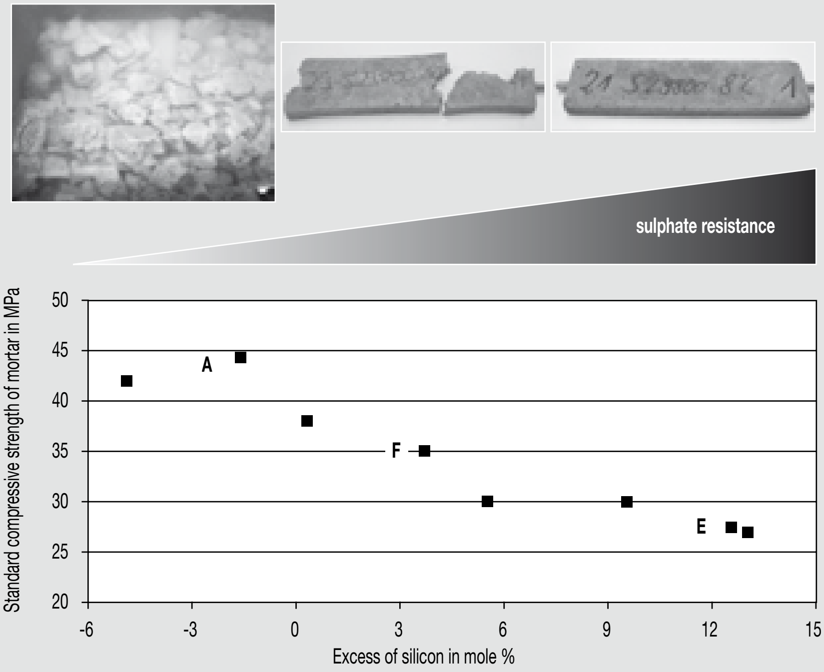


Fig. III-17: Connection between an excess of silicon and the standard compressive strength or sulphate resistance behaviour respectively

Effect of fly ash on the pore solution of concrete ■

The use of fly ash in concrete can reduce the risk of a damaging alkali-silica reaction. This is generally attributed to the fact that the products of the pozzolanic reaction of fly ash can bind alkalis from the pore solution chemico-mineralogically. The strength of this ability depends on several factors. This can lead to a situation where the effect of the fly ash on the alkalinity of the pore solution, and thus on the damaging alkali silica reaction (ASR), cannot be directly compared for different storage conditions. However, knowledge of these interrelations is necessary to assess the use of fly ash to prevent a damaging ASR. In addition, on this basis it is possible to assess the extent to which laboratory experiments on concrete stored at higher temperatures can be transferred to practical conditions.

In a project funded by the VGB Research Foundation and performed in the Research Institute of the Cement Industry, it was investigated how the temperature and

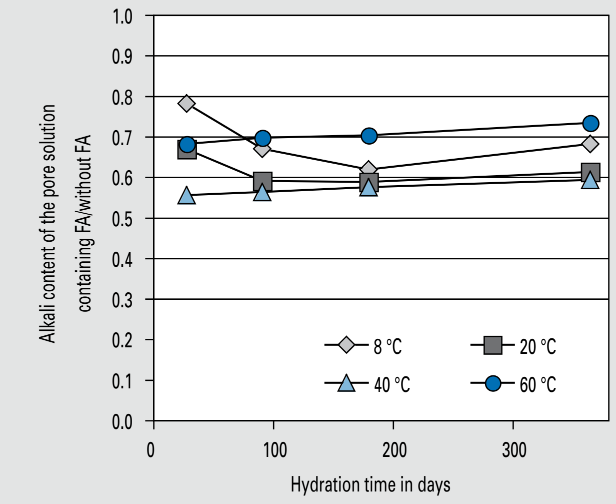


Fig. III-18: Alkali content of the pore solutions of hardened cement pastes containing fly ash after up to 365 days hydration in relation to the alkali content in hardened cement pastes containing no fly ash

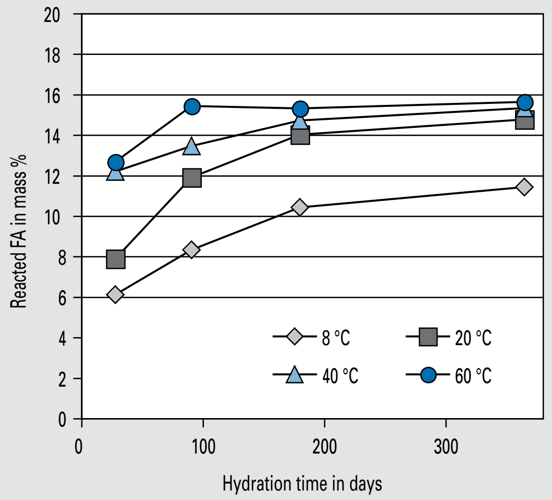


Fig. III-19: Quantity of reacted fly ash after up to 365 days hydration in mass % in relation to the cement

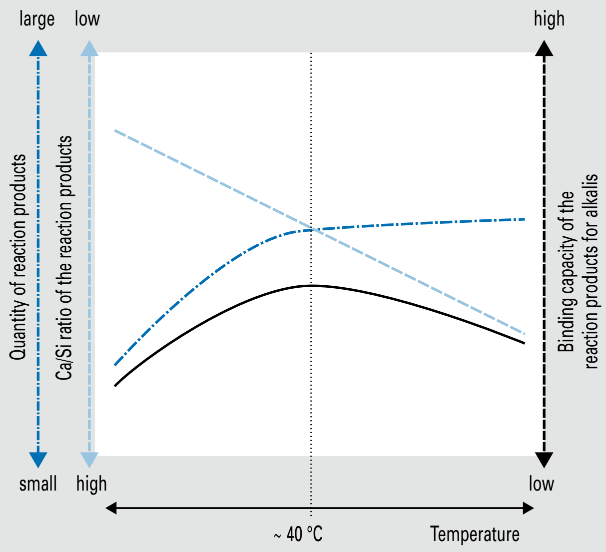


Fig. III-20: Factors influencing the alkali binding capacity of reaction products of fly ash in hardened cement pastes containing fly ash

availability of calcium affect the binding of alkalis. Hardened cement pastes were produced from mixtures of three Portland cements (CEM I 32,5 R) with different alkali contents (0.8 to 1.2 mass % Na_2O_{eq}) and three different hard coal fly ashes. The mixtures contained 30 mass % fly ash. $Ca(OH)_2$ was added to some of the mixtures to increase the availability of calcium for the pozzolanic reaction.

At specified testing times the pore solution was pressed out of the hardened cement pastes and was examined for pH-value and alkali content. From the hardened cement pastes themselves, the contents of $Ca(OH)_2$ consumed by the pozzolanic reaction and of reacted fly ash were determined by thermogravimetric analysis (TGA) and selective dissolution, respectively. This allowed the average composition of the reaction products and the degree of reaction of the respective fly ashes to be calculated. These variables were correlated with the composition of the pore solution.

Binding of alkalis in hardened cement pastes containing fly ash

In all the mixtures that were investigated the fly ash led to a reduction in total alkali contents and hydroxide ion concentrations in the pore solutions (**Fig. III-18**). In most cases the reaction products of the fly ashes actively bound alkalis that were released from the Portland cements and thus reduced the effective alkali content of the cements. During the one-year test period no subsequent increase in total alkali content was determined.

Influence of temperature on the degree of reaction of the fly ash

An important factor for the binding capacity of alkalis in hardened cement pastes containing fly ash is the degree of reaction of the fly ash. As the quantity of reaction products increases, the quantity of alkalis that can be bound by them also increases. The degree of reaction of fly ash is mainly controlled by the temperature. The results of the investigation show that the fly ash reacts quicker at high temperatures and that the total amount of reacted fly ash is higher than at low temperatures (**Fig. III-19**). However, in the samples stored at 40 and 60 °C there is little difference between the quantities of reacted fly ash.

Composition and binding capacity of the reaction products – the role of calcium

It was proven that the amount of calcium in the reaction products of fly ash had an effect on their alkali binding capacity. The higher the average Ca/Si ratio of the reaction products, the less alkali they can absorb.

The Ca/Si ratio of the reaction products depends on several factors. Firstly, in samples that were hydrated for longer periods, higher Ca/Si ratios were determined than in samples with the same composition that were stored for a shorter time at the same temperature. Secondly, in samples that are of the same age and have the same composition, the Ca/Si ratio of the reaction products increases along with the storage temperature. As opposed to the proportion of reacted fly ash, in this case considerable differences are noticeable in the samples that were stored at 40 and 60 °C. Thirdly, the Ca/Si ratio of the reaction products is dependent on the availability of Ca. In samples with the same cements and fly ashes which were stored for the same length of time at the same temperature, the Ca/Si ratio of the reaction products in samples with primarily added $Ca(OH)_2$ is higher than in samples without the addition of primary $Ca(OH)_2$, although in the latter case considerable quantities of $Ca(OH)_2$ from the hydration of the Portland cement were found.

Interaction between the quantity and the composition of the reaction products

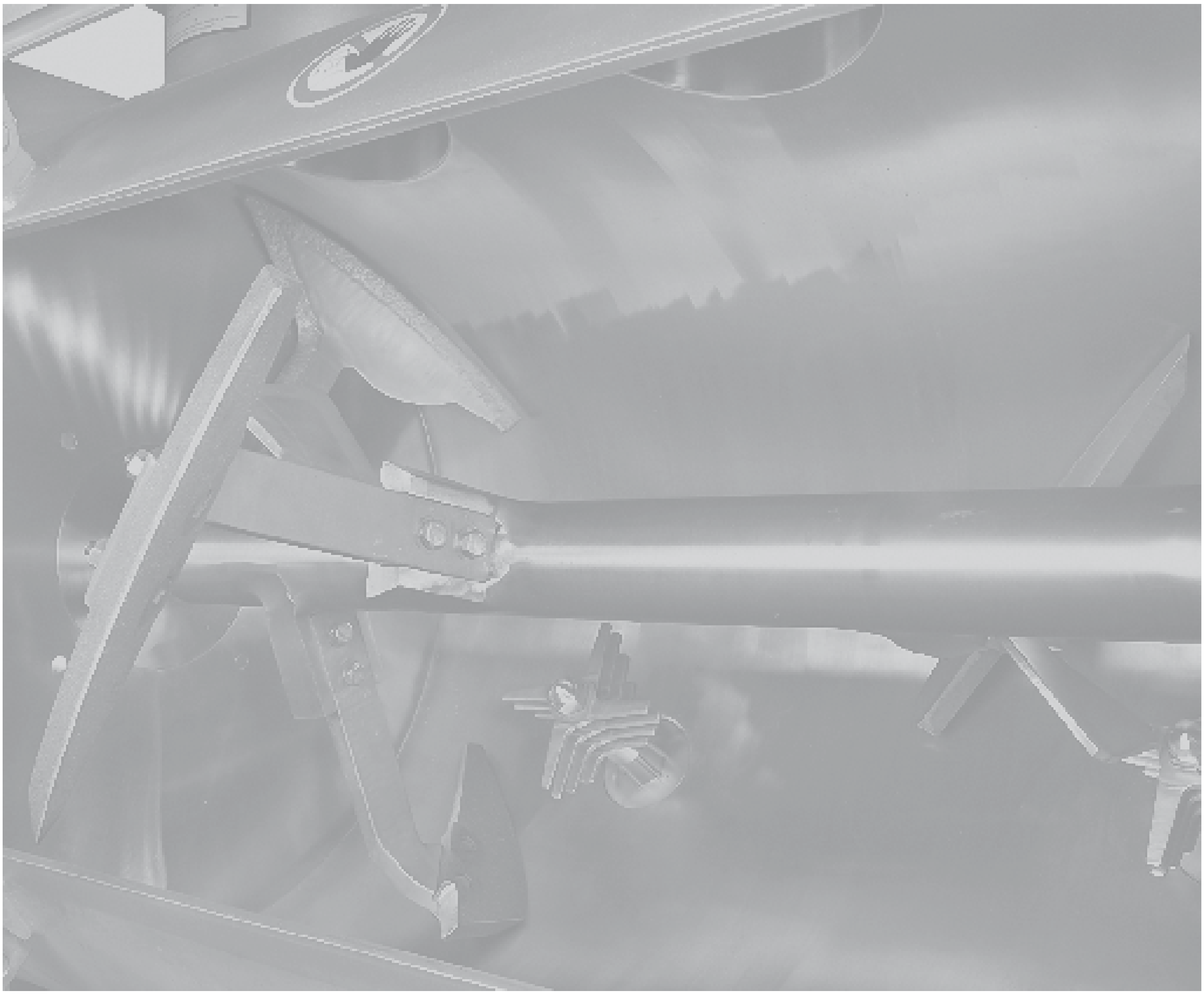
The temperature has a significant effect on two opposing factors that determine the total binding capacity of alkalis in hardened cement pastes containing fly ash; namely the total quantity of reaction products and their Ca/Si ratio (**Fig. III-20**).

In the mixtures that were investigated the alkali ion concentrations of the pore solutions were generally at their lowest at 40 °C. At lower temperatures the quantity of reaction products from the fly ash is much lower. At higher temperatures it hardly increases at all, while the Ca/Si ratio in the products increases further, causing the overall binding capacity to decrease.

Within the research project it was confirmed that the reaction products of fly ash actively bind alkalis from the pore solution. The total capacity to bind alkalis is determined by the total quantity of reaction products and also by their composition. Both factors are, however, dependent on temperature. At about 40 °C the alkali content of the pore solutions in the hardened cement pastes containing fly ash was much lower than in hardened cement pastes containing no fly ash.

IV

Quality surveillance and quality assurance of cement



Inside view of a ploughshare mixer for the production of binders in a cement factory

VDZ's quality surveillance organisation ■

VDZ's functions include testing, inspection and certification of cements and cement-type binders to meet the protective goals set by the state building regulations, the Construction Products Directive and their implementation in national law and also in terms of the Construction Products Law. For this purpose, the association operates the quality surveillance organisation as a testing laboratory, inspection body and certification body (PÜZ body). The associated inspection and test activities are carried out in the Research Institute of the Cement Industry's Quality Assurance Department. The technical committee of the VDZ's quality surveillance organisation discusses the results of third-party inspections twice a year.

Before the introduction of the European cement standard in 2000, cement and other hydraulic binders were covered solely by national standards and regulations. Compliance with the requirements was indicated by national compliance marks. In Germany, the "Ü" mark was awarded in this respect.

These days, almost all binders carry the CE mark (**Fig. IV-1**). In particular, this includes all common cements, CEM, including the additional property low heat of hydration, and all masonry cements, MC. Cements with a high sulphate resistance and low effective alkali content fulfil the requirements for common cement and in Germany are covered by the national standard DIN 1164-10. As explained in the sub-section "Standardisation", great progress has been made in terms of a harmonised European regulation, at least for cements with a high sulphate resistance. European definitions are currently being drafted for road binders. Cement and binders covered by European harmonised standards carry the CE mark as a "technical passport" and a market access sign and can be traded freely in all countries in the European Economic Area.

Approval and accreditation

The VDZ's quality surveillance organisation works in the legally regulated area as a testing laboratory, inspection and certification body. On the one hand, approval covers the state building regulations (LBO), which are applicable at national level, where conformity is indicated by the national Ü mark. Moreover, the VDZ's quality surveillance organisation is notified according to the German Construction

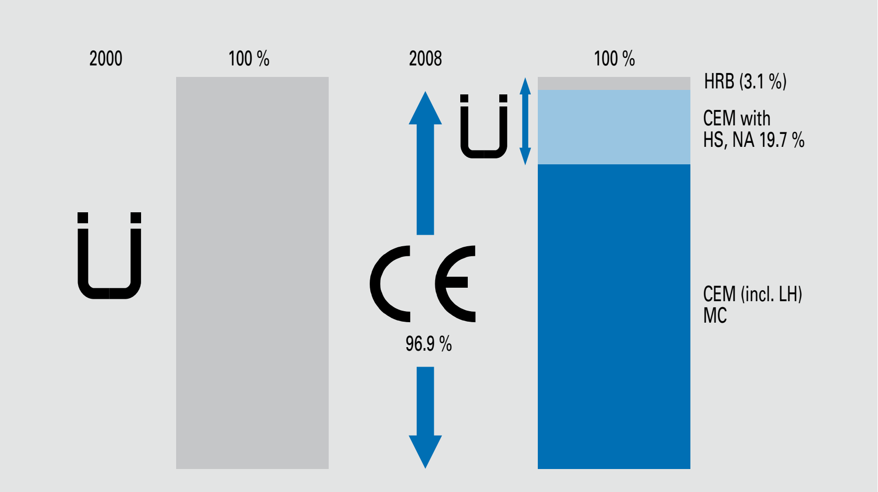


Fig. IV-1: Comparison of the certification of domestic hydraulic binders in 2000 and 2008

Table IV-1: Approval areas of VDZ's quality surveillance organisation as a testing laboratory, inspection and certification body for construction products

Construction products	Technical regulation(s)	Conformity attestation level	
		BPG	LBO
Binders			
Common cement	EN 197-1	1 +	
Cement with special properties	EN 197-4	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) 1)
Building lime	EN 459-1	2	
Other cement-type binders (incl. sprayed concrete cements)	Approval 2)		ÜZ
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 2)		ÜZ
Concrete admixtures			
	EN 934-2, -3, -4	2 +	
	DIN V 18998		ÜHP
	Approval 2)		ÜZ
Aggregates			
	EN 12620	2 +	
	EN 13055-1	2 +	
	EN 13139	2 +	
Masonry mortar			
	EN 998-2	2 +	
Grout			
	EN 447		

BPG: Construction Products Law
LBO: State building regulations
ÜZ: Conformity certificate from approved certification body
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 ÜZ

2) If the production process, the composition or the properties deviate substantially from the standard

Table IV-2: Overview of the cements and hydraulic binders inspected and certified by VDZ's quality surveillance organisation in 2008

Binder	Standard/Regulation	Scope	Type of certification	Certification body	Inspection body	Number of binders	Number of works
Cement	EN 197-1	EU	legal	VDZ	VDZ	550 [1]	58
	DIN 1164	Germany					
	Approval	Germany					
	DIN 1164	Germany			other	1	1
	TL Beton-StB	Germany		–	VDZ	54	27
	BRL 2601, NEN 3550	Netherlands	private	bmc	VDZ	111	27
	TRA 600, PTV 603, NBN B 12	Belgium		VDZ	VDZ	41	16
	Reglement NF	France		AFNOR	VDZ	36	11
	DS/INF 135	Denmark		Dancert	VDZ	7	6
Masonry cement	EN 413	Germany	legal	VDZ	VDZ	19	17
	BRL 2601	Netherlands	private	bmc	VDZ	4	3
Hydraulic road binders	DIN 18506	Germany	(legal)	VDZ	VDZ	16	15

[1] These figures include 88 multiple certificates for identical cements and 21 cements approved by the building authorities

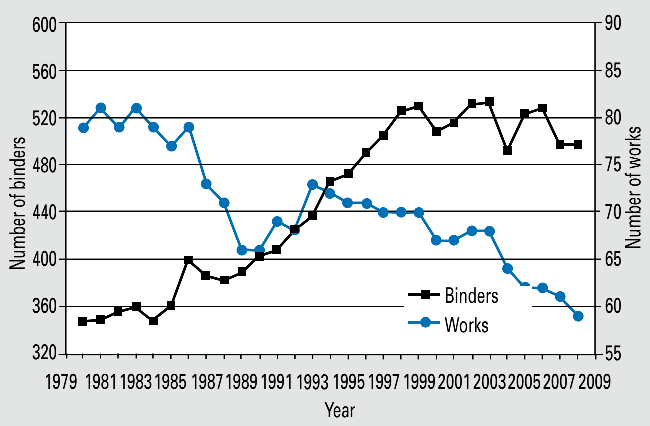


Fig. IV-2: Number of binders inspected

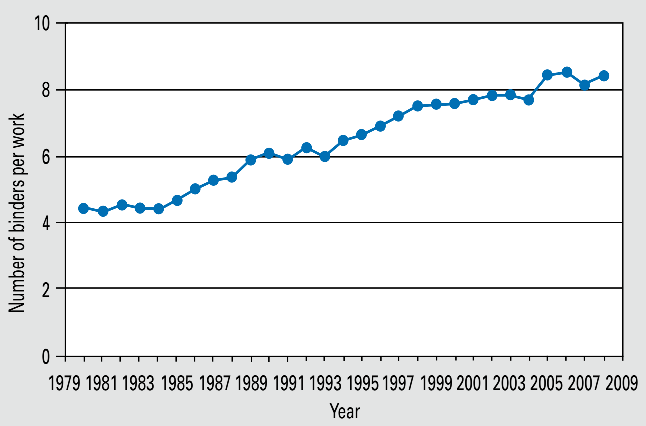


Fig. IV-3: Average number of binders inspected per works for the works inspected by VDZ's quality surveillance organisation (without multiple certificates)

Products Law (BauPG), which implements the EU Construction Products Directive, and is registered in Brussels as certification body No. 0840. Within the scope of the Construction Products Directive, the CE mark is attached to indicate conformity. In addition to that, bilateral agreements exist with foreign bodies. Corresponding marks under private law are used to attest conformity.

In addition to the requirements deriving from the domain regulated by law, the VDZ's quality surveillance organisation has also been accredited as a product certification body under private law according to EN 45011 since 2002. Moreover, all relevant laboratory tests were accredited in accordance with ISO 17025. Under the terms of accreditation, the quality surveillance organisation is regularly assessed by third parties (see Chapter VDZ/FIZ).

Approval of the VDZ's quality surveillance organisation by the competent building authorities (**Table IV-1**) primarily covers cements and cement-type binders. It also includes approvals for other mortar and concrete constituents (concrete additions, admixtures, aggregates) and cementitious mixtures (e.g. masonry mortar). It refers to both standardised products as well as products regulated by the building authorities. In the period under review, an application was submitted for additional approval for ground granulated blastfurnace slag according to EN 15167-1.

Third-party inspection of cement according to statutory regulations

Table IV-2 presents an overview of the cements and hydraulic binders that VDZ's quality surveillance organisation certified and inspected in 2008. A total of 585 binders were inspected and certified according to statutory regulations. Totalling 550 (94 %), cements accounted for the largest share. The figures include eight cements from four foreign cement works. In 88 of 550 cases, multiple certificates were issued for identical cements. They obtained certificates for EC conformity (EN 197-1) and also conformity certificates according to DIN 1164-10.

Without the multiple certificates for identical cements, 497 binders from 59 cement

Table IV-3: Number of domestic cements inspected by VDZ's quality surveillance organisation in 2008 (2006)

Cement	Number of cements				Share of cement dispatch (domestic) in mass %			
	32.5	42.5	52.5	Total	32.5	42.5	52.5	Total
Portland cement CEM I	36 (51)	78 (80)	61 (56)	175 (187)	5.6 (12.3)	16.6 (21.5)	8.0 (8.3)	30.2 (42.1)
Portland-composite cement CEM II	64 (79)	71 (60)	32 (31)	167 (170)	24.3 (24.0)	20.0 (12.4)	4.8 (3.6)	49.1 (40.0)
Blastfurnace cement CEM III	56 (72)	44 (44)	8 (7)	108 (123)	7.0 (9.9)	13.4 (7.5)	0.3 (0.5)	20.7 (17.9)
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	159 (205)	193 (184)	102 (95)	454 (484)	36.9 (46.2)	50.0 (41.4)	13.1 (12.4)	100.0 (100.0)
Cements with high early strength (R)	95 (124)	103 (102)	54 (50)	252 (276)	29.5 (37.0)	26.0 (27.6)	9.0 (8.5)	64.5 (73.1)
Cements with normal early strength (N)	64 (81)	90 (82)	48 (45)	202 (208)	7.4 (9.2)	24.0 (13.8)	4.1 (3.9)	35.5 (26.9)
Cements with special properties (LH, HS, NA)	46 (60)	48 (45)	7 (6)	101 (111)	no data			

factories were inspected in 2008. The number of binders that were inspected was slightly lower than in 2006 (**Fig. IV-2**). The average number of binders inspected per cement factory has increased over the last 20 years or so and is now constant at roughly 8.4 binders per works (**Fig. IV-3**).

In 2008, 54 cements with approvals for concrete paving were also inspected. In 2008, VDZ's quality surveillance organisation also inspected 19 masonry cements according to EN 413-1; four of those were in Class MC 12.5 and 16 hydraulic road binders according to DIN 18506.

Table IV-3 summarises the number of certificates (also without multiple certificates for identical cements) for domestically produced cements inspected by VDZ's quality surveillance organisation as well as the corresponding domestic dispatch quantities for 2008 compared to 2006 (figures in brackets). The cements were graded in the main cement types CEM I, CEM II, CEM III, CEM IV and CEM V, and the strength classes 32,5, 42,5 and 52,5. The table shows that the number of domestic cements that were inspected decreased by 30 from the number in 2006 and now stands at 454. The number of Portland cements and also the number of blastfurnace cements both decreased. However, the number of Portland-composite cements remained virtually constant.

There was also a significant drop in the dispatch quantities of Portland cements (see Table IV-3). However, on the other hand, the dispatch quantities of Portland-composite cements CEM II and blastfurnace cements CEM III increased. Noticeable is the significant shift in the dispatch quantity of cements in strength class 32,5 R in the direction of cements in strength class 42,5 N.

Fig. IV-4 confirms that over the last years there has been a marked shift in the domestic dispatch of the cements. As a comparison, the figure shows the proportions of cement types and strength classes in domestic dispatch in 2000 and 2008. It can be seen that the share of cements in strength class 32,5 has declined from 60.1 % to 36.9 %. At the same time, the cements in the top strength classes have increased accordingly. More cement in strength class 42,5 is now manufactured than in strength class 32,5.

A similar shift can be seen as regards the cement types. In the course of increasing attempts to reduce CO_2 emissions, the dispatch quantity of Portland cements has more than halved over the last eight years. Since 2000, the absolute share has dropped by 31.5 % from 61.7 % to 30.2 %. At the same time, the absolute share of CEM II cements has increased by 25.2 % from 23.9 % to 49.1 %. This is especially noticeable in cements in strength class 42.5. Here, about 40 % of the cements are now CEM II cements. The dispatch quantity of CEM III cements has also increased.

Third-party inspection of cement according to voluntary regulations

Bilateral agreements exist between VDZ's quality surveillance organisation and the corresponding Belgian, Danish, French, Dutch and Russian inspection bodies on the mutual recognition of testing, inspection and certification activities. These relate to third-party inspection according to national regulations and standards over and above the requirements of EN 197 (see Fig. IV-1). VDZ's quality surveillance organisation performs the supplementary tests and inspections required at the German manufacturers' sites in agreement with the corresponding foreign body. This reduces the additional costs for the cement manufacturers.

In 2008, VDZ's quality surveillance organisation also inspected 111 cements and four masonry cements from 27 works according to Dutch assessment guideline (BRL 2601) (see Table IV-2). The certificates were issued by BMC.

VDZ's quality surveillance organisation also certified and inspected 41 cements from 16 works according to Belgian regulations, which permit these cements to carry the Belgian BENOR mark.

In 2008, VDZ's quality surveillance organisation tested and inspected 36 cements with the NF mark from eleven cement works. The NF mark is issued according to French regulations. Agreement has been reached with the French certification body, AFNOR, according to which VDZ's quality surveillance organisation carries out third-party inspection tests and inspections in German cement works as a sub-contractor of AFNOR.

In 2008, an additional seven cements from six works were inspected according to Danish regulations. All cements obtained a Dancert certificate according to DS/INF 135.

Other construction products

Since the new pigment standard, EN 12878, was adopted by the building authorities in 2006, VDZ's quality surveillance organisation has also been certifying and inspecting the factory production control systems of pigment manufacturers. This relates to the manufacture of 53 different pigments from four European works.

In 2008, the organisation began testing, inspecting and certifying ground granulated blastfurnace slag according to DIN EN 15167-1. Currently, two ground granulated blastfurnace slags are being certified.

Since a harmonised product standard was introduced for masonry mortar in 2003 (DIN EN 998-2), it is now also possible to issue a CE mark for this mortar. Instructions for factory production control systems for CE marking of masonry mortars after a suitability test are contained in the new DIN 18581. This standard was developed in collaboration with Research Institute staff and was introduced in 2008.

In the period under review, various commissioned tests on grouts according to DIN EN 447 were conducted. Initial experiences with the new test procedure and requirements pursuant to DIN EN 445 or DIN EN 447 respectively have shown that some grouts that were suitable according to the 1996 version did not fulfil the requirements, especially as regards bleeding, volume changes and the sieve test. This means that the 1996 version will largely remain valid in the construction area. The manufacture of grout on the building site and grouting of tensioning ducts can be inspected by the VDZ's quality surveillance organisation.

Comparative tests

To ensure a constant level of testing and to fulfil the respective requirements from standards and accreditation, the testing body of VDZ's quality surveillance organisation regularly takes part in several round robin tests. In particular, the standard tests for cement are compared at national and international levels several times each year.

Among other things, Stichting BMC organises weekly comparative tests with a Dutch reference cement and these are evaluated each quarter. The results are discussed among representatives from the participating third-party inspection institutions at an annual meeting. At the same time, the results of the weekly tests of the reference cement are documented in a quality control chart to determine fluctuations so that a quick response can be initiated.

In addition, the Research Institute takes part in the annual cement comparison test organised by Association Technique de L'Industrie des Liants Hydrauliques (ATILH), in which about 200 test laboratories from 59 countries regularly participate. Similar national round robin tests are carried out on other building materials, such as fly ash and concrete admixtures.

Test laboratory

In connection with third-party inspection tests and the associated commissioned and comparison tests, each year about 3 500 binder samples are tested in the Research Institute's laboratories. With around ten properties on average to be tested, that corresponds to roughly 35 000 individual tests. With this high sample throughput rational test processes are indispensable and a constant testing level and a high testing quality must be ensured. This is achieved by standardising many of the test processes. The physical tests are carried out in the quality surveillance laboratory; while the chemical tests are sub-contracted to the cement chemistry department.

Quality assurance ■

Unique legal regulations are a basic requirement for the fact that cement is no longer dealt with just nationally, but at an European level. The EU Construction Products Directive is one of 26 directives according to the so-called "New Approach" aimed at reducing trade barriers in the European Union. In this respect, the Construction Products Directive has an excep-

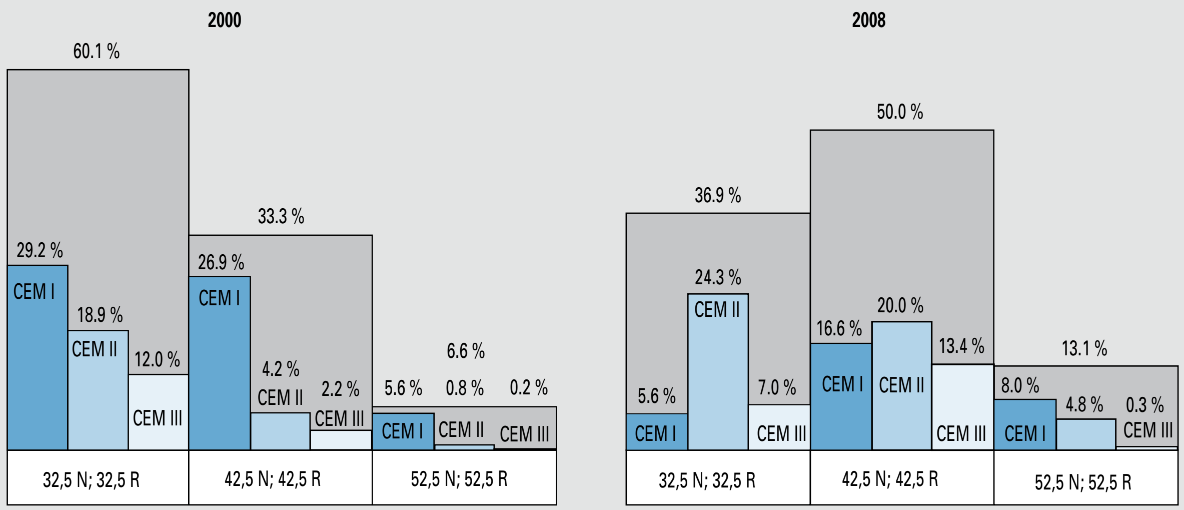


Fig. IV-4: Comparison of the share of cement types and strength classses of cements manufactured and dispatched in Germany in 2000 and 2008

tional position, because the main requirements refer not to the construction products themselves but to the buildings constructed using the products. It regulates trading in construction products throughout Europe but not the manufacture of building elements or structures, which are still subject to national law.

Proof of conformity according to the EU Construction Products Directive

The Construction Products Directive is currently being revised. The aim is to simplify and deregulate the directive, which is thought to be too complicated. The previous directive is also to be issued as an EU regulation, which will make it more difficult to have special national regulations.

The European Construction Products Directive demands that only construction products that are suitable for their intended use may be traded in the Single European Market. Placing products on the market is linked to six "essential requirements"; these are

- Mechanical resistance and stability,
- Safety in case of fire,
- Hygiene, health and environment,
- Safety in use,
- Protection against noise,
- Energy economy and heat retention.

The inclusion of a seventh requirement is being considered in the revision regarding the sustainable use (recyclability) of natural resources (see Chapter VI).

As mentioned above, proof must be provided that construction products are suitable for their intended use. As opposed to other European directives, the specifications for the product are not formulated directly in the directive. This is covered by harmonised European standards that are compiled by the European Committee for Standardisation, CEN (see sub-section on standardisation) and the European technical approvals that are pursued under the umbrella of the European Organisation for Technical Approvals, EOTA (see Chapter V).

As regards proof of conformity with the respective requirements, the Construction Products Directive currently specifies four conformity attestation systems (**Table IV-4**). Two of these have modifications, which are marked with a "plus". When the Construction Products Directive is revised, these systems are to be maintained. Only System 2, which was used for just one construction product (building lime), is to be omitted without replacement. It is also conceivable that certain exemptions will be created for smaller companies with less than ten employees and a turnover of less than € 2 million per annum.

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

System	Conformity attestation	Tasks of the notified body	Binder 1)	
1+	Certification by certification body	Third-party inspection **with** testing spot samples	Cement 1)	EN 197-2
1		Third-party inspection **without** testing spot samples	–	
2+	Declaration of conformity by the manufacturer	Initial inspection and **continuous surveillance**	Road binder	prEN 13282-3
2		Only **initial inspection**	Building lime 2)	
3		Only initial test	–	
4		–	–	

1) Common cement, cements with special properties, special binders
2) Future system 2+ according to prEN 459-3

Product certification by a notified body (System 1+) is required for just a few construction products. Because of their importance for construction safety, these include common cement, cements with special properties and special binders. System 2+ is specified only for hydraulic road binders, in which external surveillance of the factory production control is carried out by a notified body. During the period under review, a corresponding draft standard was developed with the participation of staff in the Research Institute of the Cement Industry.

The conformity of cement is assessed according to conformity evaluation standard EN 197-2. Undoubtedly the standard has proven its worth and is a model for corresponding definitions for concrete additions, such as fly ash, silica fume and ground granulated blastfurnace slag. Because of this, this standard will not be revised for the present.

In the revision of the Construction Products Directive, modified competency requirements will also be given to the approved bodies. These concern, for example, the legal structure, impartiality requirements and the general duties of a body as well as professional liability insurance cover. Some changes are the result of the restructuring of the European accreditation system.

Restructuring of the European accreditation system

Several years ago, a revision of the legal framework of the New Approach was initiated. The aim was to simplify and deregulate as a prerequisite for the free movement of goods. One result of the revision was a regulation on accreditation and market surveillance from the European Parliament and Council, which was published in August 2008 and which will take effect on 1 January 2010. This regulation necessitated a restructuring of the German accreditation system.

In Germany, there are many certification bodies and laboratories that carry out many different tests on products and services. Five different accreditation bodies, such as DACH, DAP, TGA, exist to assess the competency and qualifications of these bodies. At present the individual bodies focus on different competencies and tasks, such as accreditation of laboratories, test and certification bodies for many different products and certification bodies for management systems. There are also nine national and four state bodies in the legally regulated area (approval authorities). The different bodies work together in the German Accreditation Council (DAR).

Due to the European regulation, one single accreditation body must be established by

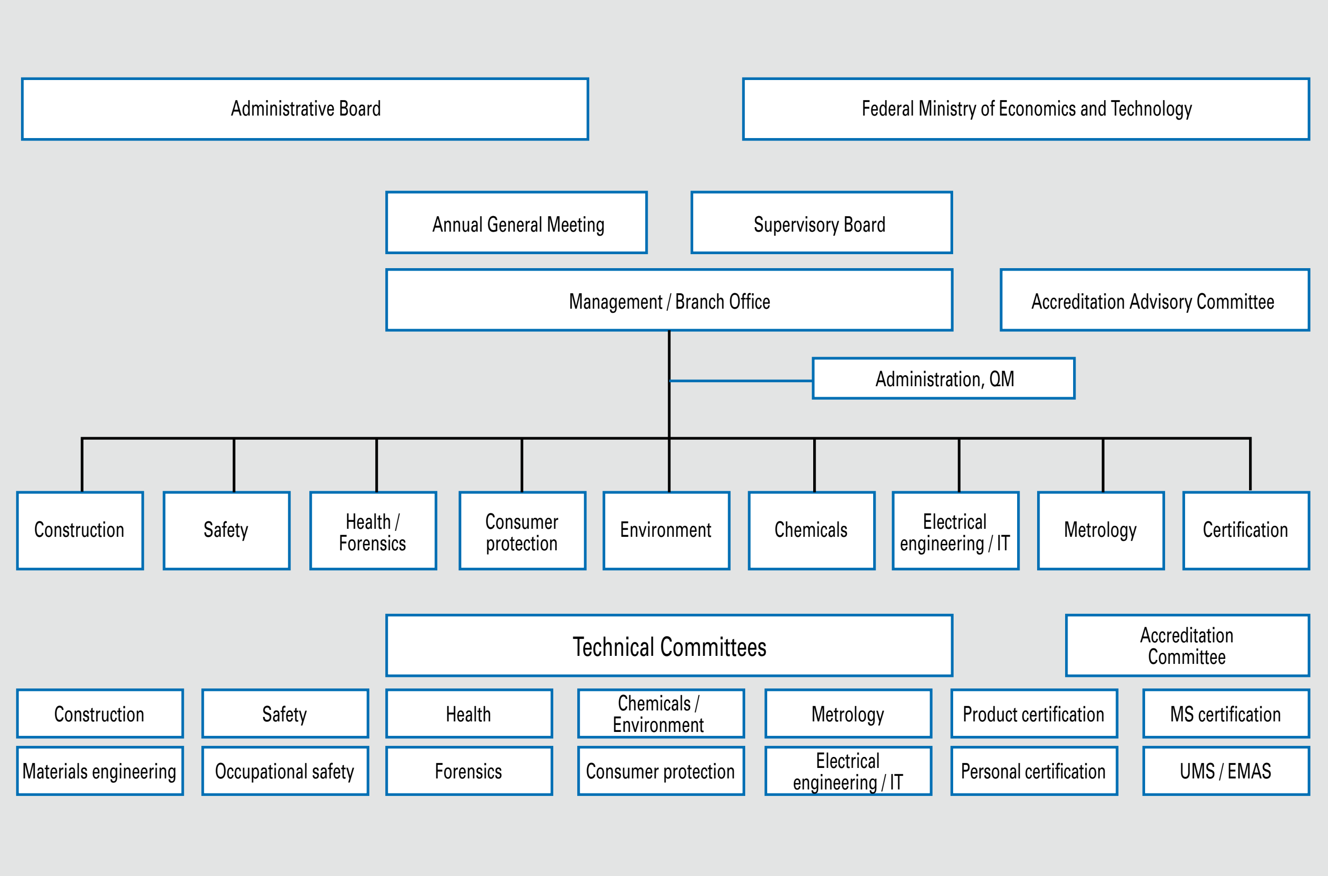


Fig. IV-5: Concept of a German accreditation body

1 January 2010. Therefore, in Germany an accreditation law was drawn up to create a single German accreditation body. The corresponding draft was passed by the federal cabinet in April 2009.

On 20 August 2008, the Federal Ministry of the Economy presented the concept of a privately-run accreditation body, which will be authorised in the form of entrusting by the public sector (**Fig. IV- 5**). This accreditation body will then be responsible for all accreditations within the scope of the 26 directives of the New Approach. The EU Construction Products Directive, which is currently being revised, is one of these directives. The present competencies of the existing accreditation bodies are to be integrated. A functional separation of the granting of authorities (approval, notification, announcement, etc.) and formal confirmation of a body's competency (accreditation) is planned.

The accreditation body will cover various areas, such as construction, safety, environment, metrology, certification, etc. It must support itself with the fees it charges and may not work in a profit-oriented manner.

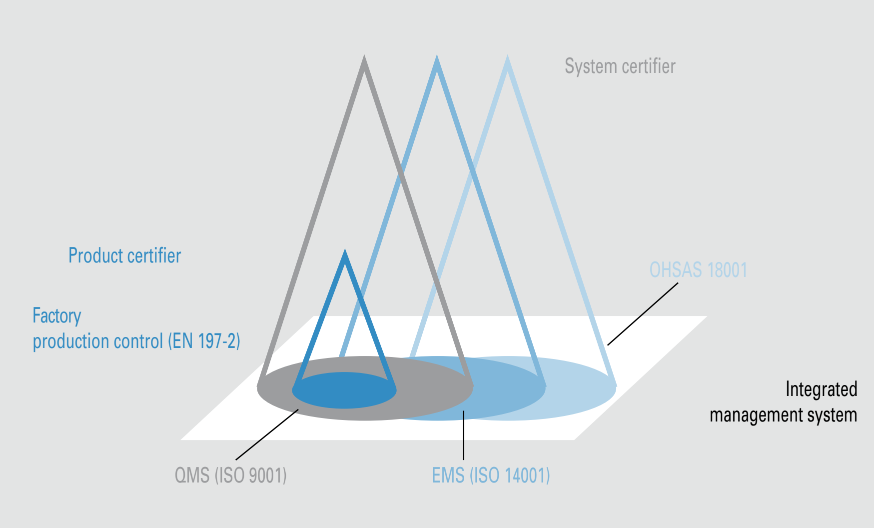


Fig. IV-6: Different view of product and system certifiers on integrated management systems

The Research Institute adjusted to this situation at an early stage and, in addition to the legally stipulated recognition and notification, has also had itself accredited privately for the corresponding areas (see Chapter 0).

Cooperation between the notified bodies

One main requirement for approval of notified bodies according to the Construction Products Directive is that they regularly exchange experiences with each other. For this purpose there are horizontal and sector-related committees in the notified bodies. Since in Germany a lot of bodies exist, the work will also be mirrored nationally. As in previous reporting periods, VDZ's quality surveillance organisation regularly took part in the exchanges of experience in the relevant European and national committees.

Certification of management systems

In addition to the factory production control system that is legally required in the areas of product inspection and certification, some companies in the cement and construction material industries operate management systems. Over the last years there has been a clear trend towards integrated management systems that simultaneously cover the specific requirements in terms of quality (ISO 9001), environment (ISO 14001) and occupational health and safety (OHSAS 18001) (**Fig. IV-6**). Although the systems are similar, there are differences in the content between product and system certifications. Product certifiers work in a legally regulated area and control in detail that the formal specifications of standards are fulfilled. Management systems have more the character of a management or control tool. Here, system certifiers work in the private area and audit systems chosen by the manufacturers themselves in spot samples and in dialogue with the manufacturer.

The Research Institute has operated a corresponding certification body for management systems, FIZ-Zert, for more than ten years. In the period under review it was reaccredited by the accreditation body (see Chapter 0).

Standardisation ■

The Research Institute of the Cement Industry is represented on almost all CEN/TC 51 standardisation committees. Some activities associated with the revision and extension of cement standards are described below.

Product standards for common cements

Table IV-5 summarises the current status of existing and planned product standards for cements and other hydraulic binders. Since being published originally in 2000, the European Cement Standard EN 197-1 has been amended and supplemented several times.

During the period under review, an amendment, A3, for fly ash as a cement constituent was completed and published. This is a formal harmonisation in line with the regulations for fly ash as a concrete addition. With the corresponding declaration, it is now possible to have higher losses on ignition for fly ash that is used as a main constituent of cement.

In addition, the planned amendment A2 for cements with a high sulphate resistance (SR) has been further specified. The proposed change takes account of almost 90 % of cements manufactured in Europe with high sulphate resistance. The proposed amendment covers seven types of cement: Portland cements with three different C_3A contents, blastfurnace cements with at least 66 % blastfurnace slag and CEM IV cements. National cements that were not included are to be listed in an appendix to the standard. These may not be labelled SR, but they may still be used. The drafts were presented to a representative of the EU Commission in July 2008. As soon as a written comment from the Commission is available, the formal vote of the two drafts will be carried out.

Parallel to these amendments, work was commenced on the formal revision of EN 197-1, which is to be carried out about every 5 years. As the standard has so far proven its worth, the changes will essentially be limited to the formal integration of all the previous changes (A1, prA2, A3) and of EN 197-4, which refers to blastfurnace cements with low early strength, including amendment A1 (the blue area in Table IV-5). The levels and classes

- low early strength (L)
- low hydration heat (LH), and
- high sulphate resistance (SR)

will be included in the standard. A corresponding consolidated version of EN 197-1 has already been compiled.

Only minor changes will be made to the content. These relate to such things as updating the requirements for cement constituents. For instance, new or revised standards for the concrete additions fly ash (as described above), ground granulated blastfurnace slag and silica fume have already been drafted or are in preparation. The specifications are to be harmonised with each other more than in the past. The requirements for cement additives are also to be revised to take account of requirements from the drinking water area. The cements manufactured in Germany already fulfil this requirement.

In future, the requirements of the Construction Products Directive are to be considered more in terms of hygiene, health and environmental protection. However, initially this subject has to be prepared in terms of content before the corresponding concepts are put forward for standardisation.

Special binders

In the past, standardisation activities focused primarily on common cements. However, six further standards and draft standards have now been adopted for special cements and special binders. Accordingly, binders that were previously used only regionally or for special areas of application may be used (see Table IV-5). For several years, standards have been completed and published for:

- cements with very low hydration heat that can be used for mass concrete,
- calcium aluminate cements that can be used for special applications, such as repair mortar, and
- masonry cements.

In the meantime

- supersulphated cements and
- hydraulic binders for non-structural applications have been added and
- the regulations for hydraulic road binders have been systematically supplemented and extended.

A new project concerns cements with a blastfurnace slag proportion of between 30 and 50 % and a limestone or fly ash content of 6 to 20 %. As the applications for these cements have not yet been defined, they have been given the working name CEM X. One reason for this is the possible CO_2 reduction in the manufacture of these binders.

Supersulfated cement

Some time ago, a standard was compiled for supersulfated cements. These are cements containing up to 75 % granulated blastfurnace slag and which are stimulated by up to 20 % calcium sulfate. The Portland cement clinker proportion is maximum 5 mass %. These cements were also standardised in Germany in the past and were manufactured and used up until the 1960s. After many years of development work, supersulfated cements are again being manufactured in some countries in the European Union. These cements are char-

Table IV-5: Existing and planned European product standards for cement and other hydraulic binders

Standard No.	Cement/binder	Type of cement/binder		Strength class	Additional classes	Status
		Number	Designation			
EN 197-1	Common cements	27	CEM I CEM II CEM III CEM IV CEM V	32,5 N/R 42,5 N/R 52,5 N/R	–	2000, Revision initiated, CEN enquiry in preparation
A1	Common cements with low heat of hydration				LH (≤ 270 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, formal vote only after reply from the EU Commission
A3	Fly ash as a cement constituent					2007
EN 197-4	Blastfurnace cements with low early strength	3	CEM III	32.5 L 42.5 L 52.5 L	LH (≤ 270 J/g)	2004
prA1	Sulphate resisting blastfurnace cement					2008, formal vote only after reply from the EU Commission
open	Cement with increased quantities of blastfurnace slag and limestone or fly ash		CEM X			Pre-standard investigation
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
EN 14647	Calcium aluminate cement	1	CAC	40	–	2005
prEN 15743	Supersulfated cement	1	CSS	30 40 50	–	Formal vote in preparation
prEN 13282-1 prEN 13282-2	Hydraulic road binder	1 [1]	HRB	N1 E2 N2 E3 N3 E4 N4	RS [2]	CEN enquiry initiated
EN 413-1	Masonry cement	1	MC	5 12.5 22.5	X (without air entraining agent)	2004, Revision initiated
prEN 15368	Hydraulic binders for non-structural applications	2	BHB	2.0 3.5	–	2008

[1] Declaration of the composition within given limits

[2] RS rapid setting

🟦 Revision of EN 197-1

acterised by low hydration heat, high sulphate resistance and increased resistance to acids.

These binders have a variable consistency depending on their composition. Some of the mortars have a very low viscosity, as can be seen in **Fig. IV-7** in the manufacture of a mortar mould. Therefore, it was originally considered to manufacture the mortar with a lower water-cement ratio of 0.40. Round robin tests were carried out with several water-cement ratios to discover the best test conditions. Ultimately, it was decided to use a normal standard test procedure with a water/cement ratio of 0.50 in order to connect this with the strength classes of common cement. Because of their slow hardening, supersulfated cements are always classified in early strength classes L or N – a draft standard now exists and will soon be considered as a CEN standard.

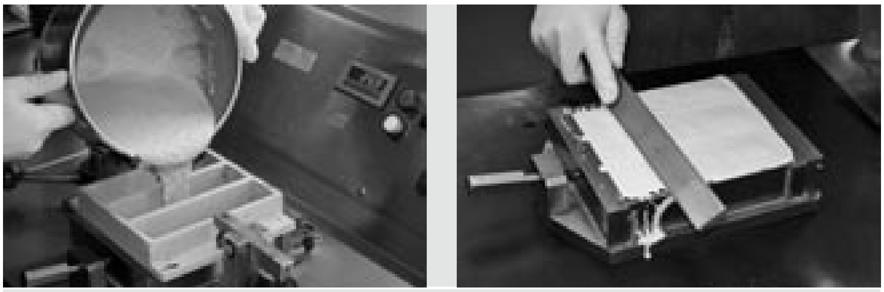


Fig. IV-7: Testing super-sulfated cement according to prEN 15743 – filling the mortar mould (left) and wiping off the matrix (right)

Table IV-6: Test standards for cement according to DIN EN 196

DIN EN 196 Part	Content	Valid version	Corresponding ISO standards
1	Strength	2005	ISO 679
2	Chemical analysis	2005 [1]	ISO 29581-1
3	Setting, soundness	2005	ISO 9597
(4) [2]	Composition	2007	–
5	Pozzolanicity	2005	ISO 863
6	Fineness	1990	–
7	Sampling	2008	–
8, 9	Heat of hydration	2004	ISO/DIS 29582-1/-2
10	Water-soluble chromate	2006	–

[1] In addition, EN 196-2.2 (ISO/DIS 29581-2) for X-ray fluorescence analysis in preparation

[2] Published as CEN Report CEN/TR 196-4

Hydraulic road binders

Another project deals with the completion of a European road binder standard. The standard envisages various constituent materials and allows a variable composition with different binder components. This allows more adjustment to the respective local conditions. The draft standard has now been extended to cover slow hardening binders, which only have to provide proof of strength after two months. A new feature is that the binders are not only to be used for the road base, but also more for soil improvement and stabilisation. It is planned to also make the standard accessible for so-called mixed binders (Mischbindemittel). This will require a corresponding modification of the test procedure that was tested in the round robin tests. It is planned to pre-slake the lime components in a pretest and then use the usual standard procedure.

Test procedure

Parallel to the product standards, the test standards are also revised and updated at regular intervals. **Table IV-6** presents an overview of the current status of the test procedures for the EN 196 series. Not included in this presentation are the performance test procedures that are developed together with the concrete standardisation committee CEN/TC 104. The main test procedures according to EN 196 have been converted into the corresponding ISO standards, so that similar test procedures can be used in many different countries.

In the period under review, further developments were made on the test standards to determine fineness according to EN 196-6 using air-jet sieve, a test standard to determine hydration heat with heat flow calorimetry, a CEN report on determining the composition, the test procedure for chemical analysis using X-ray fluorescence and the sampling procedure (see also Chapter III).

Chromate reduction in cement and cementitious mixtures ■

Since October 2006, a harmonised European test procedure has been available to determine water-soluble chromate in cement. This method, described in European Standard EN 196-10, is the reference procedure for checking the limit value of 2 ppm water-soluble chromate in cement.

The limit value also applies to cementitious mixtures. However, the proportion of water-soluble chromate does not refer to the entire mass of the formulation but only to the dry mass of the cement contained in the formulation.

When the proportion of water-soluble chromate in cementitious mixtures was being tested, it was found that even in mixtures where the content of water-soluble chromate had been reduced to less than 0.1 ppm with the addition of chromate reducers, the amount of chromate measured in the formulation in relation to the proportion of cement could still be above 2 ppm.

Investigations into the suitability of the test method based on DIN EN 196-10 for cementitious mixtures

The test procedure according to EN 196-10 can also be used for cementitious mixtures when the recommendations in the informative annex B of EN 196-10 are taken into account.

According to experiences made by various laboratories, the determination limit of the test procedure based on EN 196-10 is in the magnitude of 0.1 to 0.3 ppm Cr (VI). The cement to be tested is mixed with water and standard sand to form standard mortar according to EN 196-10; its cement proportion is 25 mass % of the dry mortar mass. The analyses were carried out on the filtrate of this mortar.

In the investigation of cementitious mixtures no further sand is added; instead the mixture is suspended with water. For example, with a cement proportion of 10 mass % in a cementitious mixture, in the worst case scenario the theoretical determination limit would be approx. 2.5 x 0.3 ppm = 0.75 ppm. However, it is possible to use a suitably adjusted larger amount of aqueous extract from the formulation that is produced for the analysis. This allows the absolute quantity of analysed chromate in the measured solution to be increased, which improves the determination limit of the analysis process.

Instead of the very toxic bromine water used in the former Technical Rules for Hazardous Substances, TRGS 613, the test procedure based on EN 196-10 proposes that sodium persulphate is used to oxidize reducing substances in the measured solution. In the investigations that were carried out, it was seen that opacifying organic components in cementitious mixtures can be destroyed and separated with this oxidising agent, producing the clear measuring solution required for the analysis.

Investigations into the effects on the content of water-soluble chromate from other components in cementitious mixtures

The proportion of water-soluble chromate in cement and cementitious mixtures is a component of a chemical equilibrium. When a pure cement clinker is suspended in water, almost the entire chromate of the clinker is dissolved. However, at the same time, especially in mixtures containing aluminium (e.g. chromate ettringite), the dissolved chromate is bonded. The chemical equilibrium between bonded and dissolved chromate can be influenced by other constituents. For example, sulphate ions that are introduced into the cement via the setting regulator, calcium sulphate, displace the chromate ions from their bonds and this is ultimately measured as water-soluble chromate in the actual cement. In particular, dissolved carbonate ions from the respective components of cementitious mixtures (e.g. alkali carbonates) can increase the proportion of dissolved chromate ions from cement clinker. If a Portland cement is extracted not with pure water but with water containing sodium carbonate, this produces not just approx. 20 to 30 mass %, but more than 80 mass % of the entire chromium content of the cement as chromate in the solution. Therefore, tests were carried out to see whether the components other than cement in normal mixtures can affect the solubility of chromate.

Influence of individual components in cementitious mixtures on chromate solubility

For the investigations a Portland cement with the various individual components that were provided and also with the compounds (total ingredients of conventional cementitious mixtures) was used. The ingredients of the cement corresponded to the mixtures that are generally found in practice. In additional investigations, a calcium aluminate cement was mixed with the test cement at 50 % and 5 % of the amount normally used in practice. The water-soluble chromate content of these mixtures was then determined after different storage times based on EN 196-10 and also according to the analysis regulation from the appendix of the former TRGS 613. If not stated otherwise, the results of the analysis refer to the proportion of cement in the mixture.

Fig. IV-8 shows the results of this chromate determination according to TRGS 613 on the test cement with the individual components of cementitious mixtures. In a number of mixtures, the proportion of water-soluble chromate in the test cement was up to 4 ppm higher when it was tested immediately after it was produced (0 months). In some mixtures, the dissolved chromate content was up to 6 ppm lower than in pure test cement.

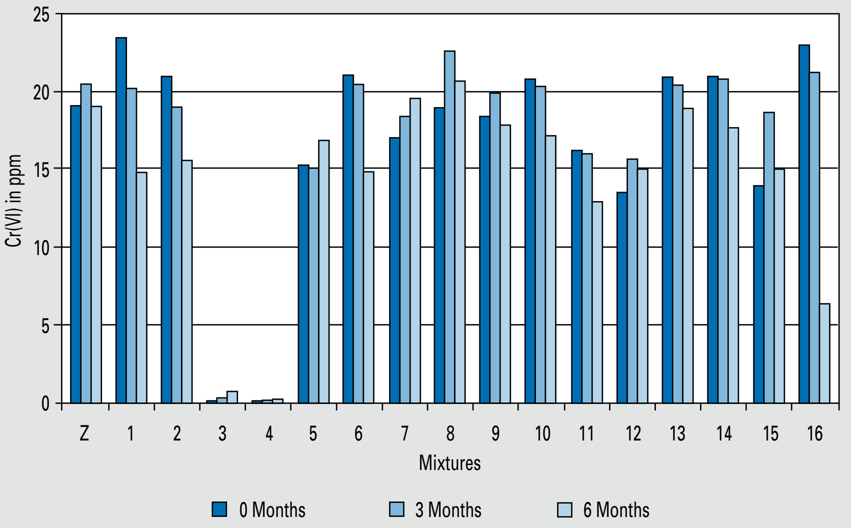


Fig. IV-8: Water-soluble chromate content in mixtures of the test cement (Z) with various components of cementitious preparations (determination based on TRGS 613; analysis results in relation to cement proportion)

1: Z + tartaric acid;
2: Z + citric acid S40;
3: Z + calcium aluminate cement (50 mass %);
4: Z + calcium aluminate cement (100 mass %);
5: Z + calcium aluminate cement (5 mass %);
6: Z + Melment F 10 plasticiser;
7: Z + lithium carbonate;
8: Z + Vinnapas 5044 N;
9: Z + zinc stearate;
10: Z + sodium maleate;
11: Z + methyl cellulose 1;
12: Z + methyl cellulose 2;
13: Z + air entraining admixtures;
14: Z + limestone meal;
15: Z + methyl hydroxy ethyl cellulose;
16: Z + mixture of citric acid (0.3 mass %) and limestone meal (4 mass %)

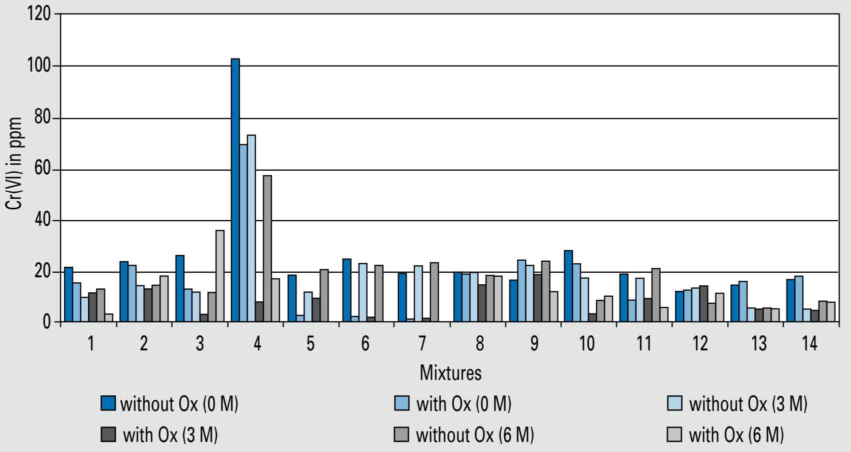


Fig. IV-9: Water-soluble chromate proportion of mixtures of the test cement with various compounds of cementitious preparations (determination according to TRGS 613; analysis results in relation to cement proportion; # M = storage time of the test cement/compound mixture in months; Ox = oxidation with sodium persulphate; broken line = water-soluble chromate proportion of pure test cement)

The water-soluble chromate proportion in the mixture with the normal amount of calcium aluminate cement (Mixture 4) was particularly low, namely below the determination limit of the analysis method. With a dosage of 50 mass % of the normal amount, the calcium aluminate cement reduced the water-soluble chromate proportion by almost the same extent. Even adding just 5 mass % of the normal amount produced a marked reduction in the proportion of water-soluble chromate. The reason for this strong reduction in the proportion of water-soluble chromate is not that it is chemically reduced to trivalent chromium but is due to the increased bonding of chromate because of its reaction with the reactive aluminates of the calcium aluminate cement discussed above. The results of the analysis show that the components of cementitious mixtures that were investigated do not cause any serious increase in the water-soluble chromate. However, with a combination of two components (Fig. IV-8, Mixture 16) the effects of the individual components can accumulate.

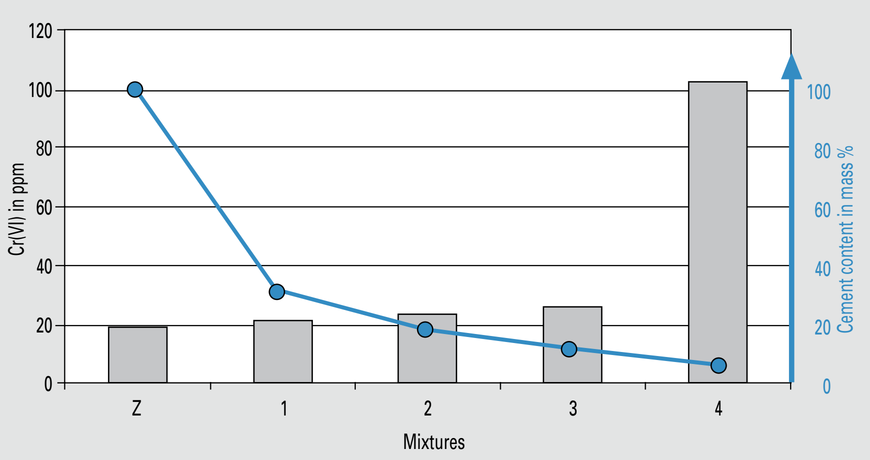


Fig. IV-10: Water-soluble chromate proportion (bar) and cement content (curve) of mixtures of the test cement (Z) with the compounds 1, 2, 3 and 4 (determination according to TRGS 613 without oxidation; analysis results based on the cement proportion)

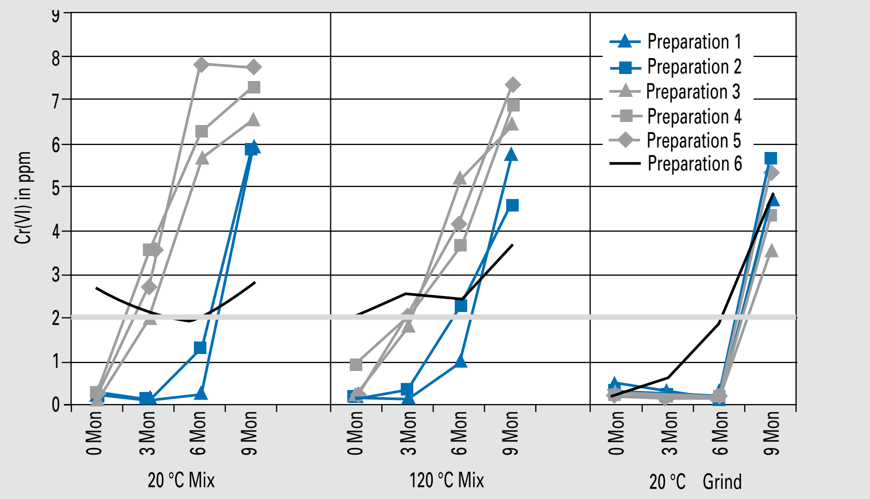


Fig. IV-11: Results of the Cr(VI) determination of the test cement/tin (II) preparation mixtures according to DIN EN 196-10 (“Mix”: produced by mixing; “Grind”: produced by grinding materials together; temperatures: mixing and grinding temperatures; # Mon: test date in months after the tin (II) preparation was added

Effect of all components in cementitious mixtures

Cementitious mixtures generally contain only small amounts of cement. These proportions are often in the magnitude of 10-20 mass %, in some cases well below 10 mass %. In comparison to cement, the total of all components contained in the formulation apart from cement, otherwise referred to as compounds, is clearly the main component of the mixtures. Consequently, it can have a significant influence on the release of chromate. To investigate this, a test cement with compounds was mixed according to the mass ratios in the authentic products and the content of the water-soluble chromate of these mixtures was determined (**Fig. IV-9**). Most compounds do not significantly increase the chromate released from the cement. The only obvious exception to this is Compound 4. Moreover, during the time the mixtures are stored the measured chromate content decreases in most mixtures.

Reducing substances have to be destroyed in an oxidation stage, as otherwise in the analysis they would produce an incorrect (too low) chromate content in the sample. However, some compounds (e.g. 4, 5, 6, 7 and 11) produce lower chromate contents only when the analysis is carried out with such an oxidation stage. It could be that critical reducing substances are only produced as a result of incomplete oxidation. From the results of the analysis of compounds 1 to 4, it is possible to deduce the conditions under which the proportion of soluble chromate could increase considerably (**Fig. IV-10**). Among other things, these four compounds contain finely ground limestone. The lower the cement content in the formulation, the higher the measured chromate content in relation to this cement proportion. Even just a low proportion of dissolved carbonate from the limestone meal changes the equilibrium as regards dissolved and bonded chromate in the suspension of these mixtures.

Influencing the efficiency of chromate reducers

Interactions are observed not only between the components of cementitious mixtures and cement but also between these components and the chromate reducers. Tin (II) sulphate preparations are very efficient chromate reducers. However, in many cases the chromate content increases again considerably after just a few months. The decreasing effectiveness of chromate reducers can be due to several reasons:

- continuing oxidation of the reducing agent (e.g. by atmospheric oxygen)
- reactions of the reducing agent with other components in the formulation
- reduced solubility of the reducing agent over time (e.g. due to retarding crusts)

Because of this, various tin (II) preparations were investigated as regards their reduction effect on water-soluble chromate in cement and their durability. The aim was to determine what properties a chromate reducer based on tin (II) salts has to have to remain effective over a long period of time. A total of seven tin (II) preparations were tested; they differed as regards the amount of residual sulphuric acid they contained and in terms of their preliminary storage time conditions and the amount that was added (**Table IV-7**). The chromate reducers were added to a test cement in various ways. In relation to their tin (II) content, all preparations were added in amounts corresponding to 0.02 mass % tin (II) sulphate. This dosage did not completely reduce the water-soluble chromate in the test cement, which allowed the effectiveness of the individual preparations to be compared. During the nine month storage period, all preparations lost much of their effectiveness; this can be seen in the increasing chromate content shown in **Fig. IV-11**. The powdery preparations 1 and 2 exhibited a good reduction effect over a period of six months. However, at the latest after nine months the effectiveness of these two preparations fell to the same level as that of the other preparations.

Compared to preparations 1 and 2, the effectiveness of the crystalline preparations 3 to 5 decreased continuously during the storage time when they were added to the test cement by mixing at 20 °C or 120 °C. However, if they are added by being ground together with the test cement at 120 °C, they are just as effective as preparations 1 and 2. This good conformity of effectiveness can be attributed to the similarity of the particle sizes as a result of grinding.

Summary

The components other than cement in cementitious mixtures can increase the proportion of water-soluble chromate in the cement. With low cement content in the presence of large amounts of these components, the increase in the proportion of water-soluble chromate can be quite considerable. In this connection, components with soluble carbonate must be regarded as especially critical. To reliably reduce the additional chromate dissolved in this way additional chromate reduction is recommended.

Table IV-7: Tin (II) preparations that were used for the durability tests

Name	Composition	Free sulphuric acid in mass %	Other properties
1	Pure tin (II)-sulphate	0.3	Powder
2	Pure tin (II)-sulphate	0.1	Powder
3	Pure tin (II)-sulphate	< 0.1	Crystalline
4	Pure tin (II)-sulphate	0.01	Crystalline
5	Pure tin (II)-sulphate	0.1	Crystalline
6	Pure tin (II)-sulphate	Unknown	3 years old

Tin (II) sulphate preparations should be added to cement at high temperatures by grinding both together. Normally, tin (II) sulphate is added to cementitious mixtures only by mixing at low temperatures. The extent to which conditioning tin (II) sulphates under increased mechanical and thermal loading would produce the same effect as grinding cement and chromate reducer together at higher temperatures must be examined on a case-by-case basis.

Certain properties of tin (II) sulphates can affect their (long-term) effectiveness in different ways, depending on the dosing strategy (temperature, mechanics). Based on these results, the decisive factors in this regard are the fineness of the reducer and the amount of free sulphuric acid it contains. However, the effectiveness of the chromate reducers was considerably reduced after nine months at the latest in all the test cement/reducer mixtures that were examined.

These results show the complexity of the chemical and physical impacting factors in the reduction of water-soluble chromate in cementitious mixtures. However, they also allow strategies to be developed for the successful production of adequately durable low chromate cementitious mixtures.

V

Concrete constituents, concrete technology and concrete engineering

First concrete roundabout in Germany (Bad Sobernheim)

Cements with several main constituents ■

Historically, raw materials that were available in the various regions have been used to manufacture efficient cements that ensure safe and reliable concrete structures. Consequently, there has been a long tradition of using cements containing several main constituents. These days, because of increasing demands in terms of environmental protection, the manufacture and use of cements with several main constituents has taken on a new level of significance due to their ecological benefits.

With reference to conditions in Germany, the successful use in the building industry has proven the efficiency of CEM II and CEM III cements for challenging and durable concrete structures. The technical application properties of these cements, the ecological advantages of using them and examples of practical applications were described in a customer-oriented manner in the VDZ brochure “CEM II- und CEM III/A-Zemente im Betonbau – Nachhaltige Lösungen für das Bauen mit Beton”[CEM II- and CEM III/A cements in concrete constructions – sustainable solutions for building with concrete] from the German Cement Works Association (can be purchased from www.beton.org).

Ecological advantages

The positive ecological effect gained from the increasing use of cements with several main constituents can be seen in the changes in the building material profile for a metric ton of cement in Germany (**Table V-1**). In 2006, the contribution to the greenhouse effect and other environmental impacts was determined for an average German cement, consisting of the average proportions of cement clinker and other main constituents. The environmental impacts of upstream supply chains, for example the electricity used to produce the material, were also considered. Compared to 1996, the contribution to the greenhouse effect had been reduced by 23 % and consumption of non-renewable energies had fallen by 38 %; contributions to other environmental impacts were also drastically reduced. These reductions reflect the fact that in Germany more cement is produced with several main constituents and that the increased use of secondary fuels has also had a positive effect on many key values.

Table V-1: Building material profile for cement: potential effects and consumption of primary energy (from non-renewable energies) for the manufacture of 1 t of cement in Germany (average)

			1996	2006	
Effect category	global	Greenhouse effect (GWP)	872	670	kg CO_2 equiv.
		Ozone depletion (ODP) [1]	0	1.6 x 10^{-5}	kg R11 equiv.
	regional	Acidification (AP)	1.68	0.92	kg SO_2 equiv
		Overfertilisation (NP)	0.20	0.12	kg PO_4^{3-} equiv.
		Summer smog (POCP) [2]	0.07	0.10	kg C_2H_4 equiv.
Primary energy (not renewable)			4 355	2 713	MJ

[1] Indicator was set to zero in 1996

[2] In 1996 the indicator was based on a different calculation method

Application regulations in Germany

The current concrete standards DIN EN 206-1 and the German DIN 1045-2 contain the application regulations for standard cements in relation to exposure classes. When these standards were introduced, application restrictions applied to some standard cements – based mainly on the lack of practical experience with these cements in Germany. In these cases, proof of suitability for use in specific exposure classes was provided by a general building authority approval (Technical Approval, TA) from the German Institute for Building Technology (DIBt).

Currently, in Germany the following cement types may be used in all exposure classes:

- Portland cement CEM I
- Portland-blastfurnace cements CEM II/A-S and CEM II/B-S
- Portland-burnt shale cements CEM II/A-T and CEM II/B-T
- Portland-limestone cements CEM II/A-LL
- Portland-fly ash cements CEM II/A-V and CEM II/B-V
- Portland-composite cements CEM II/A-M with other main constituents S, LL, T, D and V
- Portland-composite cements CEM II/B-M with national technical approval for application
- Blastfurnace cements CEM III/A *)

Since 2003, 18 general building authority approvals have been granted for CEM II/B-M (S-LL) and 4 approvals for CEM II/B-M (V-LL) in Germany. Apart from the approvals for CEM II/B-M (V-LL), 16 approvals are currently valid for CEM II/B-M (S-LL). In all the approvals, use is approved for concrete, reinforced concrete and pre-stressed concrete according to DIN EN 206-1 in conjunction with DIN 1045-2 for exposure classes XC3, XC4, XD1 to XD3, XS1 to XS3, XF1 to XF4, XA1 to XA3, XM1 to XM3 as a supplement to the exposure classes X0, XC1 and XC2 already permitted in DIN 1045-2. In all approvals reference is made to use in mortar and concrete according to the old DIN 1045:1988 and the former pre-stressed concrete standard DIN 4227-1. Not permitted is use in grout for pre-stressing tendons according to DIN EN 447. In the meantime, uses for the manufacture of bore piles according to DIN EN 1536 in conjunction with DIN Technical Report 129 and for the manufacture of water-impermeable concrete according to the DAfStb Guideline on concrete structures with water-endangering materials have been included in four approvals. From a technical point of view, the extension applies to all these approvals. However, the owner of the approval must make a formal request to the DIBt. In addition to the above list of applications, CEM II-M cements with general building authority approval may be used in all areas where the corresponding regulations refer to cement according to DIN EN 197-1, DIN 1164 or include cement general building authority approval and with no specific usage restrictions. The following list contains several examples

- DIN 1053-1 Masonry
- DIN 4158 Filler concrete joists for reinforced and pre-stressed concrete floors
- DIN EN 12843 Concrete masts and poles
- DIN 4261-1 Small sewage treatment plants
- DIN 18551 Sprayed concrete
- DIN 18148 (DIN 18162) Hollow lightweight concrete blocks for walls (not reinforced)
- DAfStb Guideline “Manufacture and use of dry concrete and dry mortar” (dry concrete guideline)
- DAfStb Guideline “Manufacture and use of cement-based flowable concrete and flowable mortar”

*) Exposure class XF4: CEM III/A in strength class ≥ 42,5 N or strength class 32,5 R with up to 50 mass % blastfurnace slag

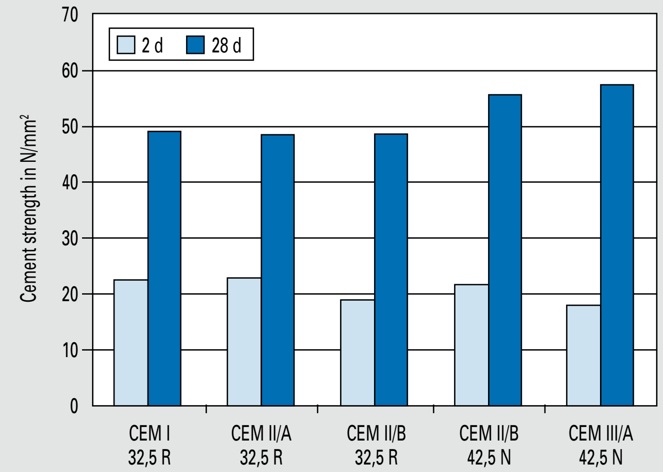


Fig. V-1: Average standard compressive strengths of different types of cement based on the results of third-party inspection

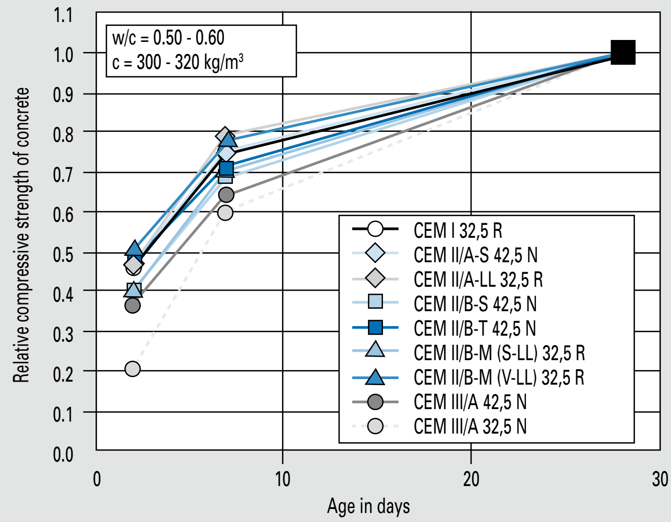


Fig. V-2: Relative compressive strength of concretes with various CEM II and CEM III/A cements compared to CEM I concrete

More information on uses of cement according to EN 197-1 can be found in Building Rules List A, Part 1, Appendix 1.33 (2006/1). When engineering structures are built near highways in Germany (ZTV-ING) the customer must agree to the use of CEM II-M cements. Despite the restriction, numerous practical examples have also proven the suitability of CEM II/B-M cements with technical approval in this area of application. In the long term it should be possible to remove this addendum.

A working group of CEN/TC 104/SC1 "Concrete" has developed a synopsis of the national application documents (NAD) for the European concrete standard EN 206-1. It describes some considerable differences in the use of cement. Apart from the traditional differences in market conditions and construction practice, it also reflects the philosophies underlying the imposition of rules (see VDZ Activity Report 2005-2007). While the German application standard DIN 1045-2 lays down specifications for the application of all 27 basic cement types and for a number of CEM II-M cements, other NADs only regulate the application of a few cement types that have traditionally played a role in the respective national markets.

Cement properties

The properties of CEM II and CEM III/A cements have been continuously improved in the course of technical developments in the manufacturing process. They have also been adapted to suit current requirements, which has, in turn, considerably increased the bandwidth of potential applications. In particular, as regards early strength the manufacturers have adjusted the CEM II and CEM III/A cements so that they can be used in a similar way to the CEM I cements (**Fig. V-1**).

Properties of concrete in construction practice

In addition to the environmentally compatible manufacture of CEM II and CEM III/A cements, because of their composition and especially considering the many different technological guidelines for concrete, they also have several advantages when used in fresh concrete and hardened concrete. For specific applications – including bridge and tunnel construction and road and building construction – it is possible to produce optimally adjusted concretes. A number of important properties are described below:

Strength development

Under practical building conditions, the strength development of concrete with CEM II and CEM III/A cements is similar to that of CEM I concretes. To satisfy practical requirements for early strength CEM II/B and CEM III/A cements are also available in strength class 42,5 N. **Fig. V-2** shows the relative compressive strength development of concretes based on conventional CEM I, CEM II and CEM III/A cements with similar concrete compositions and curing conditions. The relative values result from the relation of the compressive strength of concrete after 2, 7 and 28 days to the 28-day compressive strength of the concrete. The test values for a CEM III/A 32,5 N are shown as a comparison. These results allow the investigated concretes to be classified into medium and slow strength development classes. Accordingly, the concrete with the CEM III/A 32,5 N cement can be classified as a slow strength developer. This classification is important to define the time needed for after-treatment.

Durability

The durability of the concrete is one of the key requirements for every structure. The most important feature is that the concrete element used must be resistant to loads and environmental impacts for its intended period of use, assuming it is maintained and repaired adequately.

Carbonation

Investigations of reinforced concrete and pre-stressed concrete structures that were constructed with concretes of different strength classes and with different com-

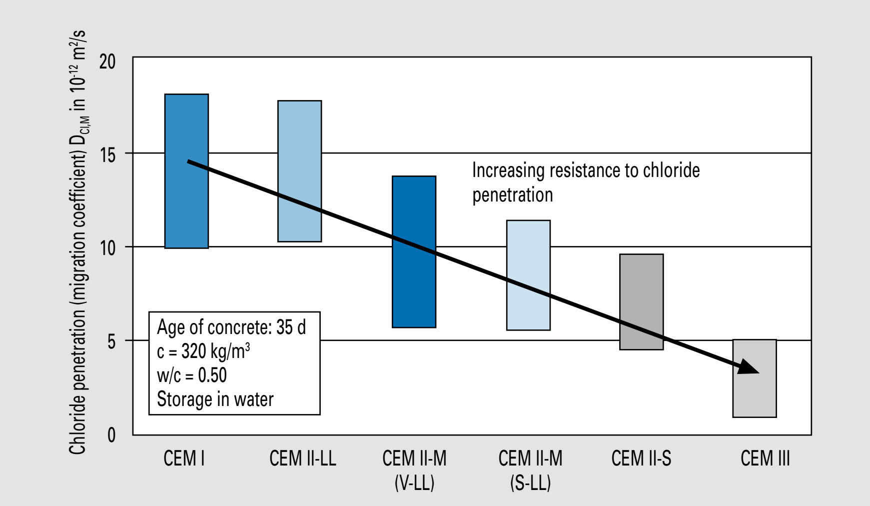


Fig. V-3: Influence of the cement type on the resistance to chloride penetration of concrete using the rapid test method

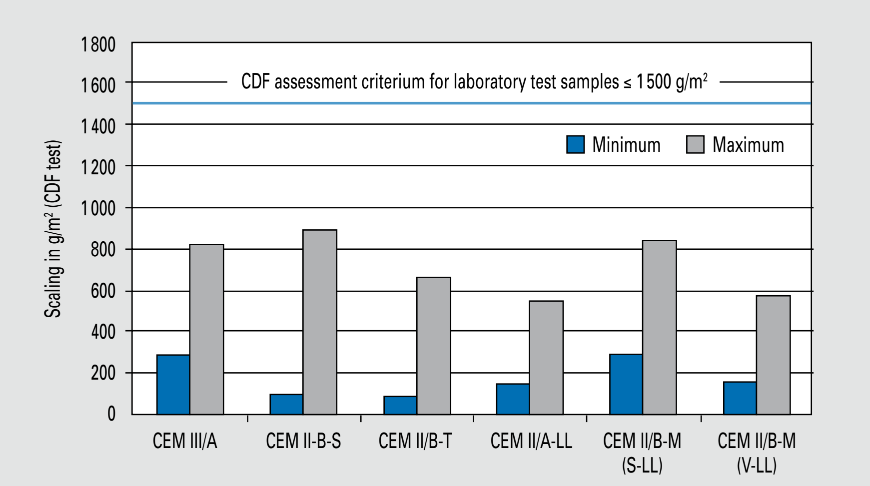


Fig. V-4: Freeze thaw resistance with de-icing salt of air-entrained concretes using the CDF method, cement content 320 to 365 kg/m³; w/c ratio 0.41 to 0.50; strength classes of the cements: 32,5 R and 42,5 N

positions have shown that with construction components that were weathered outdoors, the type of cements used in Germany generally have no effect on the carbonation behaviour. Although higher carbonation depths may be found on dry, interior elements, because of the lower moisture content of these elements there is no risk of the reinforcement corroding.

Chloride penetration resistance

Due to the finer pore system, in some cases the use of cements containing blastfurnace slag and fly ash can cause a marked increase in the concrete's resistance to the penetration of chlorides (**Fig. V-3**). With concretes intended for massive construction components according to the DAfStb Guideline and when a CEM III/A or CEM III/B cement of exposure class XD3 or XS3 is used, the highest permissible water-cement ratio of 0.45 may be increased to 0.50 with no change in the corrosion protection for the reinforcement.

Freeze-thaw resistance with or without de-icing salt

With the correct composition, processing and after-treatment according to DIN 1045, concretes with CEM II and CEM III/A cements have a high freeze-thaw resistance with or without de-icing salt. Consequently, they are very suitable for engineering structures and traffic areas. Only CEM III/A in strength class 32,5 N and CEM III/A 32,5 R with more than 50 mass % blastfurnace slag are excluded for exposure class XF4. **Fig. V-4** shows some results from freeze-thaw-test with de-icing salt on concretes containing different cement types using the CDF method. If freeze-thaw resistance with de-icing salt has to be tested, as a general rule the following criterion is applied to evaluate the results: after 28 freeze-thaw cycles, scaling must not exceed 1 500 g/m² for a concrete that is meant to have adequate freeze-thaw resistance with de-icing salt. This corresponds to a scaling depth of around just 0.6 mm. This criterion may not be applied to samples taken from structures.

Application examples

In terms of the workability characteristics, strength development and durability of concrete, the CEM II and CEM III/A cements that have been produced in Germany to date have proven their reliability in practical applications over many decades. The current VDZ brochure "CEM II- und CEM III/A-Zemente im Betonbau – Nachhaltige Lösungen für das Bauen mit Beton" [CEM II- and CEM III/A cements in concrete constructions – sustainable solutions for building with concrete] contains many practical examples from different areas of concrete construction.

Outlook

As an industry that uses a high volume of energy and raw materials, the cement industry is very much affected by demands to conserve resources and reduce the use of energy and also by the global issue of climate control. Cement manufacturers are facing these challenges by continuously improving their production processes in terms of energy and raw materials consumption.

If the industry wishes to continue along this path consistently, this raises the issue of producing cement types that have, in the past, only been produced and used in small quantities or which are not even included in the European cement standard DIN EN 197-1, even if their compositions are not vastly different from the cements covered by DIN EN 197-1. A current research project entitled "Ecologically and technically optimised cements with several main constituents" is involved in investigating these and similar cement compositions. This project is being carried out within the framework of the "klimazwei" research measure which is carrying out research work into climate control and controlling the effects of climate change (www.klimazwei.de) and is funded by the German Federal Ministry for Education and Research (BMBF).

The investigations are focussing on Portland-limestone cements with 30 and 35 mass % limestone and cements with 10 to 25 mass % limestone in combination with blastfurnace slag and siliceous fly ash. The

Table V-2: Composition of the test cements with several main constituents

Cement	Limestone fineness approx. 7 000 cm^2/g (Blaine)	Blastfurnace slag fineness approx. 4 000 cm^2/g (Blaine)	Fly ash fineness approx. 4 000 cm^2/g (Blaine)	Fineness of cement in cm^2/g (Blaine)	Water demand in mass %	Origin of the constituents
30 % LL	30 mass % limestone with 70 mass % $CaCO_3$	-	-	6 265	31.5	Region 1
10 % S 25 % LL	25 mass % limestone with 70 mass % $CaCO_3$	10 mass % blastfurnace slag	-	6 195	30.5	Region 1
20 % S 20 % LL	20 mass % limestone with 80 mass % $CaCO_3$	20 mass % blastfurnace slag	-	5 150	30.5	Region 2
40 % S 10 % LL	10 mass % limestone with 80 mass % $CaCO_3$	40 mass % blastfurnace slag	-	4 970	30.0	Region 2
10 % V 25 % LL	25 mass % limestone with 70 mass % $CaCO_3$	-	10 mass % siliceous fly ash	6 325	30.0	Region 1
20 % V 20 % LL	20 mass % limestone with 70 mass % $CaCO_3$	-	20 mass % siliceous fly ash	5 955	29.0	Region 1

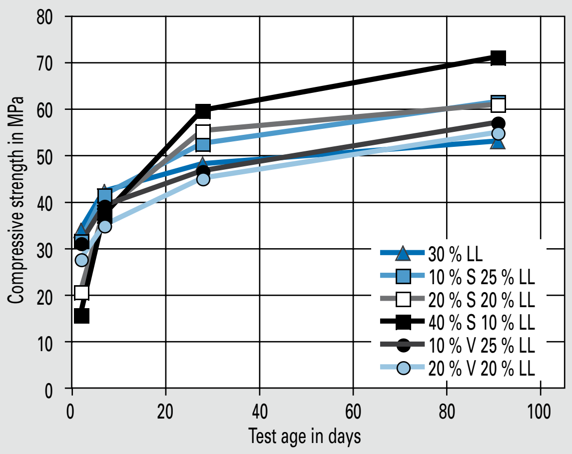


Fig. V-5: Compressive strength of cements in relation to test age

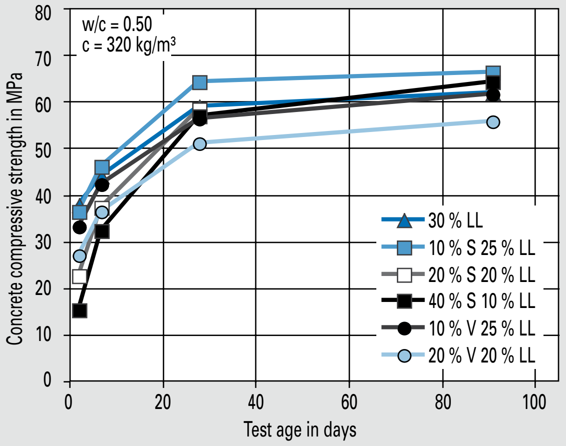


Fig. V-6: Compressive strength of concrete in relation to test age

cements to be investigated were manufactured in the laboratory and also by large-scale cement works. During the manufacturing process granulometric optimisation of the main constituents of the cement and optimisation of the sulphur agents were carried out with consideration of the cements' setting behaviour. Moreover, different types of main constituents were varied (for example, according to origin). The focus of the investigations was placed on the durability of concretes manufactured using these cement types. The results of several selected investigations that provide an overview of the cements and their compositions are presented below **Table V-2**. The following results cannot be generalized. They can, however, be used for further development work.

Compressive strength development

The development of compressive strength in several cements produced in the laboratory is shown in **Fig. V-5**. The results show that, in general, the strength of the cements produced in the laboratory for the durability investigations develops in the same way as in normal practice. To manufacture the concretes, aggregate (coarse Rhine sand from the research facility's stocks) with a grain composition A16/B16 according to DIN 1045-2, Annex L was used. The compositions of the concrete mixtures are based on the limit values for the composition and properties of concretes according to DIN Technical Report 100 "Concrete".

Fig. V-6 presents examples of the development of compressive strength in concrete with a water-cement ratio w/c = 0.50 and a cement content c = 320 kg/m^3 using selected cements produced in the laboratory. As expected, the early strengths of the concretes with CEM II cements were higher than concretes manufactured with cements not included in DIN EN 197-1. Apart from two exceptions, the concretes at the age of 28 days had a similar strength level. Thus, it is generally possible to make a direct comparison of the properties that are relevant for durability even after this time.

Carbonation

Fig. V-7 shows examples of the development of carbonation depths over time in several concretes that were investigated. The concretes were manufactured with a cement content of c = 260 kg/m^3 and a water-cement ratio of w/c = 0.65. The carbonation depths of the concretes containing the laboratory cements investigated here were almost all below the values of the CEM III/A concrete given as a reference. CEM III/A can be used for all applications (exposure classes).

Chloride penetration resistance

The concrete's resistance to chloride penetration was determined with a rapid test

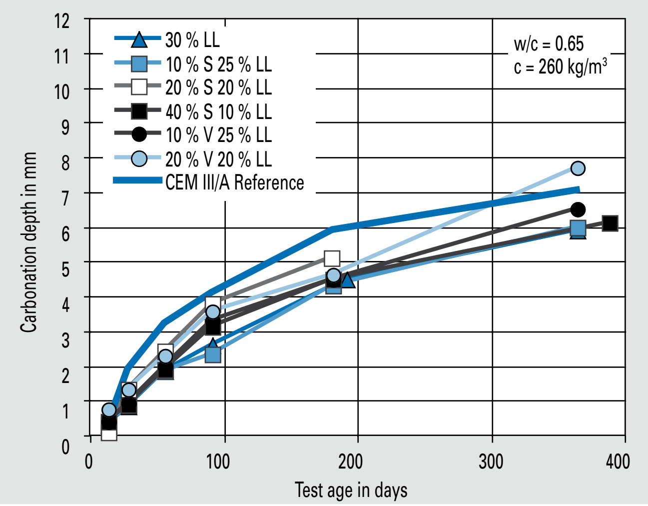


Fig. V-7: Carbonation depth of concrete in relation to test age

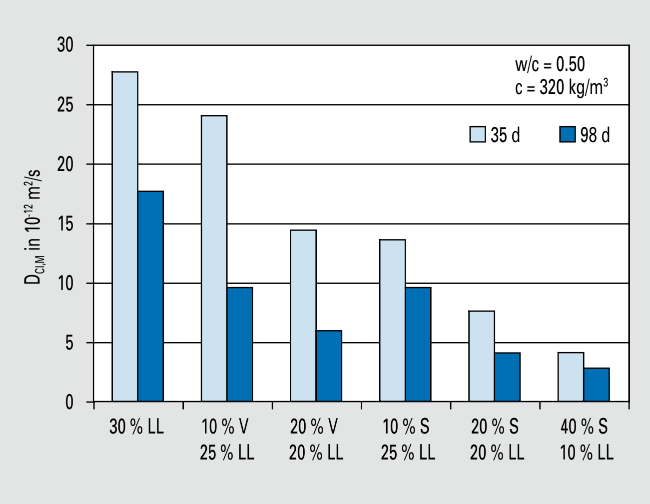


Fig. V-8: Chloride migration coefficients of the concretes in relation to test age

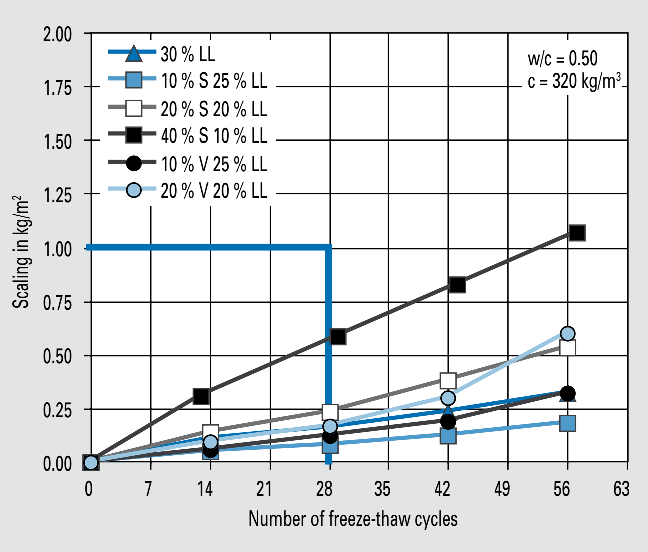


Fig. V-9: Scaling of concretes in the CF method in relation to the number of freeze-thaw cycles

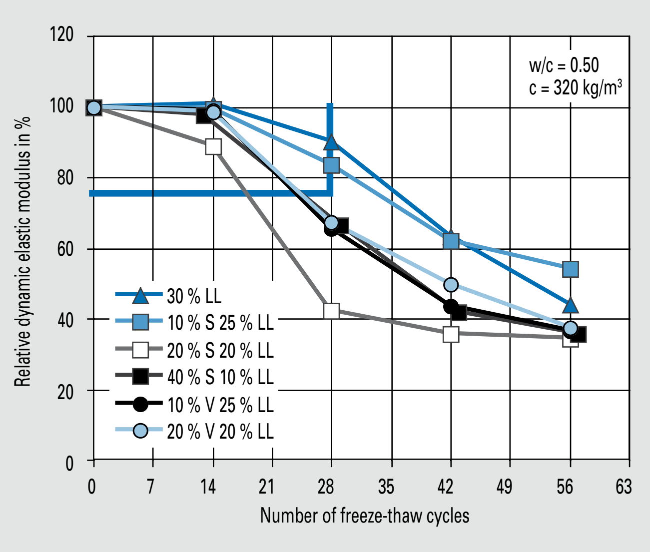


Fig. V-10: Relative dynamic elastic modulus of concretes in the CIF method in relation to the number of freeze-thaw cycles

method (migration test). The test samples were cured in water for 35 and 98 days respectively. Concretes in exposure class XD2/XS2 were manufactured with a water-cement ratio of w/c = 0.50 and a cement content of c = 320 kg/m³. The chloride migration coefficients $D_{Cl,M}$ (**Fig. V-8**) that were determined when laboratory cements containing 30 mass % limestone was used were approximately 28 · 10^{-12} m²/s after 35 days and approx. 18 · 10^{-12} m²/s after 98 days, and are thus in the same range as concretes made with Portland cement. The concretes that were manufactured with cements containing fly ash or blastfurnace slag exhibited a lower chloride migration coefficient $D_{Cl,M}$, which was in the range of approx. 4 to 24 · 10^{-12} m²/s after 35 days and approx. 3 to 10 · 10^{-12} m²/s after 98 days.

Freeze-thaw resistance with or without de-icing salt

Results of the frost resistance tests according to the CF/CIF method and results of the tests into frost de-icing salt resistance according to the CDF method are presented and evaluated below. In Germany, assessment criterions for scaling (CF/CDF method) and assesment criterions for internal structural damage (CIF method) are defined by the German Federal Waterways Engineering and Research Institute (BAW) in the “Frost test of concrete” fact sheet.

In the investigations that were conducted with the CF method, the concretes (cement content c = 320 kg/m³, water-cement ratio w/c = 0.50) exhibited scaling well below the assessment criterion of 1.0 kg/m² after 28 frost-thawing sequences that is defined in the “Freeze-thaw test of concrete” fact sheet issued by the German Federal Waterways Engineering and Research Institute (BAW) (**Fig. V-9**). The BAW assessment criterion for the CIF method is a relative dynamic elastic modulus of 75 % after 28 freeze-thaw cycles. As **Fig. V-10** shows, the concretes containing cements with 30 mass % limestone and 10 mass % blastfurnace slag and 25 mass % limestone exhibited a relative dynamic elastic modulus of more than 80 % after 28 freeze-thaw cycles. When cements with a composition outside the standard were used, the criterion was not fulfilled within the scope of the investigations conducted by the Research Institute.

The CDF test is used to test resistance to freeze-thaw attack with simultaneous de-icing agent stress. Generally, a defined de-icing salt solution is used (3 % NaCl solution). In the test for freeze-thaw resistance with de-icing salt (CDF) of air-entrained concrete surface scaling is dominant and has priority for the assessment. The CDF-method was tested on concretes with a cement content of c = 320 kg/m³ and a water-cement ratio of w/c = 0.50. The results are shown in **Fig. V-11**. Concrete scaling was between 0.35 and 1.25 kg/m² after 28 freeze-thaw cycles and was thus below the assessment criterion of 1.5 kg/m² after 28 freeze-thaw cycles which applies to this method.

Figures V-12 and **V-13** show comparative results of further investigations of concretes manufactured using cements produced in the laboratory and in cement works. A requirement for the large-scale manufacture of cements in the works was that the manufacturing process had to be adapted to suit constituents that were available locally. As the figures show, the durability of concretes containing cements with 30 mass % limestone and 20 mass % fly ash in combination with 20 mass % limestone was improved in some cases. Field site tests using the works cements under XF3 conditions will show how the concretes behave in practice.

Cement and admixtures

The use of concrete admixtures to control the properties of the fresh and hardened concrete is state of the art in concrete production today. Some 90 % of the concrete produced in Germany contains concrete admixtures. In 2007, consumption of admixtures in Germany was about 12 kg per metric tonne of cement. Overall, more than 550 concrete admixtures which can be classified in 15 different functional groups are presently available in Germany. At approx. 75 %, concrete plasticisers and super-plasticisers account for the lion’s share.

There is still a substantial lack of scientifically backed understanding of the precise working mechanisms of some concrete admixtures. The influence that concrete admixtures have on the hydration of cement and thus on the properties of fresh and/or hardened concrete is usually determined empirically and is the subject of some controversial discussion. This applies especially to super-plasticisers based on polycarboxylate ether, shrinkage reducing admixtures and new air-entraining concrete admixtures. These have been extensively investigated by the Research Institute.

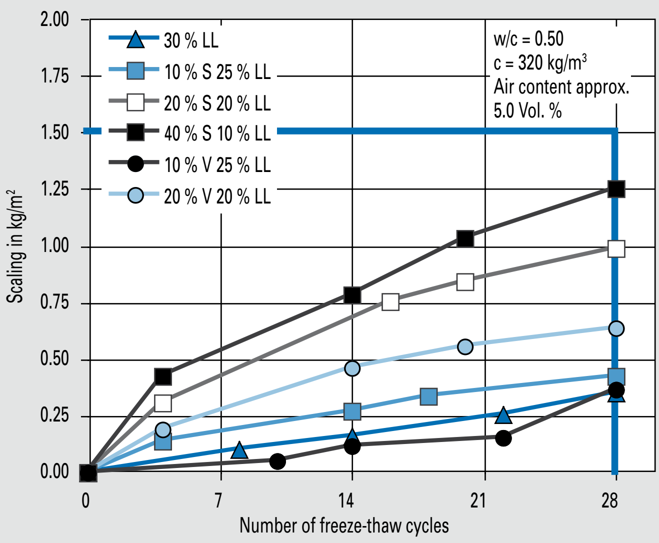


Fig. V-11: Scaling of air-entrained concretes in the CDF method in relation to the number of freeze-thaw cycles

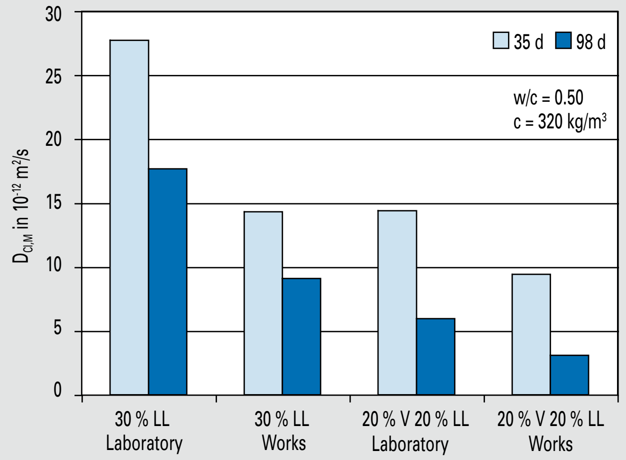


Fig. V-12: Chloride migration coefficients of concretes containing laboratory and works cements in relation to test age

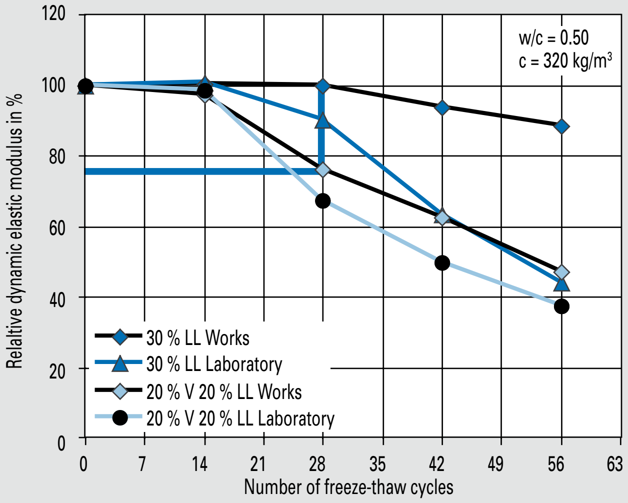
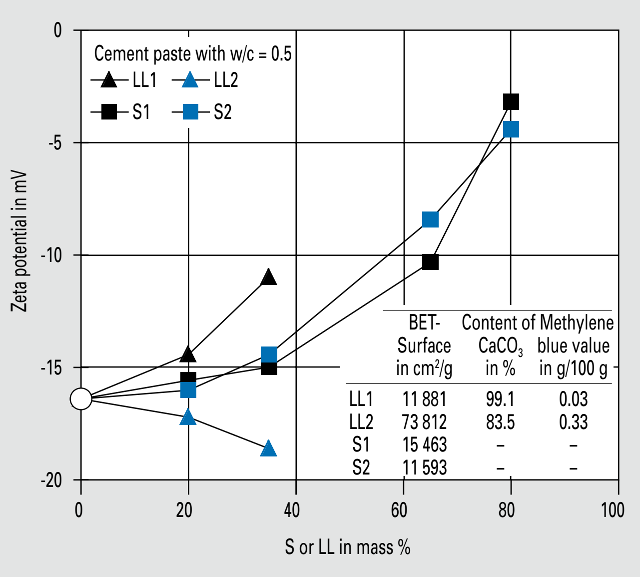


Fig. V-13: Relative dynamic elastic modulus of concretes containing laboratory and works cements in the CIF method in relation to the number of freeze-thaw cycles

Super-plasticisers

Synthetic organic polymers with carboxylic groups, such as polycarboxylate ethers (PCE), constitute an advance in the field of active ingredients contained in super-plasticisers. Some 45 % of the super-plasticisers used today are based on PCE, and the tendency is rising. PCEs consist of main chain molecules, such as polyacrylic acid, and side chain molecules, such as polyethylene oxide, which are fixed to the main chain. Via their negatively charged main chain,



	BET-Surface in cm^2/g	Content of $CaCO_3$ in %	Methylene blue value in g/100 g
LL1	11 881	99.1	0.03
LL2	73 812	83.5	0.33
S1	15 463	–	–
S2	11 593	–	–

Fig. V-14: Zeta potential of pastes from Portland-composite and blastfurnace cements manufactured in the laboratory with the same clinker components

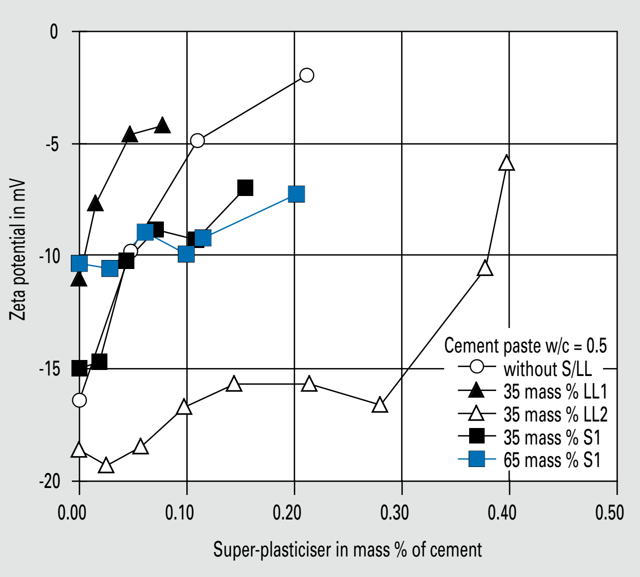


Fig.V-15: Zeta potential of pastes from Portland-composite and blastfurnace cements manufactured in the laboratory with the same clinker components in relation to the amount of PCE super-plasticiser that was added

the PCEs adsorb on the positively charged surfaces of the cement, its hydration products and other fine solids particles. The dispersing effect is largely attributable to the steric repulsion of the side chains. Variation of the charge and the length ratio of the main chain and the side chains allows adjustment of different properties, such as a strong initial plasticising effect and/or extended workability of fresh concrete.

In addition to parameters such as the exact point when the material is added, the mixing time and the temperature of the fresh concrete, the effects of the super-plasticisers are also affected by the cement that is used. Practical experience has shown that even if the same type and quantity of super-plasticiser and the same type of cement are used, in unfavourable cases effects such as rapid loss of consistency, segregation, intensive bleeding and delayed strength development may occur. While knowledge of the effects that traditional super-plasticisers have on Portland cement exists, there is still need for more research into the interactions between Portland-composite/blastfurnace cements and super-plasticisers based on polycarboxylate ether.

The Research Institute is investigating the effects of the main constituents of cement (clinker, blastfurnace slag and limestone) on super-plasticiser adsorption. In combination with rheological measurements it is being determined whether conclusions can be drawn as regards initial plasticising and the duration of plasticising of super-plasticisers on the basis of the zeta potential. The aim is to determine substance parameters that must be known to understand the methodical interaction between cement and super-plasticisers e.g. in order to prevent discolouration of fair-faced concrete surfaces as a result of sedimentation.

Zeta potential investigations

The zeta potential is an electro-kinetic potential in the interface between the mobile and the rigid part of the double layer formed at the transition zone between solids and aqueous solutions. The potential indicates the charge conditions on the particle surface. Changing this potential by adding super-plasticisers allows to investigate the adsorption of the super-plasticiser molecules on the surfaces of various main constituents of cement. In the Research Institute the zeta potential can be determined on suspensions rich in solids with normal w/c ratios using an electro-acoustic measuring method.

Fig. V-14 shows the effect that various proportions of blastfurnace slag (S1, S2) and limestone (LL1, LL2) have on the zeta potential of laboratory cement pastes containing the same Portland cement clinker components. The zeta potential of the cement paste with no main constituents other than clinker was approx. -17 mV. The zeta potential of the cement pastes containing blastfurnace slag shifted in the same manner from the negative range towards the isoelectric point (0 mV) as the content of S1 and S2 was increased. The reduction in zeta potential did not correlate with the increase in blastfurnace slag. In water the blastfurnace slags exhibited a zeta potential of approx. -15 mV. LL1 reduced the negative zeta potential of the pastes. This course is generally expected in limestone with a very high $CaCO_3$ content, which usually exhibits a positive zeta potential in water. On the other hand, LL2 caused an increase in the negative zeta potential of the pastes. Based on initial findings, this can be attributed to the clay constituents in LL2.

The results show that blastfurnace slag and limestone can have a considerable influence on the zeta potential of cement pastes. Consequently, the sorption of super-plasticiser molecules can also be affected.

Fig. V-15 presents the course of the zeta potential in pastes of selected laboratory cements containing blastfurnace slag and limestone respectively with increasing quantities of super-plasticiser (PCE). As the quantity of anionic PCE increased, the negative zeta potential of the cement paste with no other main constituents shifted towards the isoelectric point. This contradictory behaviour is attributed to a shift in the measuring level of the zeta potential caused by the adsorbed PCE molecules.

The zeta potential of the cement paste with 35 mass % S1 and 35 mass % LL1 was already reduced considerably in the same way as the cement with no other main constituents with small quantities of super-plasticiser. The zeta potential of the cement paste with 65 mass % S1 was affected slightly by the addition of super-plasticiser. It is likely that the molecules adsorb mainly on the clinker components and not on the blastfurnace slag S1 or limestone LL1.

The zeta potential of the paste with 35 mass % LL2 changed only slightly when about 0.3 mass % super-plasticiser was added. This is attributed to the large surface area of the clay constituents on to which a certain proportion of the super-plasticiser molecules adsorb non-specifically. When more super-plasticiser was added, this produced a marked shift of the zeta potential in the direction of the isoelectric point.

Shrinkage reducing admixtures

Shrinkage is caused by changes in the moisture content in concrete which result in changes in the inner forces in the structure of the hardened cement paste matrix due to environmental effects or drying in the concrete. This creates tensile stress that causes the hardened cement paste matrix to contract. Shrinkage of concrete leads to deformations that may cause stress in structural elements in case of constraint. As a consequence, cracks can occur that have a negative effect on the durability of the concrete. The Research Institute of the Cement Industry is currently investigating whether potentially negative effects can be significantly reduced through the use of shrinkage reducing admixtures.

To reduce shrinkage of concrete, shrinkage reducing admixtures (SRA) were developed in Japan at the start of the 1980s and have also been used in Europe since about 1997. In Germany, SRAs have been used only in the manufacture of screeds and cement-based mixtures. Since at present no general building inspectorate approvals have been issued for this type of admixture, SRAs may not be used in load-bearing structural elements made from concrete, reinforced concrete or pre-stressed concrete.

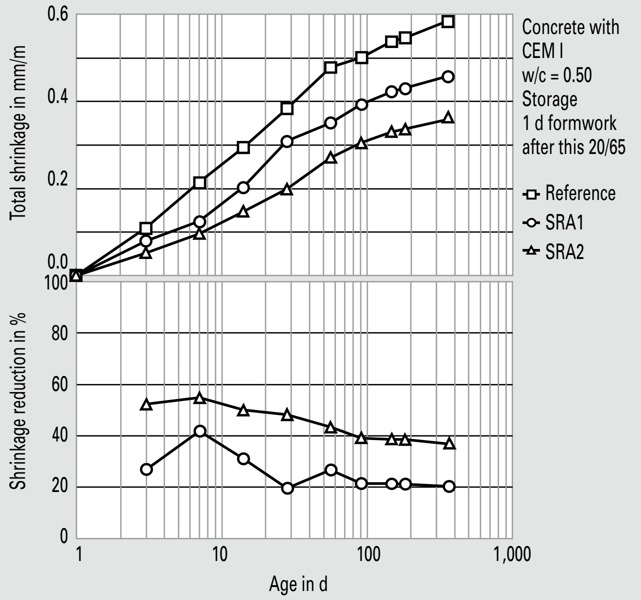


Fig. V-16: Total shrinkage (top) and shrinkage reduction (bottom) of concrete with Portland cement and w/c = 0.50 after dry curing in a 20/65 climate; SRA amount: 4.5 mass % of water

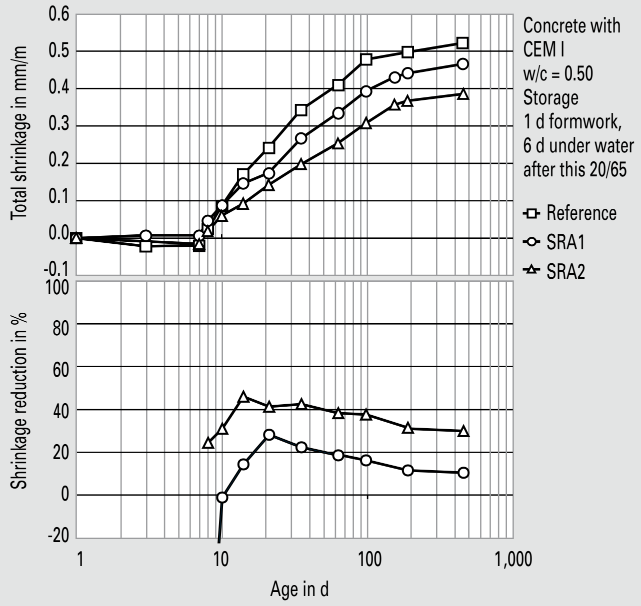


Fig. V-17: Total shrinkage (top) and shrinkage reduction (bottom) of concrete with Portland cement and w/c = 0.50 after curing for six days under water and then in a 20/65 climate; SRA amount: 4.5 mass % of water

The Research Institute of the Cement Industry conducted investigations into the working mechanisms of shrinkage reducing admixtures as part of an AiF-sponsored research project. The results show that the shrinkage reducing effect does not correlate with the reduction in surface tension as assumed in a number of other investigations. Active substances in the SRAs may increase the so-called disjoining pressure effect of the pore solution, the reduction of which is essentially responsible for shrinkage of cement paste. Increased relative moisture in hardened cement paste may intensify the disjoining pressure effect of the pore solution. However, some active substances exhibit no shrinkage reducing effect. In fact, they increase shrinkage of hardened cement paste under sealed conditions and also when the paste is dried at 20 °C and 65 % relative humidity (dry curing). One of the reasons for this could be the considerable increase in the gel pore content compared to hardened cement pastes with no SRA. On the basis of these findings, the Research Institute is currently conducting a subsequent research project funded by AiF. In this project the effect of SRA on shrinkage, the mechanical properties and the durability of concrete are being investigated.

Effect of SRA on concrete shrinkage

The first results show that the properties of fresh concrete are not significantly affected by SRA, regardless of the water/cement ratio or the cement paste content.

Total shrinkage of concrete containing Portland cement can be reduced by up to about 40 % by SRA depending on the cement paste content and the form of curing. **Fig. V-16** shows an example of total shrinkage (top) and shrinkage reduction (bottom) when the concrete was cured at 20 °C and 65 % relative humidity (20/65). The reduction in shrinkage is the shrinkage of concretes containing SRA in relation to the reference sample without SRA. During curing (L1), the test samples dry directly after demoulding within 24 hours. After one year, total shrinkage was reduced by shrinkage reducing admixture SRA1 and SRA2 respectively by about 20 % and 40 % respectively (see Fig. V-16, bottom). **Fig. V-17** presents total shrinkage (top) and the corresponding shrinkage reduction (bottom) of concrete containing Portland cement after being cured for six days under water, followed by curing in a 20/65 climate (L2). In the top picture it can be seen that the subsequent curing of the concretes in water had only a minor effect on the extent of reduction after one year. When the sample was cured in water for seven days, the respective reduction in shrinkage (see Fig. V-17, bottom) was slightly less than with dry curing after one year and was approx. 10 % with SRA1 and approx. 30 % with SRA2. In the research project it is currently being investigated whether this behaviour also occurs in concretes containing different cements and different water/cement ratios. The results of investigations into the effect of SRA on the shrinkage of concrete with varying cement paste contents show that the increased extent of shrinkage associated with increasing cement paste content can be reduced with SRA. Hence, easily workable concretes rich in cement paste can be manufactured with low shrinkage.

Effect of SRA on the mechanical properties of concretes

Many publications state that the compressive strength of concretes can be reduced through SRA. The effect of SRA on the compressive strength of concrete was been investigated so far on Portland cement concretes with a water/cement ratio of w/c = 0.50. The concretes were cured in climates (L1), (L2) and sealed (L3). The concretes with SRA1 and SRA2 exhibited roughly 20 % (SRA2) less compressive strength than the respective reference concrete without SRA – largely regardless of age and curing method. The concrete with shrinkage reducing admixture SRA1 exhibited a higher compressive strength than the concrete with shrinkage reducing admixture SRA2 at all ages and with all three methods of curing.

The static modulus of elasticity of concrete with Portland cement and a water/cement ratio of w/c = 0.50 was reduced by up to 7 % with shrinkage reducing admixtures SRA1 and SRA2 with curing method L2 and after 91 days. With curing method L1 after 2 days the flexural tensile strength was about 12 % (SRA2) and approx. 20 % (SRA1) higher than in the concrete without SRA. In contrast, after 2 days curing in water the flexural tensile strength of the concretes with SRA was about 15 % lower than the reference sample with no SRA. After 91 days the effect of the SRA on flexural tensile strength was insignificant.

The results of the investigations into the effect of SRA on the mechanical properties of concrete largely confirm the results already determined for cement paste (see VDZ Activity Report 2005-2007).

Air-entraining admixtures

In unset concrete air-entraining admixtures are added to create a lot of small, evenly distributed air voids with a diameter ≤ 300 µm. In hardened concrete these voids serve as an expansion space to relieve the pressure created when the pore solution freezes. The air voids also interrupt the capillary pore system and reduce water absorption in the concrete. Both mechanisms of action contribute to the adequacy of the concrete's resistance to freeze-thaw with de-icing salt. Road paving concrete which is covered with de-icing salt in winter must be manufactured as air-entrained concrete. Other areas of application are bridge caps, scraper tracks and concretes used in hydraulic engineering (exposure class XF3).

Manufacturing of proper air-entrained concrete requires a suitability test in which the main effects that the composition of the concrete, the temperature of the unset concrete and the mixing time have on the formation of air voids are determined. Suitable regulations for the composition and manufacture of air-entrained concrete are defined and have proven their worth in the past. Traditional super-plasticisers based on melamine, naphthalene and lignin sulphonate have long been used to regulate consistency for the manufacture of air-entrained concrete.

When super-plasticisers based on polycarboxylate ether (PCE) are used, it has been determined that the requirements for the formation of the air void system are not always fulfilled. Accordingly, in some cases the air void structure is not stable, which means that the total air content and the air void distribution can change. In a few cases, despite compliance with the total air content in the fresh concrete, the requirements for the air void parameters measured on hardened concrete (spacing factor and micro air void content) are not achieved. In cases such as this, the accurate adjustment of the micro air void content, which prevents frost and de-icing salt damage, is no longer guaranteed. To clarify the facts, in 2006 the German Committee for Structural Concrete (DAfStb) formed a working group headed by the Research Institute. Extensive research work was also commenced.

Research at the Institute

Insufficient information is available about the precise interactions between air-entraining admixtures and super plasticisers, especially PCE. Because of this, during the period under review the Research Institute started work on an AiF-funded research project. The investigations will provide fundamental knowledge about the effects and interactions between the air-entraining admixtures and super plasticisers in combination with cement. The aim is to manufacture appropriate air-entrained concrete containing super plasticisers by identifying "robust" admixture combinations that enable the specific formation of air voids.

The formation of air voids is being investigated in cement pastes, mortar and concrete with different combinations of air-entraining admixtures, super plasticisers and cement. In cement paste and mortar, the formation of air voids and foam is being analysed in relation to the admixture-cement combination. Sorption of the super plasticiser on cement particles is determined with paste and flotation experiments. In addition, the formation of air voids on unset and hardened concrete will be determined using selected admixture-cement combinations. In the course of these experiments, the air entraining parameters will be determined for hardened concrete and the concretes' de-icing resistance will be analysed using the CDF method. The research project is being carried out in close collaboration with the Institute of Building Materials Research (IBAC) at Aachen University in Germany. One of the focuses here is research into the interactions between air-entraining admixtures and super plasticisers when fly ash is used.

Formation of foam

Initial research has been carried out on the foam formation capacity of air-entraining admixture/super plasticiser combinations in cement suspensions. The maximum permissible amount of super plasticiser was added (3 mass % of cement). In a standardised experiment water, cement and admixture were mixed in a plain cylinder, fine air bubbles were introduced to the suspension and the height of the foam that formed was measured. **Fig. V-18** shows the formation of foam in relation to the amount of active agent in the air-entraining admixture and super plasticiser (PCE for ready-mixed concrete) that was added. The experiment was stopped when the foam overflowed from the cylinder (height of foam > 16 cm). This status is shown by the arrow in Figure V-18. First, in a "reference experiment" the formation of foam of a synthetic air-entraining admixture (syn. surfactant) and a natural air-entraining admixture (modified wood resin) with no added super plasticiser (only air-entraining admixture) were determined. Subsequently, the effect of the time when the super plasticiser was added was also investigated. In one case the super plasticiser was added before the air-entraining admixture (first SP) and in the second case the air-entraining admixture was added (height of foam approx. 8 cm) before the super plasticiser (first AEA). In the second option the aim was also to investigate whether the formation of foam was affected by the subsequent addition of super plasticiser.

With the same concentration of active agents, the synthetic air-entraining admixture exhibited a much stronger foam formation than the air-entraining admixture based on a natural active agent. Apart from this, the sequence in which the admixtures were added also had a major effect on the formation of foam. If about 8 cm of foam was produced by adding the air-entraining admixture first before the super plasticiser was added, there was less overall formation of foam. The formation of foam was hardly affected at all by the subsequent addition of the super plasticiser and the foam height of approximately 8 cm fell only slightly. If the super plasticiser was added before the air-entraining admixture, much more foam formed. A possible reason for this is the reduced sorption of the air-entraining admixture molecules on the cement particles when the sorption places are already filled by the super plasticiser molecules. The air-entraining admixture molecules can stabilise more air bubbles and more foam forms. It is possible that in practice the effects that occur during the formation of air voids in concrete can be attributed to these differences in the sequence in which the admixtures are added. Generally, when concrete is being manufactured the air-entraining admixture is added before the super plasticiser.

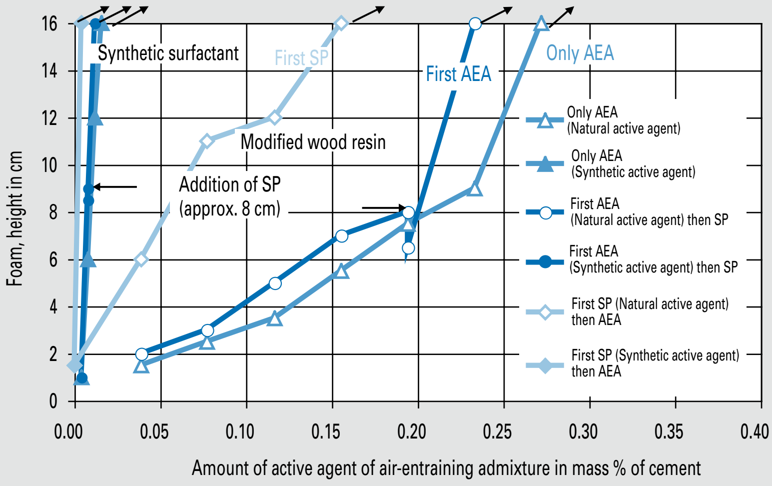


Fig. V-18: Formation of foam in a cement suspension in relation to the type and amount of air-entraining admixture (AEA) added and the time when the super plasticiser (SP) is added.

Alkali-silica reaction ■

In an alkali-silica reaction (ASR), all constituents in the aggregate containing silica that is sensitive to alkalis react with the alkalis of the pore solution in the cement paste. The reaction product is an alkali silica gel that endeavours to absorb water. The associated increase in volume is described as concrete expansion and can cause cracks in the concrete. In many concretes an ASR takes place with no damage. The triggers for and the course of a damaging ASR in concrete depend on the type, reactivity, quantity and particle size distribution of the alkali-reactive aggregate, the effective alkali content in the pore solution and on sufficient moisture being present. If one of the three requirements is missing, no damaging ASR occurs. If the conditions for a damaging ASR exist, visible cracks can appear in the concrete. However, it is not always possible to distinguish these cracks from other cracks that are the result of other damage, such as frost attack. If a damaging ASR is suspected, it is imperative that an expert carries out a thorough examination to clarify whether a damaging ASR has taken place.

Regulations

In Germany, the German Committee for Structural Concrete (DAfStb) issues guidelines – "Preventive measures against a damaging alkali reaction in concrete" – to prevent ASR damage, these guidelines are generally known simply as the Alkali Guidelines. The latest version of the Alkali Guidelines was published in February 2007. The guidelines are introduced by the building authorities with publication in Version 2008/1 of Construction Products List A, Part 1.

The Alkali Guidelines are split into three parts:
Part 1: General
Part 2: Aggregates containing opaline sandstone and flint
Part 3: Crushed alkali-reactive aggregates

Effects on building with concrete

The guidelines offer practical solutions for building with concrete which, however, must be applied. In this connection, it must be mentioned that there is also the option of classifying an aggregate as non-reactive (E I) on the basis of a petrographic description with no other test being required. This applies to aggregates that are not listed in the guidelines or which are not excavated in regions listed in the guidelines. A requirement is that no damaging ASR has occurred with the aggregate when used under normal building conditions (**Fig. V-19**).

With the concrete formulations and cement contents generally used these days, there are also many uses in civil engineering and engineering structures (moisture classes WO, WF, and WA, **Table V-3**) for

Aggregate is
- not from a region according to Part 2 of the Alkali Guidelines
- not crushed aggregate according to Part 3 and is not gravel with more than 10% crushed aggregate according to Part 3

No damage caused by ASR in real concrete structures – petrographic description

E I (non-reactive)

No restrictions
Cement/cement content
aggregate

WO, WF, WA, WS 1)

1) Use of road paving cements
Follow the regulations of TL Beton-StB 07 and ARS

Fig. V-19: Requirements for classifying an aggregate as non-reactive (E I) on the basis of a petrographic description with no other tests

Aggregate is
- from a region according to Part 2 of the Alkali Guidelines

Test according to the Alkali Guidelines:
test method according to Part 2 of the Guidelines

E I-O/OF (non-reactive)	**E II**-O/OF (medium reactive)		**EI III**-O/OF 2) (reactive)	
No restrictions Cements / cement contents aggregates **WO** **WF** **WA** **WS** 1)	**No restrictions** Cements / aggregates		**No restrictions** Cements / aggregates	
	E II-O	**E II**-OF	**E III**-O	**E III**-OF
	c ≤ 330 kg/m^3	c ≤ 330 kg/m^3 **WO, WF** (WA with NA)	**WO** (WF with NA)	
	WO, WF (WA with NA)	c ≤ 330 kg/m^3 **WO** (WF, WA w. NA)		

1) Use of road paving cements
Follow the regulations of TL Beton-StB 07 and ARS

2) Applies also to aggregates that have not been assessed

Fig. V-20: ASR effects on building with concrete when using aggregates from a region according to Part 2 of the Alkali Guidelines (c = cement content, NA = NA cement according to DIN 1164-10)

Aggregate is
- crushed aggregate according to Part 3 or is gravel with more than 10% crushed aggregate according to Part 3

Test according to Alkali Guidelines
accelerated mortar bar test/concrete prism test

E I-S (non-reactive)	**E III**-S 2) (reactive)
No restrictions Cements / cement contents aggregates **WO, WF, WA, WS** 1)	**No restrictions** Cements / aggregates c ≤ 300 kg/m^3: **WO, WF, WA, WS** 1) 300 < c ≤ 350 kg/m^3: **WO, WF** (WA with NA) c > 350 kg/m^3: **WO** (WF with NA)

1) Use of road paving cements
Follow the regulations of TL Beton-StB 07 and ARS

2) Applies also to aggregates that have not been assessed

Fig. V-21: ASR effects on building with concrete when using aggregates according to Part 3 of the Alkali Guidelines (c = cement content, NA = NA cement according to DIN 1164-10)

aggregates that are classified as E II (medium reactive) or E III (reactive). **Figures V-20** and **V-21** illustrate the fact that in many cases even for aggregates classified as E II or E III according to Parts 2 and 3 of the Alkali Guidelines either no measures at all are required or that technically reliable and economically feasible solutions are available. Moisture class WA applies to concrete structural elements that are often moist or moist for long periods of time while they are in use and which are exposed to an external alkali supply often or for long periods. Examples of this are structural elements exposed to seawater and elements that are exposed to de-icing salt with no additional high dynamic stress, such as paved and parking areas in multi-storey car parks or bridge caps (Table V-3).

Concrete road pavements and airfields require special treatment in the regulations because of the particular stress that they are subject to. Therefore, General Circulars on Road Constructions issued by the German Federal Ministry of Transport, Construction and Housing will continue to include requirements above and beyond the regulations contained in the Alkali Guidelines. These circulars allow flexible responses to new developments – such as the recent introduction of exposed aggregate concrete. In future, the Alkali Guidelines will thus include a description of moisture class WS. But the regulations for this moisture class will be included in TL Beton (German technical requirements of delivery for concrete) (see the section on road construction) and perhaps also in the General Circulars on Road Constructions. Preventive measures regarding concrete for airfields are not covered by the Alkali Guidelines, but have to be determined by experts because special de-icing agents are applied on airfields.

Alkali reactivity of concrete compositions

For aggregates that are classified as medium reactive (E II-O, E II-OF) or reactive (E III-O, E III-OF, E III-S), the Alkali Guidelines require that measures must be taken depending on the moisture class of the structural element and the cement content. In the past, these measures have included replacing the aggregate or using cements with a low effective alkali content (NA cement). So as not to unnecessarily exclude aggregates or cements from being used, the suitability of a concrete composition can be investigated in performance tests within the scope of expert opinions. The test allows a statement to be made as to whether for a specific concrete composition there is a risk of an ASR damaging the concrete in relation to its exposure (moisture class). To simulate impingement with de-icing agents or salts, concretes for moisture classes WA and WS and for airfields are tested with an external alkali supply.

In Germany, the accelerated concrete prism test at 60 °C with and without external alkali supply and the alternating climate method are currently used as performance test procedures. The procedure may be included in a future Part 4 of the Alkali Guidelines.

Comparative investigations for the performance test were conducted at the Research Institute (accelerated concrete prism test at 60 °C with and without external alkali supply) and at Bauhaus University Weimar (climate simulation chamber). As a basis for the performance tests a practice-oriented concrete formulation with w/c = 0.42, c = 370 kg/m^3, air-

Table V-3: Moisture classes according to the Alkali Guidelines or DIN 1045-2

Name of class	Description of the environment	Examples for allocating exposure classes (informative)
WO	Concrete, which after normal curing is not moist for long periods and which remains largely dry after it has dried out under normal use.	Interior elements in building construction; Building elements which are exposed to outdoor air but not, for example, atmospheric water, surface water or soil moisture and/or which are not constantly exposed to relative humidity of more than 80 %.
WF	Concrete that is moist often or for long periods during normal use.	Unprotected outdoor building elements that are subject, for example, to atmospheric water, surface water or soil moisture; Interior building elements in building construction for wet rooms, such as indoor swimming pools, laundries and commercial wet rooms in which relative humidity is generally higher than 80 %; Building elements that are regularly below the dew point, such as chimneys, heat transfer stations, filter chambers and cattle sheds; Bulky building elements according to the DAfStb Guideline “Bulky concrete building elements”, whose smallest dimension is larger than 0.80 m (regardless of the presence of moisture).
WA	Concrete which, in addition to stress according to Class WF is subjected to an external alkali supply frequently or for long periods.	Building elements exposed to seawater; Building elements exposed to de-icing salt with no additional high dynamic stress (e.g. spray water areas, driving and parking areas in multi-storey car parks); Building elements in industrial and agricultural buildings (e.g. manure tank) exposed to alkali salts. Concrete road surfaces in Class IV -VI [1]
WS	Concrete that is subjected to high dynamic stress and an external alkali supply.	Building elements exposed to de-icing salt with additional high dynamic stress (concrete road pavements in Classes SV and I -III) [1]

[1] Building classes according to RStO; according to TL Beton-StB 07

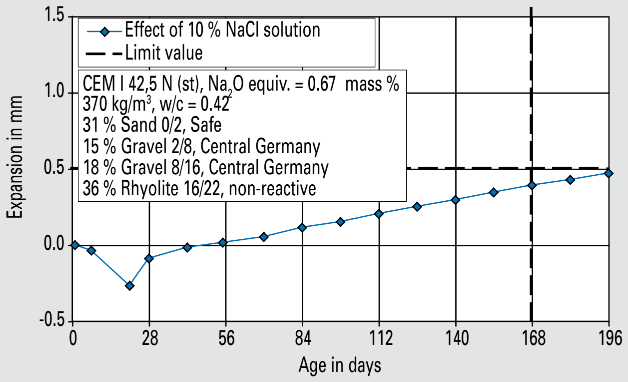


Fig. V-22: Expansion of concrete in accelerated concrete prism test with external alkali supply

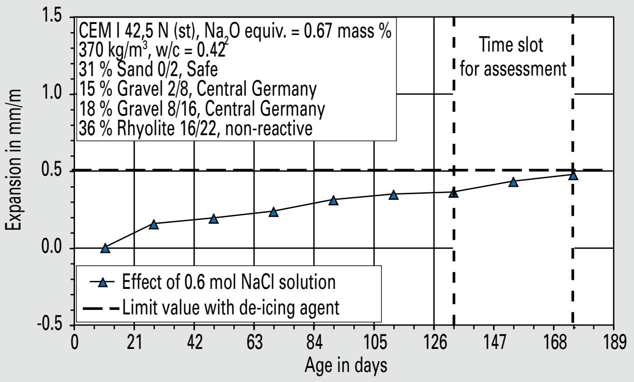


Fig. V-23: Expansion of concrete in FIB alternating climate test with de-icing effect

entraining admixture (air content 4.5 ± 0.5 % by volume) was used.

As variables, five different alkali-reactive aggregates and four Portland cements CEM I (32,5 R and 42,5 N) with Na_2O equivalent values in the range between 0.56 and 0.89 mass % were included in the test programme. **Figures V-22** and **V-23** show the expansion of a concrete during the accelerated concrete prism test at 60 °C with a 10 % sodium chloride solution and in the climate simulation chamber with a 0.6 mole sodium chloride solution. To summarise, the investigations produced the following picture:

- A total of 12 concrete compositions for concrete road pavings were tested with FIB alternating climate test (ASR performance test) and the accelerated concrete prism test at 60 °C with and without external alkali supply (NaCl).
- In the examination of concrete compositions in moisture class WS in performance tests with external alkali supply, similar results were obtained for 11 concrete compositions with both methods; the results differed for only one concrete composition
- The same results were obtained when 12 concretes were tested for moisture class WF (without alkali supply).

Test cement

A test cement with a high alkali content was used to test the alkali reactivity of aggregates according to Part 3 of the Alkali Guidelines. Cement that fulfils the re-

Table V-4: Cements and alkali contents

Cement	Cement type	Works	K_2O in mass %	Na_2O in mass %	Na_2O equiv. in mass %
Test cement A	CEM 32,5 R	C	1.52	0.26	1.26
Test cement B	CEM 32,5 R	D	1.55	0.18	1.20
Cement 1	CEM 32,5 R	A	1.02	0.20	0.86
Cement 2	CEM 32,5 R	B	1.21	0.13	0.93
Cement 3	CEM 32,5 R	C	1.19	0.24	1.02

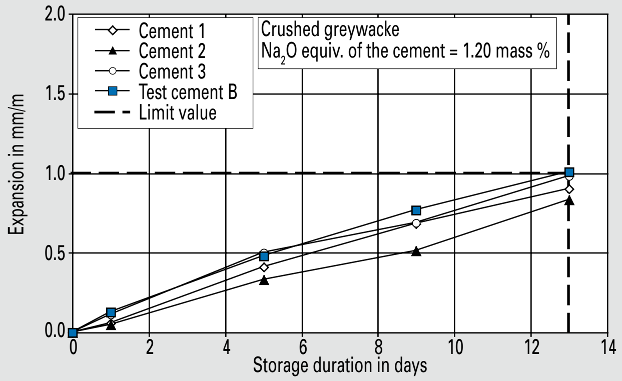


Fig. V-24: Expansion of mortar bars in the accelerated mortar bar test with the reference method according to the Alkali Guidelines

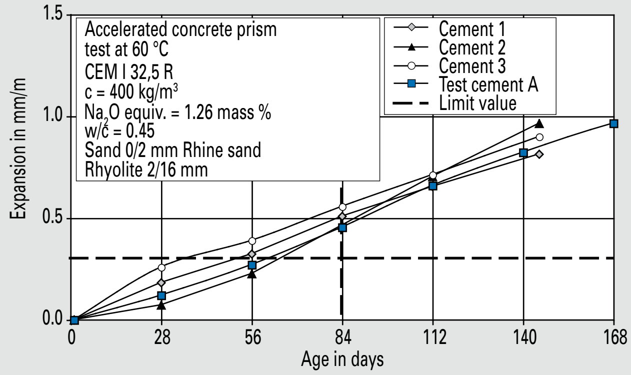


Fig. V-25: Expansion of concrete prisms in the accelerated concrete prism test at 60 °C with concrete containing different cements and an Na_2O equivalent of 1.26 mass % in relation to the cement

quirements of a test cement according to Part 3 of the Alkali Guidelines is no longer available in Germany. The Research Institute conducted experiments in order to make recommendations for future requirements for a test cement according to the Alkali Guidelines.

For this purpose three Portland cements with an Na_2O equivalent of (0.90 ± 0.15) mass % were chosen (**Table V-4**). The cements were boosted with potassium sulphate to obtain an Na_2O equivalent of 1.20 and 1.26 mass % (alkali content of earlier delivery batches of the test cement, described below as Test cement A and Test cement B).

Cement pastes were manufactured with the boosted cements. The chemical compositions of extruded pore solutions and supernatant solutions according to TGL 28104/17 were determined. The pH values of the boosted cements were similar to those of Test cement A. The addition of potassium sulphate is suitable to obtain a similar pH value in the pore solution to that of the unboosted cement.

Accelerated mortar bar tests (reference method according to Alkali Guidelines) were carried out using a crushed greywacke and the boosted cement. In all cases, the investigations would lead to the aggregate having the same classification in the alkali reactivity class E I-S (**Fig. V-24**). The accelerated mortar bar test with Cement 3 reproduced the results of the test with the test cement best of all.

Accelerated concrete prism tests at 60 °C according to Part 3 of the Alkali Guidelines, informative appendix B, were carried out with crushed rhyolite (**Fig. V-25**). In the case of the boosted cements, expansion after 84 days at 0.47 mm/m, 0.51 mm/m and 0.56 mm/m was slightly higher than the expansion of 0.45 mm/m in the event of Test cement A. Cement 3 exhibited the most expansion. In the accelerated concrete prism test at 60 °C using boosted cements and unboosted Test cement A, the aggregate was identified as being alkali reactive.

Effect of alkali reactivity of test sands on the assessment of potentially alkali-reactive aggregates

To test potentially alkali-reactive aggregates the Alkali Guidelines specify, among other things, concrete tests in which the aggregates with a particle size of > 2 mm are used. As a particle fraction < 2 mm an "inert natural sand" is to be used. Test samples are made from the concrete which are investigated in aggregate tests (concrete prism test with fog chamber curing (40 °C), accelerated concrete prism test at 60 °C).

In a previous test of an aggregate in combination with different sands, different expansion behaviour was observed in the concrete, which may be attributable to alkali reactivity of the quartz sand fraction in laboratory tests, which should actually be inert. According to our current knowledge, there are no adequate criteria that could prove the suitability of a test sand for aggregate tests. Consequently, assessments of coarse aggregates in which an unsuitable sand is used could have systematic errors.

To quantify the effects of a not completely inert test sand on the results of ASR concrete prism tests, a research project was initiated and funded by the German Federation of Industrial Research Associations (AiF).

Firstly, natural sands rich in quartz from various regions were selected, which differed in terms of their mineralogy and particle size distribution. In addition, crushed aggregates < 2 mm from pure limestone were used as an inert sand and crushed aggregates from alkali-reactive greywacke with a similar particle size were used as reactive sand. The characterisation of the

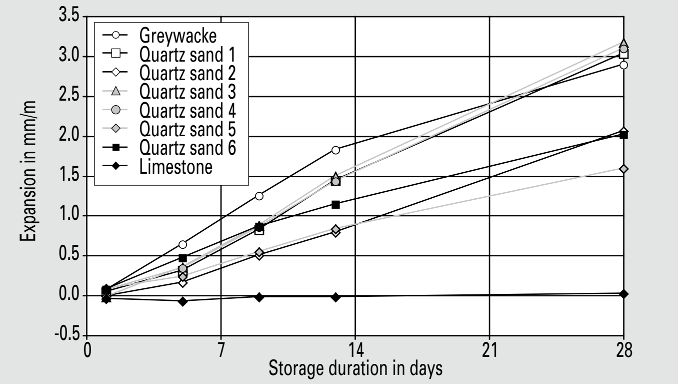


Fig. V-26: Expansion of mortar bars in the accelerated mortar bar test with the reference method according to Part 3 of the Alkali Guidelines for different sands

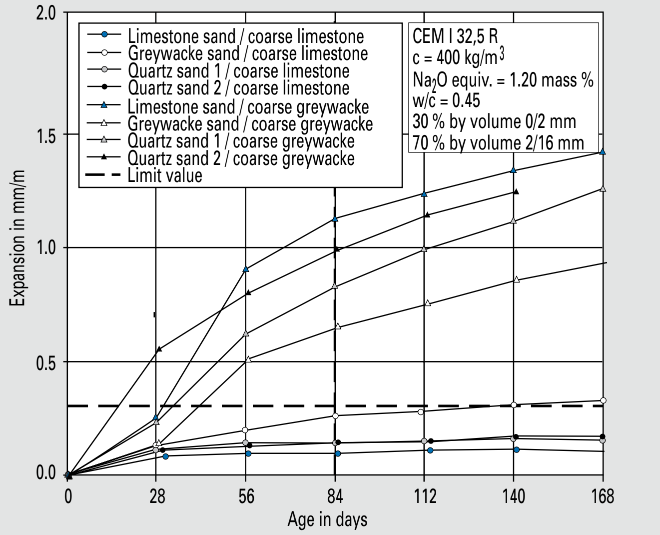


Fig. V-27: Expansion of concrete prisms in the accelerated concrete prism test at 60 °C for different combinations of sand and coarse aggregates

sands (petrography, alkali solubility, calcium-binding capacity) show differences in the detail, but it is not possible to clearly identify reactive sands. The test according to ASTM C289 (soluble silica) also showed no differences between the sands. In the accelerated mortar bar test the use of sands instead of crushed aggregate produced different expansion behaviour in some cases (**Fig. V-26**). All quartzitic sands caused increased expansion in the mortar; however, in some types a degressive tendency was exhibited. Other sands produced a constant increase in expansion, so that with an extended testing period even the expansion of the mortar with the reactive crushed greywacke sand was exceeded.

These sands were chosen for the accelerated concrete prism test and were combined with inert limestone or reactive coarse aggregate in a ratio of 30 % sand to 70 % coarse aggregate. The concretes were manufactured with a test cement according to the Alkali Guidelines. The concretes were tested according to the Alkali Guidelines with fog chamber storage at 40 °C, with storage in an outdoor exposure site and with the accelerated concrete prism test at 60 °C. Regardless of the test method used, the reactivity of the sands suggested in the accelerated mortar bar test had no effect on the assessment of the aggregate (**Fig. V-27**). Concrete expansion was achieved only with the reactive crushed greywacke sand in combination with inert limestone, which was in the range of the preliminary limit value. In some cases, the combination of quartzitic sands with the reactive aggregates led to less concrete expansion than when inert crushed limestone sand was used. However, in every case the expansion values were well above the limit value set for the test method. In other words, there is no need to fear incorrect classification of alkali-reactive aggregates as a non-reactive aggregate because of the reactivity of quartzitic test sand. To estimate whether the observed minor effects have any effect on the performance test of concrete compositions, more investigations are currently being carried out on concrete made with road paving cement (CEM I with Na_2O equivalent ≤ 0.80 mass %) and CEM II/B-S.

Field site tests

As with all laboratory tests on concrete that are relevant to the durability of the concrete, it is important to ensure that the results from these tests can be transferred to how the concrete actually behaves in actual construction situations. The EU PARTNER project, partially funded by the European Union, had the overall objective of establishing a unified test procedure for evaluating the alkali reactivity of aggregates. In the project, the suitability of RILEM test methods and some regional test procedures have been investigated with different aggregates and types of aggregates that are excavated throughout Europe. The results of the accelerated laboratory tests were compared with the behaviour of these aggregates in real concrete structures and in concrete samples stored in field test sites. The Research Institute was in charge of the field tests.

To take account of different climatic conditions in Europe, the behaviour of concrete samples in various field sites was investigated. One of the issues pursued in the project was whether concrete that is partially submerged in water is damaged faster and more severely as a result of an ASR than concrete that is only exposed to ambient rainfall. Laboratory tests in the past have also shown that concrete samples containing reactive aggregates expand more when they are exposed to a de-icing salt solution rather than water. Therefore, it is generally assumed that de-icing salt could facilitate a damaging ASR in concretes containing reactive aggregate.

For the field site tests all the concrete cubes were manufactured for every aggregate combination and every aggregate. These were then transported to the laboratories and field sites of the participating partners. 13 aggregate combinations with which concrete was manufactured in 5 laboratories were monitored and investigated in 8 different field sites from Norway to Spain. (**Fig. V-28**). In Sweden, samples were stored in a forest in Borås and beside a motorway between Borås and Goteborg to examine the added effects of external alkali supply.

For each field site two 300 mm concrete cubes were made for each aggregate combination that was to be investigated. The concrete composition corresponded to that of the concrete prisms in the RILEM tests AAR-3 (concrete prism test at 38 °C) and AAR-4 (accelerated concrete prism test at 60 °C).

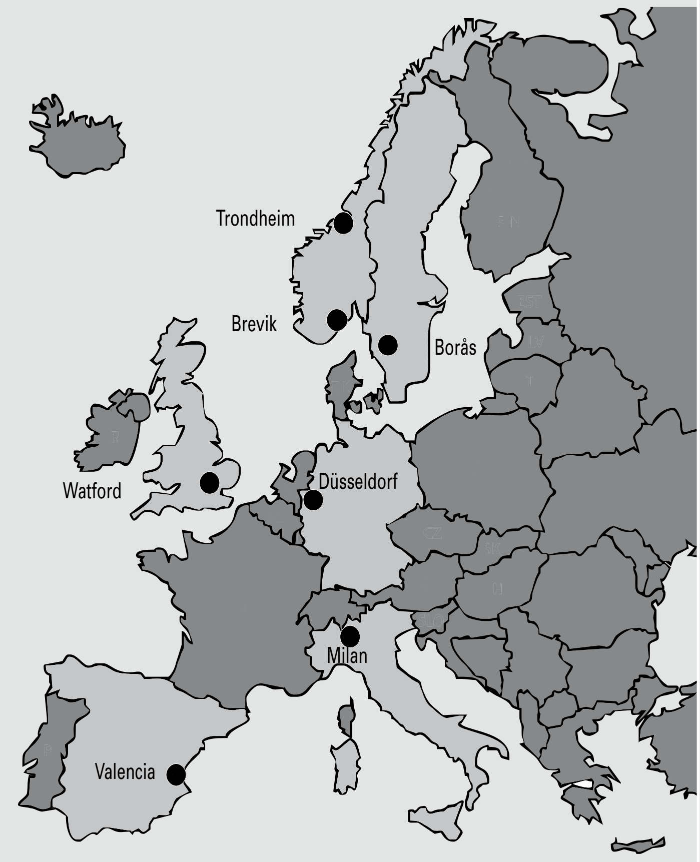


Fig. V-28: Location of outdoor exposure sites

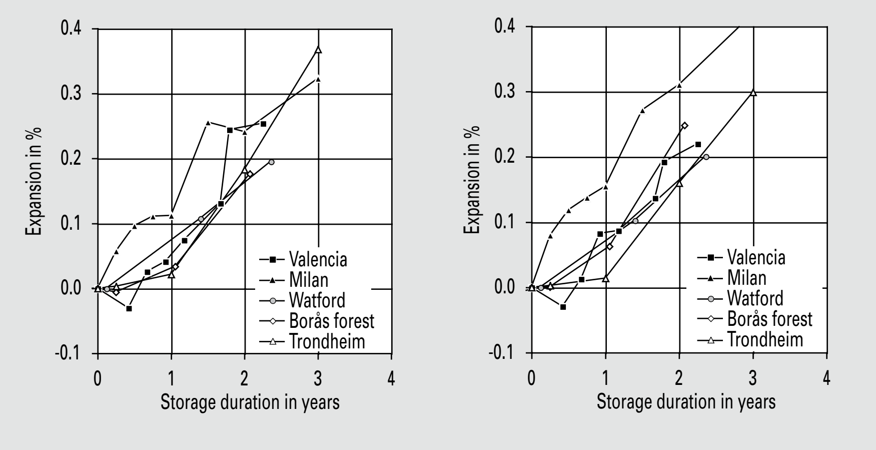


Fig. V-29: Average expansion of concrete cubes B1(C+NRF); left: the bottom of the cube is submerged in water to about 5 cm; right: the cube is exposed only to ambient rainfall

The samples were manufactured with a cement content of 440 kg/m³ and a Portland cement with a high alkali content (1.26 mass % Na_2O equivalent). To record any damage resulting from an ASR, the length changes on the top side and on two opposite sides as well as the width of any cracks were periodically recorded.

In 2008, the samples had been stored outdoors for about 4 years. For slowly reacting aggregates this period is too short to cause a damaging ASR. Because of this, it is only possible to draw preliminary conclusions. **Table V-5** shows the current results of the field site tests and the laboratory experiments together so that a comparison can be made. The results of the accelerated laboratory tests were taken from other subprojects of the PARTNER project.

The concrete cubes with aggregate composition B1(C+NRF) exhibit a lot of expansion > 0.04% (**Fig. V-29**) and cracks with a maximum width of ≥ 0.20 mm in all field sites from Norway to Spain, regardless of how they were stored.

Aggregate mixtures D2, G1, N1 and UK1 expanded more and had larger cracks in mild (Düsseldorf, Watford) and in warm climates (Milan, Valencia). **Fig. V-30** illustrates this for aggregate mixture N1, which showed high expansion in Valencia, Düsseldorf and Watford, but which, to date, has not expanded in cold climates (Borås, Trondheim). The increase in expansion was higher in Southern Europe (Valencia) than in Central Europe (Düsseldorf, Watford). **Fig. V-31** illustrates the expansion of aggregate composition G1, the crushed gravel from the Upper Rhine Valley.

The results suggest that a damaging ASR occurs in a similar manner in North and Southern Europe, the only difference being that with the same concrete composition the reaction can take place quicker in Southern Europe – which can probably be attributed to the higher average temperature.

It is also noteworthy and surprising that the samples which were exposed only to ambient rainfall expanded more and exhibited larger cracks than the samples that were stored partly immersed in water.

To date no differences have been detected in the behaviour of the concretes stored in a forest in Borås (without alkali supply) and alongside a motorway between Borås and Goteborg in Sweden (with external alkali supply).

After 4 years outdoor storage, the slowly reacting aggregates IT2, N2, N4, S1 and P1 and the non-reactive aggregates F1 and F2 are not exhibiting any noticeable expansion or cracks.

One of the conclusions of the PARTNER project was that in most cases the RILEM test procedures were suitable for identifying the alkali reactivity of the investigated aggregates (see Table V-5). The tests were especially suitable for identifying aggregate combinations that either react within a “normal” time scale (i.e. 5 to 20 years) or which are non-reactive. There was less certainty as regards identifying slowly reacting aggregates that react after more than 20 years. Further tests must be carried out to see whether these experiences can be generalised. Generally, in the cases where differences were observed between the results from the laboratory tests and practical experience, they can be attribut-

Table V-5: Comparison of results from laboratory tests with behaviour in field sites and structures; the results are taken from other sub-projects of the PARTNER project

Aggregate	Fraction/ Combination	Reactivity/Evaluation							
		AAR-1	AAR-2	AAR-3	AAR-4/ AAR-old	TI-B51/ Chatterji	Germany/ Norway	Field site test after 4 years*	Reported reactivity in structures?
“Normally” reactive aggregate combination									
B1 - Silicified limestone	F	R	R			R/R			Yes
	C	R							
	C+F			R	R/R		R/R	R	
	C+NRF			R	R/R			R	
UK1 - Greywacke	F	R	R			R/R			Yes
	C	R							
	C+F			R	R/R		R/R	R	
G1 - Crushed Gravel with siliceous limestone and chert	C	R	R			R/-			Yes
	C+NRF			R	R/R		R/-	R	
G2 - Gravel with opaline sandstone and flint	C	R	R			R/-			Yes
N1 - Cataclasite	C	R	R			R/R			Yes
	C+NRF			R	R/R		R/R	R	
D2 - Sea Gravel with semi-dense flint	F	R	R			R/R			Yes, 10 - 15 years
	C	R	R						
	F+NRC			NR/MR	R/MR			R	
“Slowly” reactive aggregate combination									
IT2 - Gravel with quarzite	F	R	R			NR/-			Yes, 50 years
	C	R	R						
	C+F			NR	R/R			n.r.	
N2 - Sandstone	C	R	R			NR/R			Yes, 15 - 20 years
	C+NRF			R			-/R	n.r..	
N4 - Gravel with sandstone and cataclastic rocks	F	R	R			R/R			Yes, 20 - 25 years
	C	R	R						
	C+F			MR	R/-		MR/MR	n.r.	
“Non-reactive” aggregate combination									
F1 - Gravel with flint	C	R	NR			NR/R			No, but known pessimum effect
	C+NRF			NR	NR/NR		NR/-	n.r.	
F2 - Non-reactive limestone	F	NR	NR						No
	C	NR							
	C+F			NR	NR/NR		NR/NR	n.r.	
S1 - Gravel with metarhyolite and greywacke	F	R	R			R/R			Yes, but source variable in composition
	C	R							
	C+F			NR	MR/-		NR/MR	n.r.	
P1 - Silicified limestone	C	R	NR			NR/-			Yes, but the information about the aggregate is uncertain
	C+NRF			NR	MR/MR			n.r.	

F = fine aggregate
C = coarse aggregate
NRF = non-reactive fine aggregate (=N3F)
NRC = non-reactive coarse aggregate (=F2C)
R = reactive (according to the limit values for the different test methods)
NR = non-reactive (according to the limit values for the different test methods)
MR = marginally reactive (i.e. expansion was just above the limit value for the different test methods)
n.r. = no rating yet possible
* = The evaluation of preliminary results from the field site tests is based on measuring the maximum width of the crack after 4 years of storage outdoors and expansion during the last 3 years (measurement of expansion was re-started in 2005 as there were problems with zero measurement in some of the field sites.)
AAR-1 = RILEM method AAR-1: petrographic method
AAR-2 = RILEM method AAR-2: accelerated mortar bar test at 80 °C in 1 mole sodium hydroxide
AAR-3 = RILEM method AAR-3: concrete prism test at 38 °C
AAR-4 = RILEM method AAR-4: accelerated concrete prism test at 60 °C
TI-B51 = Danish accelerated mortar bar test at 50 °C in a saturated sodium chloride solution
Chatterji = Chemical test method according to Chatterji
Germany = Concrete test on concrete bars and cubes with storage in the 40 °C fog chamber according to the Alkali Guidelines
Norway = Norwegian concrete prism test at 38 °C

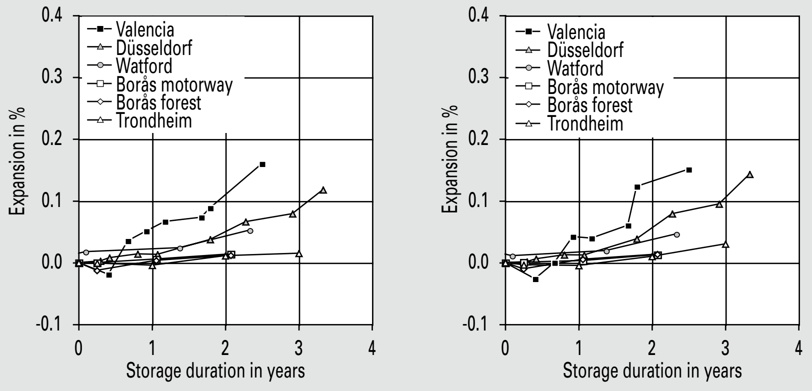


Fig. V-30: Average expansion of concrete cubes N1; left: the bottom of the cube is submerged in water to about 5 cm; right: the cube is exposed only to ambient rainfall

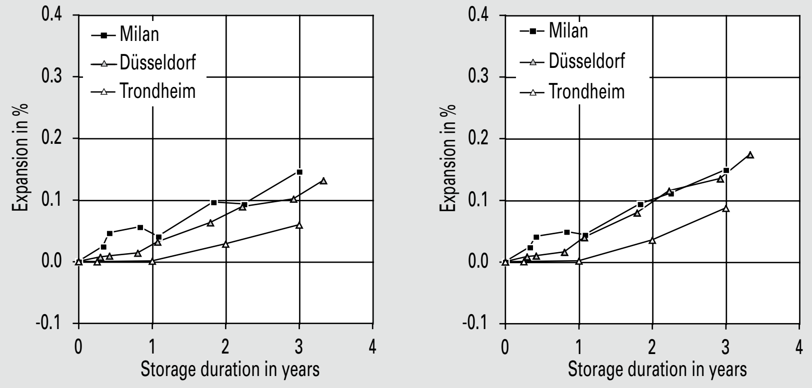


Fig. V-31: Average expansion of concrete cubes G1; left: the bottom of the cube is submerged in water to about 5 cm; right: the cube is exposed only to ambient rainfall

ed to variability in the aggregate source, pessimum behaviour or unreliable information about the behaviour of the aggregates under practical conditions. In many cases, the accelerated mortar bar test (RILEM AAR-2) and the accelerated concrete prism test at 60 °C (RILEM AAR-4) mirrored practical experience. One exception seems to be aggregates with pessimum behaviour. Thus, these procedures are suitable to assess aggregates with no pessimum behaviour against the background of local experience where these damage cases appear necessary in practice.

Sulphate resistance

In 2006, the German Committee for Structural Concrete (DAfStb) initiated a special research project entitled “An in-depth investigation into the sulphate resistance of concrete”. Funded by the German Concrete and Construction Engineering Association (DBV), the German Ready-Mixed Concrete Industry Association (BTB), VGB Power Tech and VDZ, experiments were started to underpin the existing sulphate resistance regulation when concretes containing fly ash are used. In particular, the aim was to check the results of laboratory-based experiments by means of field storage experiments under natural sulphate attack conditions. The series of experiments were started at the end of 2006. After a two-year exposure period, the findings obtained up until that point were aggregated in the form of a report at the beginning of 2009. Apart from the Research Institute of the Cement Industry (FIZ), the research programme also involved the Centre for Building Materials at the Technical University of Munich (cbm) and the F. A. Finger-Institute for Building Material Science at (FIB) Weimar University.

Effects of aggregate containing carbonate/test in synthetic soils and waters

In particular, investigations in the UK showed that in the event of a sulphate attack, carbonate from the binder or from the aggregate can act as a reaction partner, leading to damage as a result of thaumasite formation. Since these results were published, cements and aggregates containing limestone are suspected of having a negative effect on the sulphate resistance of standard concretes. Since in addition to that only quartzitic sands and gravels are used in the normal sulphate resistance tests, there is a lack of experience as regards the effect of aggregates containing carbonate. For this reason, in the Research Institute’s work package concrete test samples were manufactured with quartzitic and carbonate aggregates and subjected to a sulphate attack similar to the attacks that take place in practice. **Table V-6** shows the formulations of the concretes used in the research programme.

The Research Institute carried out the field storage experiments in a gypsum/anhydrite opencast mine in the state of Lower Saxony, Germany. A total of 60 concrete test samples were stored in a calcium sulphate saturated lake near Stadtoldendorf. After one and two years’ exposure, test samples were removed from the lake and investigated. The remaining samples are to be stored as long as possible in the sulphurous lake water (10 years storage is planned). Only then will it be possible to make statements about the long-term behaviour of the concretes.

In the second focus of the Research Institute’s investigation, concrete test samples were subjected to a defined practice-related sulphate attack in a synthetic soil. A 300-l plastic tank, called a lysimeter, was filled with alternate layers of limestone chippings, greywacke chippings and meal, quartz sand and potting soil. The concrete test samples were then stored in this “synthetic soil”. The sulphate attack was carried out using a sodium sulphate solution (1 500 mg sulphate per litre), with which the soil material was saturated. At regular intervals the sulphate solution was drained off so that the soil could be dried and then filled with a fresh solution. This simulated natural fluctuations in the groundwater. The soil was kept at 8 °C, which is the average soil temperature in Germany.

Table V-6: Names and formulations of the six concretes; Figures in kg/m³ or mass % of the cement

	M1	M2	M3	M4	M5	M6
Cement type	CEM I-SR	CEM I-SR	CEM III/B	CEM III/B	CEM I	CEM II/A-LL
Cement content	360	360	360	360	327	327
Fly ash	–	–	–	–	82	82
Water	180	180	180	180	180	180
Q 0/02	98	–	97	–	–	94
Q 0/2	409	–	407	–	–	393
Q 1/2	80	–	79	–	–	77
Q 2/8	569	–	566	–	–	547
Q 8/16	622	–	619	–	–	698
K 0/2	–	591	–	587.5	569	–
K 2/8	–	591	–	587.5	569	–
K 8/16	–	665	–	661	641	–
Q/K total	1 778	1 847	1 768	1 836	1 779	1 709
FM	–	1 %	–	0,75 %	2 %	–

Q: quartzitic aggregate
K: carbonatic aggregate (limestone)

Results

Water samples were taken and analysed at the start of the investigation and every time the samples were assessed. In the lake water the sulphate concentration fluctuated between about 1 500 and 1 800 mg/l. Apart from about 600 mg/l calcium, roughly 500 mg/l of sodium and approximately 50 to 70 mg/l magnesium were discovered as cations (**Table V-7**). According to DIN 4030, concentrations above 300 mg/l magnesium are classified as slightly severe in terms of the level of attack.

At the end of the observation period no damage was identified on the samples in the lysimeter or on those stored in the lake (**Fig. V-32**). No flaking, cracks or partial surface softening was observed. Partial surface discolouration can be attributed to algae deposits and contact with various surrounding materials (e.g. the soil). **Fig. V-33** shows the compressive strengths of the samples. Even in the second year, an increase in strength was identified in all six concretes. Although no damage was identified, investigations were carried out on hardened concrete structures near the edge using scanning electron microscopy (SEM). In all of the concrete samples, undisturbed, dense structures were observed with no signs of expansion reactions or structural weakening.

Table V-7: Sulphate and cation contents of water samples from the lake and the lysimeter

Lake		January 2007	July 2007	January 2008	July 2008	March 2009
Sulphate	mg/l	1 825	1 744	1 482	1 774	1 477
Calcium	mg/l	–	610	588	656	564
Sodium	mg/l	–	568	527	564	183
Potassium	mg/l	–	12.3	8.2	9.6	6.5
Magnesium	mg/l	–	70.2	61.3	73.8	49.8
Lysimeter		February 2007	July 2007	January 2008	July 2008	January 2009
Sulphate	mg/l	1 449	1 197	1 537	1 514	1 152
Calcium	mg/l	235	96	102	115	106
Sodium	mg/l	432	685	788	749	760
Potassium	mg/l	158	62.0	48.7	50.3	37.4
Magnesium	mg/l	–	–	13.3	12.4	17.9

Fig. V-32: Concrete test samples after two years storage in the lake of a gypsum/anhydrite opencast mine and in the lysimeter (synthetic soil)

In contrast to the results of the Research Institute, in the FIB field storage experiments damage was discovered on the concretes manufactured with Portland-limestone cement and fly ash (M6). The concrete test samples stored in water in a gypsum cave containing sulphate exhibited signs of flaking and surface weakening after just one year. Ettringite and thaumasite had formed. The reasons for these different observations are to be clarified in supplementary investigations. These investigations are being funded by the

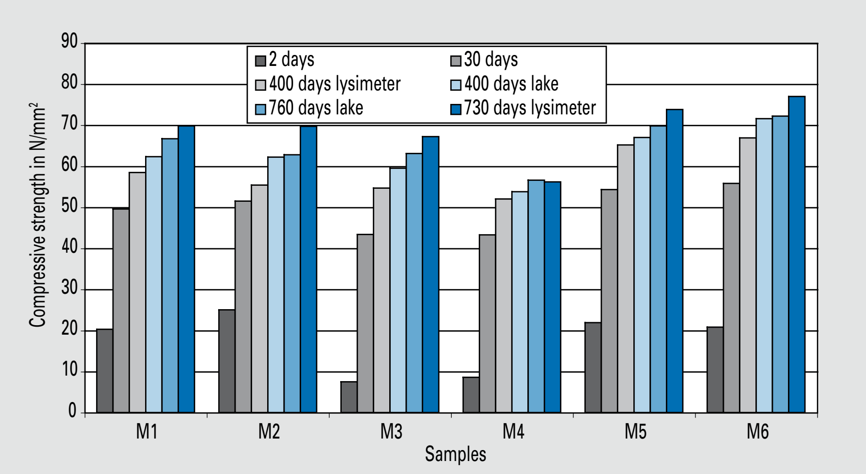


Fig. V-33: Changes in compressive strength in concrete test samples stored for two years in a lake and in synthetic soil (lysimeter)

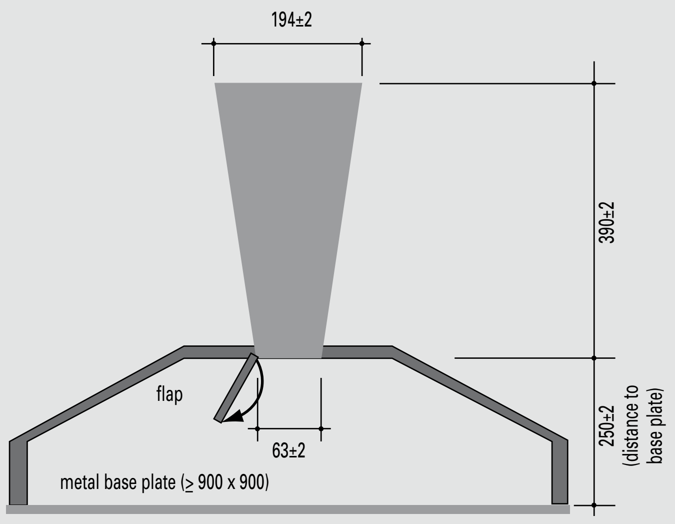


Fig. V-34: Diagram of the flow cone and the slump flow plate, dimensions in mm

Table V-8: Precise data for cone slump flow and cone flow time determined with the flow cone in mm or as a % of the average value. Values in brackets calculated from data from a European round robin test (slump flow according to EN 12350-8, flow time according to EN 12350-9)

Cone slump flow	in mm	in % of the average value
Repeatability r	29	3.9 (approx. 2.5–7.5)
Reproducibility R	81	10.8 (6.0)
Cone flow time	in s	
Repeatability r	1.1	20.8 (approx. 30–40)
Reproducibility R	1.4	28.4 (39.0)

German Committee for Structural Concrete (DAfStb). The research facilities named above are again involved in these investigations. The particular focus is on the simultaneous effect of sulphate and magnesium. In the mountain cave water (FIB investigation) magnesium concentrations of up to 180 mg/l were measured.

In conclusion, it can be said that the core statements of the DAfStb status paper “Sulphate attacks on concrete” from 2003 still apply: “Where the standard definitions for concrete with a high sulphate resistance have been complied with, no damage has been reported to date.”

Self-compacting concrete ■

To assess the workability of self-compacting concretes, according to the DAfStb Guidelines for “Self-Compacting Concrete” the slump flow and the V-funnel flow time are to be tested during the initial test, the manufacturing works’ own production control and when the concrete is delivered to the building site. According to the DIN EN 12350 series of standards, two separate test procedures are necessary, namely the slump-flow test according to Part 8 and the V-funnel test according to Part 9. An alternative to these procedures is the flow-cone test, in which a cone slump flow and a cone flow time can be determined in one experiment on a concrete sample.

Precise data for the flow cone

The flow cone (**Fig. V-34**) was developed in the Research Institute of the Cement Industry between 2002 and 2006. In earlier experiments it was shown that there was no significant difference between cone slump flow and slump flow according to DIN EN 12350-8. Cone flow time is proportional to the flow time according to DIN EN 12350-9. Previously there has been a lack of precise data that would allow the process to be standardised throughout Europe. This was determined in a round robin test managed by the Research Institute. The round robin test was funded by the German Ready-Mixed Concrete Association, the German Society for Concrete and Construction Technology and the German Cement Works Association.

Concrete testers from four companies in the ready-mixed concrete industry were invited to the Research Institute. Together with a concrete tester from the Institute, over a period of two days they tested seven mixtures of a self-compacting concrete with the flow cone. In accordance with DIN EN 12350, the self-compacting concrete (powder type) used for the tests had an average slump flow of 770 mm and an average flow time of 5.0 seconds. To determine the precise data according to ISO 5725-2, a 5 % error probability was assumed. The reproducibility R (different testers) and the repeatability r (one tester) was then 2.78 times the standard deviation. Accordingly, with a 95 % probability the maximum difference between two individual results is r or R. **Table V-8** shows the precise data that was determined for testing the cone slump flow and the cone flow time with the flow cone. The values in brackets show the results of a round robin test for corresponding tests according to DIN EN 12350 Parts 8 and 9 as a comparison.

Ultra-high performance concrete ■

Due to its very dense structure, ultra-high performance concrete (UHPC) is extremely durable when it is undamaged. However, it has not yet been clarified whether and under which conditions cracks that have a negative effect on the durability of the material can occur due to the high autogenous shrinkage of the concrete. Since the end of 2005, the Research Institute of the Cement Industry has been funded by the German Research Foundation (DFG) within the scope of the priority programme “Sustainable building with ultra-high performance concrete” to carry out research work into this aspect, which is very important for practical applications.

Tafel V-9: Investigated concrete compositions (data in kg/m^3)

	1 A	1A SAP	1 A SRA	1A HSM
Cement (c) 1)	800	800	800	200
Mixing water (w)	168	168	168	176
Silica fume (s) 2)	130	130	130	130
Super plasticiser 3)	24	24	24	13
Quartz sand 4)	1 019	1 019	1 000	1 019
Quartz meal 5)	220	220	220	220
SAP 6)	–	2.4	–	–
SRA 7)	–	–	7.56	–
GGBS 8)	–	–	–	600

1) CEM I 52,5 R-HS/NA
2) 16.2 mass % of cement; proportion of amorphous SiO_2 approx. 98%
3) Polycarboxylate ether basis (3.0 mass % of cement)
4) Particle size 0.125–0.5 mm
5) Particle size 0–0.125 mm
6) Super-absorbent polymers (0.3 mass % of cement)
7) Shrinkage-reducing admixture (4.5 mass % of cement)
8) Ground granulated blastfurnace slag

Free autogenous shrinkage

Autogenous shrinkage is the main shrinkage component in concretes that contain much less water than they require for the complete reaction of their hydraulically reactive constituents. This applies especially to UHPC. Here the equivalent water-cement ratio is usually between 0.15 and 0.25. Most autogenous shrinkage takes place in the first 24 to 48 hours. Since it is caused by inner drying and as UHPC has a very dense structure, it is difficult to affect autogenous shrinkage with external after-treatment. If deformation is prevented, which is often the case in practice, this can cause considerable restraint stress and result in a high cracking tendency.

Start and measurement of autogenous shrinkage

Autogenous shrinkage is part of the chemical shrinkage process. The latter starts when water and cement come into contact with each other; the reaction products occurring with hydration have a smaller volume than the starting materials. Autogenous shrinkage starts as soon as a solid pore system forms and the relative moisture in the initially water-saturated pores reduces due to continuing hydration. The inner drying of the increasingly solid structure causes a macroscopic volume reduction.

It is extremely difficult to determine exactly when inner drying starts. Therefore, experimental conventions are used to differentiate between autogenous chemical shrinkage and the chemical shrinkage that takes place prior to this. The start of autogenous shrinkage to be determined for specific concretes and in relation to the temperature with these conventions is called time-zero (t_0). According to the definition from the Japan Concrete Institute, the start of hardening is to be determined with the needle penetration method. However, the end of hardening is also often used as a criterion. In addition to this, numerous other methods have been proposed to determine time-zero, including the rate of shrinkage, ultrasound time-of-flight and the temperature changes. Depending on the criterion used, there can be vast differences in the determination of when autogenous shrinkage starts and, thus, on the results of the shrinkage.

Measuring the shrinkage is another difficulty. Worldwide there are many different test procedures in which autogenous shrinkage is measured linearly or volumetrically, horizontally or vertically and on test samples of different shapes and sizes. In combination with the above-mentioned issue of when to start the evaluation (time-zero), the different measuring methods have resulted in considerable variances in the past. It was thus necessary to improve the methodology. A new test procedure was therefore needed to provide evidence of good repeatability and reproducibility. It also had to be economical in order to allow as large a number of measurements as possible. Ideally, the measuring assembly needed to be a serially produced product that third parties could purchase. To investigate the effect of temperature on autogenous shrinkage, it needed to be possible to actively influence the temperature of the concrete. The experimental difficulties have prevented clarification of these connections in the past.

Against this background, a new method was developed with the help of the shrinkage cone from Schleibinger, which is usually used to investigate plastic shrinkage. With a large number of experiments, the new shrinkage cone method for determining autogenous shrinkage was optimised and its good repeat and comparison accuracy at a constant temperature of 20 °C was proven. The experiments will soon be continued for other temperatures with various European partners.

Restrained autogenous shrinkage

The “ring test” was adapted in order to investigate restraint stress and cracking tendency as a result of restrained autogenous shrinkage. This procedure is especially popular in the USA to investigate cracking tendency as a result of restrained drying shrinkage. The shrinkage reduction of a concrete ring is restrained by an internal steel ring. Strain gauges on the inside of the steel ring allow restraint deformation to be measured, from which it is possible to calculate the maximum tensile stress in concrete. To calculate cracking tendency the restraint stress that is determined is considered in relation to the tensile strength. A sudden reduction in the deformation of the steel ring indicates the formation of a larger crack.

In an extensive test programme, the cracking tendency of various ultra-high performance concretes was investigated (**Table V-9**). On the basis of a reference concrete (1A),

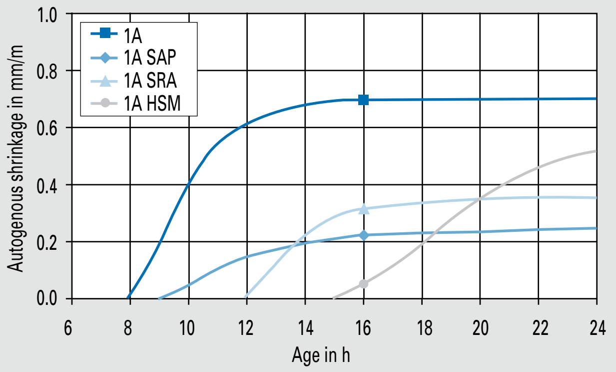


Fig. V-35: Autogenous shrinkage of concretes 1A, 1A SAP, 1A SRA and 1A HSM up to 24 hours, average values of 3 measurements with the shrinkage cone method, evaluations from the start of restraint stress in the ring test

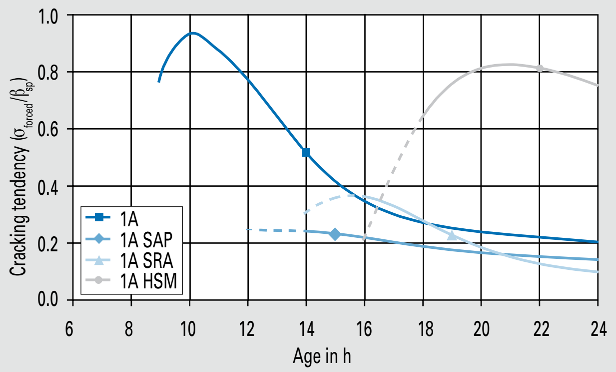


Fig. V-36: Cracking tendency as a ratio between restraint stress and tensile splitting strength, dotted area: extrapolated trend

through the use of super-absorbent polymers (1A SAP), a blastfurnace slag meal (1A HSM) and a shrinkage-reducing admixture (1A SRA), it was possible to reduce free autogenous shrinkage to various degrees (**Fig. V-35**). The cracking tendency reduced considerably in concretes 1A SAP and 1A SRA (**Fig. V-36**). In spite of less shrinkage, concrete 1A HSM still exhibited a similarly high cracking tendency to concrete 1A. This was mainly attributed to the very slow development of strength. Very small cracks, irrelevant for durability, developed in concrete 1A HSM. There were no visible cracks in the other concretes. With all concretes the maximum cracking tendency occurred in the first 24 hours. Up to about 70 % of the stress that would be expected with purely elastic behaviour of the concrete in this timeframe was compensated for by creep. With all concretes the level of restraint in the first 24 hours was in excess of 80 %.

In the investigations that were conducted the ring test proved to be a very promising method for testing autogenous shrinkage cracking tendency. This relatively simple method also has a lot of potential for further research. With the fine-particle concretes used here it was possible to choose cross-sections so small that quasi-isothermal and non-isothermal experiments would be easily possible. This is an important precondition for answering open questions about the effects of temperature. It will still have to be clarified to what extent the cracking tendencies determined here under quasi-isothermal conditions are suitable for describing the behaviour of concretes in the temperatures that are generally experienced in practice. The shrinkage cone method and the ring test are suitable methods for this purpose.

Earth-dry concrete ■

Earth-dry concrete is used for products such as paving slabs, paving blocks, kerbstones and concrete pipes. The concrete is compacted in steel moulds with an intensive vibration-compression process and can then be removed from the mould immediately, retaining the shape of the mould, due to what is known as green stability. When the composition is correctly formulated, the compressed concrete achieves a high level of stability and density as well as a high resistance to freeze-thaw with de-icing salt or chemical attack.

Modified slab test

The regulations for concrete products, standard series EN 1338, 1339 and 1340, are currently being revised. The modified slab test, a method for determining the resistance to freeze-thaw with de-icing salt attack, is on the test rig. Essentially, the method differs from the slab test according to DIN CEN/TS 12390-9 in terms of the size and properties of the test areas, the preliminary storage of the specimens, the test age and the number of freeze-thaw cycles (**Table V-10**).

The evaluation of about 40 tests by VDZ member companies using the modified slab test showed scaling of roughly 20 g/m^2 to approx. 850 g/m^2 after 28 freeze-thaw cycles. In practise no damages have been recorded for concrete products with such scaling. This would confirm that the maximum scaling of 1000 g/m^2 according to the standard is an adequate criterion for durable concrete products. In addition to the statistical variation, the main reasons for the somewhat large range of individual scaling results would appear to be the sampling procedure itself, the condition of the samples and the number of samples. Because of this, it is recommended that the number of samples be increased from the present three to at least five and that representative sampling is ensured. Experience and recommendations are being discussed intensively in the BDB-VDZ Discussion Panel „Quality of concrete construction components“ and the results of these discussions should be considered in the regulations.

Colour deviation in concrete products

The above-mentioned discussion panel also examined the possible causes of occasional colour deviations in concrete products. At present there is very little known about the causes for colour deviations in concrete products.

Currently, the discussion panel is developing an investigation programme in which the effects of the concrete composition, the cement properties and the production technology will be examined systematically.

Table V-10: Comparison between slab test according to DIN CEN/TS 12390-9 and modified slab test according to EN 1338 to 1340, Annex D

Parameter	Slab Test (DIN CEN/TS 12390-9)	Modified Slab Test (EN 1338 to 1340, Annex D)
Specimens	4 slabs 150 x 150 x 50 mm^3 A = 90 000 mm^2	7 500 < A < 25 000 mm^2, d < 103 mm, acceptance test: 3 blocks
Test area	sawn (centre of cube)	Surface
Curing	1d mould; 6d water 20 °C 21 d 20/65	–
Preliminary storage	3 d with 3 % NaCl	7 d in 20/65, 3 d H_2O, 0.25 to 0.5 h with 3 % NaCl
Test age at preliminary storage	28 d	≥ 28 d, at acceptance test: 35 d
Testing direction	one side	one side
T_{min}/T_{max}; adm. ΔT at T_{min} rate of cooling/thawing	-18 °C/+20 °C; to ± 2 K 2.5 K/h / 6.5 K/h	-18 °C/+20 °C; to ± 2 K 2.5 K/h / 6.5 K/h
Duration /number freeze-thaw cycles	24h / 56 freeze-thaw cycles	24h / 28 freeze-thaw cycles
Testing criterion (scaling)	< 1.0 kg/m^2 after 56 freeze-thaw cycles	< 1.0 kg/m^2 after 28 freeze-thaw cycles Indiv. value < 1.5 kg/m^3

Floor screeds ■

Cement-based floor screeds have been used in residential, commercial and industrial buildings for many years. Compared to other mineral bonded screeds they are superior in terms of resistance to moisture, which makes them ideal for indoor and outdoor use. The manufacture of cement screeds is a complicated process in which the choice of suitable constituents and the underlying conditions at the building site, such as transport, storage, mixing, pumping and laying at the location all play an important role.

Occasional problems in the manufacture of cement screeds in practice are still responsible for some reservations in the industry regarding the use of Portland-composite and blastfurnace cements in this area. The German Federal Association for Screeds and Coverings (BEB), based in Troisdorf, invited representatives from the cement and admixture industries to discuss their experiences as regards the use of CEM II cements in screeds. From the case studies it was not possible to show that the type of cement was the sole cause of any problems. Influences from the other constituents, the installation and the conditions at the building site must be included in the analysis. VDZ and its members examined the effects that the type of cement has on the properties of screeds.

The Research Institute assessed comparative studies of cement-based screeds with various cement compositions but otherwise with the same constituents and identical manufacturing and testing conditions. From a database of more than 700 individual results the following properties were analysed: workability and air content, strength development (**Fig. V-37**), final strength and surface strength, residual moisture (**Fig. V-38**), shrinkage and curling. No significant effect from the cement type could be identified and the structural engineering properties of cement screeds containing CEM I, CEM II and CEM III/A cements were similar in the laboratory and under practical building conditions. In the evaluated investigations any effects on the test results resulting from temperature, the shape of the test piece or the testing method were independent of the cement type used.

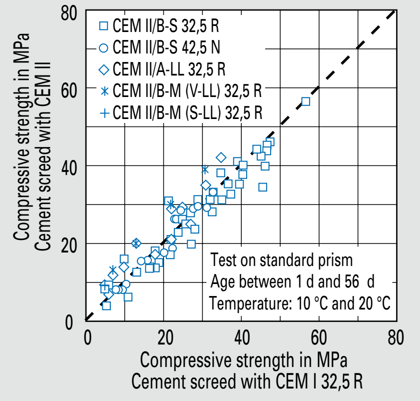


Fig. V-37: Compressive strength of cement-based screeds (c between 270 kg/m³ and 320 kg/m³; w/c between 0.42 and 0.79; with and without admixtures)

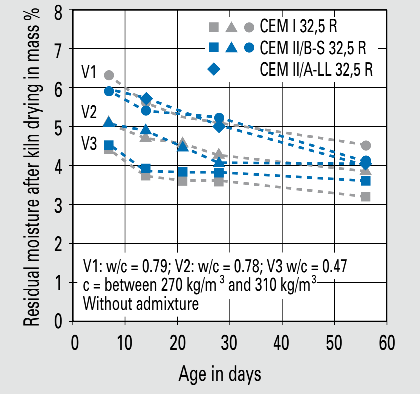


Fig. V-38: Age-related residual moisture after kiln drying at 105 °C

At present, mainly the following CEM II cements are used to manufacture cement screeds:

- Portland-limestone cement CEM II/A-LL 32,5 R
- Portland-burnt shale cement CEM II/B-T 42,5 N
- Portland slag cement CEM II/A-S 32,5 R
- Portland slag cement CEM II/B-S 32,5 R
- Portland slag cement CEM II/B-S 42,5 N
- Portland-composite cement CEM II/B-M (S- LL) 32,5 R.

In practice, screed installers have reported occasional problems (such as low surface strength, formation of cavities, slow drying) when they changed from CEM I cement to CEM II cement. In some cases reported from the industry, it appears that cements were used that are not subject to

Fig. V-39: Impregnating the concrete road surface with linseed oil

third-party inspection by the VDZ quality surveillance organisation and which were manufactured by companies that do not belong to VDZ. In some cases it has been reported that also "CEM II-M cements" were delivered with no data about the main constituents and without a conformity certificate or the national compliance marks. These products should not be used.

The meetings between the German Cement Works Association (VDZ), the German Federal Association for Screeds and Coverings (BEB) and the Federal Specialist Group for Screeds and Coverings in the Central Association of the German Construction Industry (ZDB) in May 2008 resulted in a joint statement – "Information to manufacture cement-based screeds." This statement paves the way for ensuring and disseminating high-quality methods for using cement screeds. In line with this, VDZ in collaboration with BEB and representatives of the cement and admixture industries examined the issues associated with the manufacture of cement screeds in relation to the different influences. The effects of the constituents and also of the manufacturing process, the installation and the conditions on the building site were all considered.

The basis for manufacturing screeds is the list of requirements in DIN EN 13813 as regards the construction method and the specific building project. Screed installers generally check the suitability of the screed composition with the planned constituents in the initial test at a working consistency normally found on building sites. If undesired screed properties (such as inadequate workability, inadequate strengths) are identified, suitable measures must be taken to improve the quality of the screed mortar. These measures include choosing a different aggregate (quality, supplier, grading curve), a different screed admixture (type of admixture, admixture manufacturer, amount of admixture) or a different cement (cement type, cement manufacturer, cement strength class) or changing the mixing ratio of the mortar and extending the after-treatment and the length of time that the screed must not be walked upon.

The results of the collaboration between VDZ and BEB are contained in instructions for the manufacture of cement screed mortars.

Traffic route engineering ■

It is expected that the amount of traffic on European roads will continue to increase in the long term; this is especially true for heavy transport. Despite the expansion of rail networks throughout Europe, a large proportion of the goods will still be moved by road. It is thus an advantage to have durable, low-maintenance construction methods that allow traffic to flow smoothly without any hindrances, for example due to road works. Within the scope of the infrastructure programme from 2009 funding will be provided to develop infrastructure facilities. Concrete construction methods are characterised by high load-bearing capacities and stability against deformation, low maintenance costs and a long service life and have, in the past, mainly been used to build major roads with a high proportion of heavy goods traffic. Concrete construction methods are also to be extended to cover the area of municipal road building. An important requirement for the planned expansion of the application areas is that the concrete structures are extremely durable. Because of this, durability has been one of the focuses of the Research Institute's activities.

Alkali-Silica Reaction

During the period under review the new version of the Alkali Guidelines from the German Committee for Structural Concrete (DAfStb) "Preventive measures against damaging alkali reactions in concrete" was adopted. Road surfaces made from concrete in Classes SV and I to III are to be classified in moisture class "moist + external alkali supply + strong dynamic stress" (WS), road surfaces in Classes IV to VI are to be classified in the moisture class "moist + external alkali supply" (WA). In addition, TL Beton-StB 07 contains requirements for the cements and aggregates for concrete road surfaces (see article on Alkali-Silica Reaction).

The measures taken there should prevent the occurrence of a damaging alkali-silica reaction (ASR) in future.

Early measures to maintain road surfaces already damaged as a result of an ASR could possibly prolong their service life. A working group from the German Federal Ministry of Transport with the participation of the Research Institute compiled a list of technical options to maintain these concrete road surfaces. The targeted use of suitable measures should extend the life of the affected roads and avoid them having to be renewed prematurely. The measures were defined in relation to the degree of damage.

Three damage categories were formed: 1: start of crack formation, 2: serious cracking and 3: very serious cracking and concrete breaking off (loss of load-bearing capacity). Road surfaces in damage categories 2 and 3 have to be covered with asphalt in varying thicknesses to improve their load-bearing capacity. The effectiveness of other measures is to be investigated for road surfaces in Category 1, with only shallow cracks and where the load-bearing capacity is not reduced. For this purpose, a test section was set up on the A14 motorway in Germany (built in 2000). The road surface has two layers in which a reactive aggregate was used in the top course concrete. Various test sections were set up in summer 2008. Two different methods were investigated which are used in road maintenance to e.g. improve grip: a bitumen emulsion applied as DSK slurry surfacing and an epoxy resin coating. DSK slurry or coating was applied to the road surface and then a polishing-resistant aggregate was spread over the surface. Two sections were also impregnated with linseed oil (**Fig. V-39**) and a hydrophobing agent respectively. With these four variants the moisture absorption of the concrete was reduced. If the effect is long term, this removes the conditions for a damaging ASR – swelling of the gel that occurs as a result of water absorption. In another variant the surface of the concrete road was treated with a lithium nitrate solution. Lithium bonds much better to the alkali-silicate gels than sodium or potassium. The gel that is formed does not swell as much when it comes into contact with water. A requirement is that the lithium can penetrate sufficiently deep into the roughly 7 cm thick damaged top course concrete. The fundamentals for lithium treatment were developed in a previous research project carried out by the Research Institute for the German Federal Ministry for Transport, Building and Urban Development (BMVBS). To assess the success of the measures, the test sections and additional reference sections are being monitored by the Federal Highway Research Institute (BASt). Crack development is determined at various points in time.

Concrete in municipal road construction

Areas of application for concrete road surfaces in the municipal area are, for example, roundabouts, bus stops and bus lanes, inner-city crossings, heavily used approach roads in major cities and also whitetopping, where a concrete overlay is applied to an existing asphalt surface. So far, there has been little use of concrete construction methods in these areas, which would suggest that there is a lot of potential. Consequently, pilot projects are to be carried out for the named areas to gather experience in all phases from planning through to implementation. The planned equipment engineering has to be adapted to suit the respective local conditions. If necessary, a partner-like cooperation should be established with the local concrete suppliers. The construction work can be carried out by regional construction companies. The only requirement is that these companies have sufficient experience in concrete construction. Upon completion of the pilot projects the knowledge gained from them should be documented and published.

One example of a successful pilot project is the first concrete roundabout in Germany, which was built in 2008 (**Fig. V-40**). Concrete roundabouts are now widespread in Austria, Belgium, the Netherlands and Switzerland.

Fig. V-40: Concrete roundabout in Bad Sobernheim

Regulations

To achieve a standard design of the contractual fundamentals in terms of the special needs of municipal road construction, it would be advantageous to adapt the regulations (TL and ZTV Beton-StB 07). Suitable codes of practice should be drafted, for roundabouts for example. Experience has shown that this makes implementation much easier.

Modelling ■

On the basis of 50 normal cements manufactured in Germany with different compositions, investigations were carried out in the Research Institute within the scope of AiF research project no. 14767 N to identify the boundary conditions under which it is possible to calculate the standard compressive strength of 28-day old cement based on key cement data with the help of the Virtual Cement and Concrete Testing Laboratory (VCCTL) software product.

The input data for the simulation calculation were chemical-mineralogical and physical parameters of cement and aggregate as well as key data that was determined by digital image analysis (e.g. clinker phase distribution). The simulation calculations were compared with the results from the experimental investigations (e.g. hydration heat, composition of the pore solution, porosity, compressive strength).

Simulation of cement hydration

Age-related simulation of cement hydration was carried out through iteration until a desired end point. The connection between the iteration steps and the actual progress of hydration was calculated in VCCTL for every cement via a time conversion factor, which determines the time comparison with the measured hydration heat. To simulate compressive strength after 28 days, as late a time as possible was chosen for the comparison, the hydration heat values after seven days.

Fig. V-41 shows the progress of hydration heat for two Portland cements CEM I 32,5 R from different origins. The 7-day comparison of the simulated hydration heat to the hydration heat determined by heat flow calorimetry (TAM) produced with some cements (Fig. V-41, left) a good correlation with the hydration heat trend while with others (Fig. V-41, right) the correlation was not so good.

The simulated hydration heat trend deviated from the measured hydration heat in many cements. In many cases the simulated development of hydration heat was well above the measured hydration heat. In these cases the simulated hydration proceeded faster than the actual hydration.

In the investigation as to whether groups of cements could be aggregated for the simulation calculations by choosing certain parameters, no direct connection between the strength class and the time conversion factor was identified.

While the simulation calculations for the effect of the tricalcium silicate content on compressive strength largely matched the experience values, the effect of sulphate agents on hydration heat development did not meet expectations.

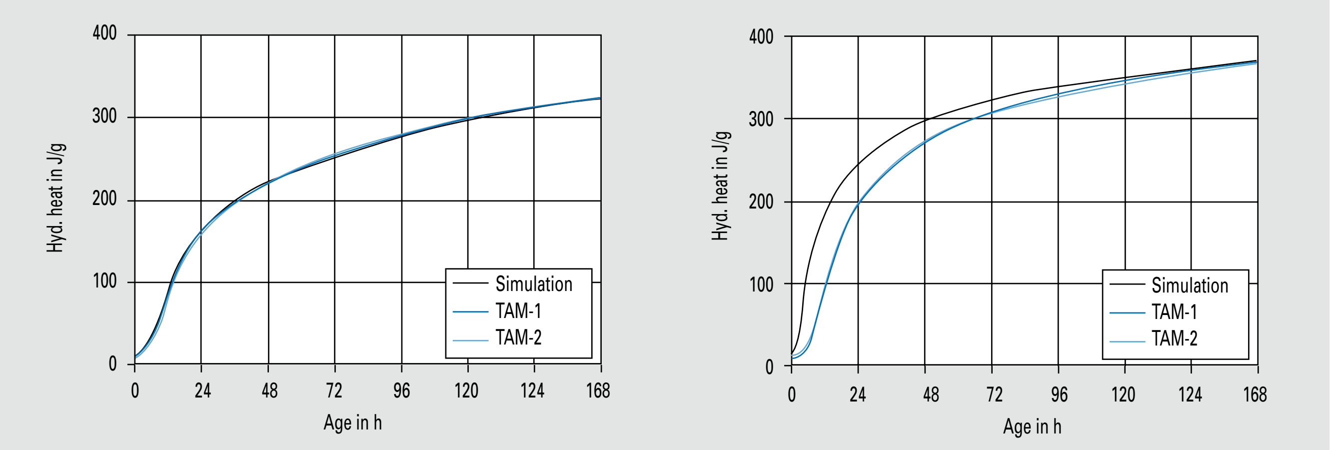


Fig. V-41: Hydration heat of two Portland cements CEM I 32,5 R from different origins simulated and determined using heat flow calorimetry (TAM); left good, right less good correlation of the hydration heat after comparison with the 7-day value (168 h)

With some cements, simulation of the composition of the pore solution produced sulphate and calcium ion concentrations in the pore solution that were clearly too high. Even when the sulphate agent was fully consumed with these cements, the simulated sulphate ion concentration in the pore solution remained at almost the same level. The programme code needs to be examined as regards consideration of the setting regulator types.

Porosity

The porosities for cement paste aged 7 and 28 days determined with mercury intrusion were up to 10 % by volume above the respective values of the simulation calculation. Among other things, this can be attributed to the fact that only "capillary porosity" is contained in the VCCTL programme. In many cases, the pore volume determined with mercury intrusion porosimetry was ≥ 0.01 µm of the simulated porosity. The measured porosities of standard mortar were, as expected, well below the measured porosity of the respective cement paste. In contrast, the mortar porosity simulated with VCCTL more or less matched the simulated porosity of the respective cement paste. This allows the conclusion to be drawn that the porosity of mortar has not been simulated correctly to date.

Compressive strength

Simulation of cement hydration provided the composition of the structure and, consequently, data about the space filling behaviour of the hydration products X(t) and about porosity P(t). With the help of Powers' approach, which assumes a basic strength of the structure D_0 which is reduced by porosity, the course of the compressive strength was calculated using the following equations

$$D(t) = D_0 \cdot X\,(t)^{n1}$$

and

$$D(t) = D_0 \cdot (1 - P(t))^{n2)})$$

The measured compressive strengths of cement paste and standard mortar were compared with the corresponding simulated development of compressive strength. To reflect the measured development of compressive strength by means of the simulated development of compressive strength, for each cement the variables D_0 and n had to be determined separately on the basis of the measured compressive strengths. Compared to the values D_0 = 203 MPa and n = 4.67 mentioned by Locher, the compressive strength of the pore-free cement paste D_0 and also the variable n were lower for most of the investigated cements. No general values for D_0 or n to approximate the development of compressive strength in different cement types and strength classes could be derived.

Alternatively, with the VCCTL software it is possible to calculate compressive strength on the basis of correlations with the modulus of elasticity independently from the simulated porosity. The values of the modulus of elasticity from the simulation calculations were, on average, about 2.6 GPa above the measured values. The compressive strengths measured on the basis of the simulated modulus of elasticity were below the measured compressive strengths and correlated with the simulated high porosities of standard mortar but not with the simulated high moduluses of elasticity.

Consideration of the aggregate

To investigate the deviations between the simulated porosity and the calculated compressive strength and the corresponding measured value for standard mortar, the influence of various parameters were considered to take account of the aggregate in simulation calculations.

On the whole it became clear that especially the choice of the modulus of elasticity for the aggregate, the particle size distribution of the standard sand and the size and properties of the contact zone are important factors for the simulation calculation of compressive strength after 28 days.

Summary

To summarise, it can be said that the simulation of the development of compressive strength in standard mortar up to 28 days old could not be predicted reliably for the different cements without using information concerning the aggregate.

Apart from the parameters of the cements used, the parameters of the aggregate and the transition zone from stone to unaffected cement matrix are also important for the result of the simulation. Simply varying these parameters within the normal fluctuation range can have a serious effect on the result of the simulation.

Basically, the VCCTL model seems suitable for mapping hydration of cement. However, the software requires further development especially in terms of simulating porosity of mortar and the composition of the pore solution and also as regards the influence of sulphate on the hydration process.

Table V-11: Exposure class-related requirements for a planned life of at least 50 years in terms of the minimum and maximum values and the most frequently used value for minimum concrete cover, the minimum compressive strength class, the maximum permissible water-cement value and the minimum cement content

Exposure class	Minimum concrete cover, mm		Minimum compressive strength class			Maximum permissible water-cement value			minimum cement content in kg/m³		
	min	max	min	max	m.f.u.v.	min	max	m.f.u.v.	min	max	m.f.u.v.
XC1	10	20	NS	C25/30	C20/25	0.60	NS	0.65	NS	300	260
XC2	15	35	NS	C28/35	C25/30	0.55	NS	0.60	150	300	280
XC3	10	35	NS	C32/40	NS, C25/30	0.45	NS	0.55	150	340	280
XC4	15	40	NS	C32/40	NS	0.45	NS	0.50	150	340	300
XD1	25	40	NS	C40/50	C30/37	0.45	0.60	0.55	150	360	300
XD2	25	55	NS	C40/50	C30/37	0.40	0.55	0.50, 0.55	150	360	300
XD3	33	55	NS	C50/60	C35/45	0.40	0.45	0.45	150	400	320
XS1	25	40	NS	C40/50	C30/37	0.45	0.55	0.50, 0.45	150	360	300
XS2	25	45	NS	C40/50	C35/45	0.40	0.55	0.45	150	360	320, 360
XS3	30	50	NS	C50/60	C35/45	0.35	0.45	0.45	150	400	320
XF1	–	–	NS	C32/40	NS	0.55	0.60	0.60	NS	300	300
XF2	–	–	NS	C35/45	NS	0.45	NS	0.55	NS	340	300
XF3	–	–	NS	C40/50	NS	0.45	0.60	0.50	NS	340	300, 320
XF4			NS	C40/50	NS	0.40	NS	0.45	NS	400	340
XA1	–	–	NS	C35/45	NS	0.40	0.60	0.55	150	380	300
XA2	–	–	NS	C40/50	C35/45	0.40	0.50	0.50	150	380	320
XA3	–	–	NS	C40/50	NS, C35/45, C40/50	0.35	0.45	0.45	150	400	360

m.f.u.v.: most frequently used value
NS: No specification

Standardisation

The European concrete standard EN 206-1

According to the CEN regulations, CEN standards have to be routinely reviewed every five years. For European concrete standard EN 206-1 this review would have been due in 2005. However, since at that time the standard had not yet been applied in some EU countries and in others had only recently been adopted, the responsible bodies had little experience with the standard. Consequently, it was decided that there would be little point in CEN/TC 104, “Concrete and related products” reviewing EN 206-1 before 2010. This decision was confirmed at the CEN meetings in Larnaca in November 2005 in the corresponding resolutions.

A working group of CEN/TC 104/SC1 “Concrete” has developed a synopsis of the national application documents (NAD) for the European concrete standard EN 206-1. This synopsis has made it clear that it will be almost impossible to further standardise definitions that are relevant to durability. **Table V-11** provides an overview of the requirements in terms of minimum and maximum values and the most frequently used values as regards minimum concrete cover, the minimum compressive strength class, the maximum permissible water-cement value and the minimum cement content. The most frequently used value is the value that has been chosen by more CEN member states than any other; but this should not immediately be interpreted as meaning that this value is actually used by most CEN member states. The following conclusions were drawn:

- In the majority of cases the values used most frequently for the maximum permissible water-cement value and the minimum cement content correspond to the values recommended in EN 206-1, Table F.1.
- In five cases (XC1, XC2, XC4, XD1 and XD3) the most frequently used values for the minimum compressive strength class, the maximum permissible water-cement value and the minimum cement content in all three categories match the values recommended in EN 206-1, Table F.1.
- In Denmark, where the lowest minimum cement contents are prescribed, compliance with a minimum powder content is also required. In Denmark, the minimum cement content cannot be reduced if Type II additions are used.

At its meeting in Stockholm in June 2007, CEN/TC 104/SC1 defined a road map for further revision of the European concrete standard EN 206-1. In June 2008, CEN/TC 104/SC1 put the road map into more specific terms. For the revision date in 2010 status papers have been compiled for issues such as the equivalent durability concept, the use of concrete additions, conformity assessment of concrete and alkali-silica reactions (ASR). These papers are the cornerstones for the subsequent new version of the standard.

Principles for revision of European concrete standard EN 206-1

- *Equivalent durability procedure (EDP)*
  - Regulation for durability-relevant aspects
  - Application possible only if put into force nationally (definition of a “reference concrete”)
- *Type II additions*
  - The currently standardised additions, fly ash, silica fume and ground-granulated blastfurnace slag are handled
  - The k-value concept can be used for all Type II additions
  - Cements with several main constituents should be considered
- In principle, *the regulations for conformity assessment and production control* for concrete should remain unchanged
- *Alkali-Silica Reaction*
  - No general classification of aggregates at an European level
  - Preventative measures regulated nationally

Equivalent durability procedure (EDP)

The concept described in Annex E of EN 206-1 has hardly been applied anywhere in Europe to date. The Dutch system of so-called “Attestbeton” or certified concrete could be described as an exception. The concept according to Annex E can be used to prove that the performance (essentially the durability) of concrete with additions is at least equivalent to a reference composed according to the descriptive rules (min c, max w/c, etc.) of the corresponding national annex. In Germany, this principle can only be applied within the scope of national technical approvals from the German Institute for Building Technology (DIBt). In the course of the revision it is now to be examined to what extent the procedure described in Annex E, which has so far been limited to proof for concrete additions, could be used in case of deviations from the descriptive approach and, at the same time, how this procedure can be put into more specific terms. This includes defining the reference situation (“reference concrete”) and the issue of which test methods are suitable and generally acceptable. The aim is to discover both opportunities (proof of equivalent durability of new concrete constituents) and challenges (softening well-tried and proven descriptive rules or negative assessments of solutions that have been proven in practice). The principle of equivalent durability should not be confused with the concept described in the UK concrete standard: the combinations principle. In the combinations principle, defined combinations of certain cements and concrete additions are to be inspected; largely corresponding to the inspection prescribed in EN 197-2. The “equivalence” of combinations of Portland cement together with GGBS, fly ash or limestone meal with cements of a suitable composition is implied on the basis of the results of a strength test pursuant to EN 196-1. Even if it is accepted that this procedure can be used only for known combinations of Portland cement and additions, in Germany it is inconceivable at the present time that it could be applied without an initial test and the corresponding durability tests. Apart from that, further national technical approvals would be required. The following principles were defined for the revision:

- A principle of equivalent durability should be included for all exposure classes.
- A detailed description will be possible for exposure classes XC, XD and XS.
- The option of specifying performance (= durability) directly on the basis of limit values should still be available. EN 206-1 may possibly recommend the test methods but will not specify any values.
- The concept can be used only when a CEN member state has defined its “reference concretes”.

Concrete additions

The general suitability of concrete additions for manufacturing concrete according to EN 206-1 is proven for stone dusts according to EN 12620, pigments according to EN 12878 (almost inactive additions Type I), the pozzolanic concrete additions fly ash according to EN 450-1 and silica fume according to EN 13263-1 (Type II). Type II additions may be counted together with the cement content and the water-cement value if they have been proven to be suitable in the concrete composition (k-value approach). The suitability of this approach is deemed to have been proven for fly ash and silica fume. However, the k-value approach in the form described in EN 206-1 is not used in many countries – and also not in Germany. Thus, the aim should be to get a general description and extend this to cements with several main constituents. The future EN 206-1 should also contain a reference to the European product standard for granulated blastfurnace slag, EN 15167-1. Apart from the k-value approach, which most countries with a national application rule have chosen for GGBS as a concrete addition, the principle of the equivalent durability concept and the UK combinations concept should also be examined. The following principles have been defined for the revision:

- The k-value concept and the equivalent durability concept will remain unchanged.
- General aspects of the combinations concept used in the UK should be added.
- A reference to GGBS should be made in combination with the above-mentioned concepts.
- The concepts for using additions should be described together with CEM II cements and in a general form. Detailed rules for their use will continue to be regulated nationally.

Alkali-Silica Reaction (ASR)

To coordinate further activities in regard to ASR (see section on Alkali-Silica Reaction), a joint working group of the CEN standardisation committees for cement and building lime (TC 51), aggregates (TC 154) and concrete (TC 104) has been set up under the leadership of the Research Institute of the Cement Industry. The working group makes the following recommendations:

- A (complete) specification to prevent damaging ASR is not possible within the scope of European concrete standard EN 206-1. Only principles can be described.
- Alkali reactivity of aggregates can be classified only on a national level.
- EN 206-1 cannot contain any limit values for effective alkali contents in concrete, as this requires a classification of aggregate combinations with consideration of national experience.

A2 and A3 changes to DIN 1045-2

The European concrete standard EN 206-1 “Concrete – Part 1: Specification, performance, production and conformity; German version of EN 206-1:2000” allows as a non-mandated and, thus, non-harmonised standard National Application Documents (NAD) with various sections in order to take account of different climatic and geographical conditions, different protection levels and long-established regional customs and experience. In Germany, these National Application rules are defined in DIN 1045-2. The national standards committee on concrete technology has voted on a list of changes to be made to DIN 1045-2. This was necessary due to application experience and the updating of other product standards for concrete constitu-ents and their national application regulations. The A2 changes were published in June 2007.

Within the scope of the A2 changes the standard was revised with regard to the following points:

- *Adaptation to the new and revised European standards for concrete constituents*
  In the meantime, European standards for silica fume (EN 13263) and an amended version of the standard for fly ash (EN 450) have been published. Reference is made to these standards. The application regulations from the drafts of the E DIN V 20000-106/107 series of standards envisaged for Germany in terms of the environmental compatibility of fly ash and the application regulations for silica fume and silica suspensions have been adopted.

- *K-value concept for fly ash also in exposure classes XF2 and XF4 for frost attack with de-icing agents and the corresponding change to the application regulations for cements containing fly ash*
  It is now also possible to use the k-value concept for fly ash for exposure classes XF2 and XF4 (frost with de-icing agent) with the known regulations. In this connection the use of cements containing fly ash is no longer excluded in these and other exposure classes. For example, in the past if Portland-fly ash cement CEM II/A-V or Portland-composite cement CEM II/A-M (P-V) were used in concrete for exposure class XF3, it was not permissible use the k-value concept with fly ash used as a concrete addition for the water-cement value or for the minimum cement content. This restriction no longer exists, nor do the usage restrictions for CEM II/A-V in exposure classes XF2 and XF4 or CEM II/B-V in exposure classes XF2, XF3 and XF4. In addition, CEM II/A-M (S-V) and CEM II/A-M (V-T) can now be used in concretes according to DIN EN 206-1 and DIN 1045-2 with no restrictions. For cements CEM II/B-M (D-V) and CEM II/B-M (P-V) there is no longer any restriction on use for exposure class XF3. The application regulation for fly ash as a concrete addition goes further than the ZTV-ING regulations. In these regulations fly ash can be counted only for exposure class XF2 and only for tunnel construction. In the ZTV-ING area, the “saturation value“ of the concrete must also be determined within the scope of an extended initial test (see ZTV-ING, Part 3 “Massive Construction”, Section 1 “Concrete”, Paragraph 3.2 (7) “Use of additions“).

- *Consideration of the definitions of the Alkali Guidelines from the German Committee for Structural Concrete (DAfStb). Integration of the moisture classes on the basis of the exposure classes*
  The German Committee for Structural Concrete (DAfStb) has revised and issued a new version of the “Alkali Guidelines”. The regulations were integrated into the respective points of DIN 1045-2/A2. The so-called moisture class must now be stated in the definition of a concrete. The “Exposure Class” table of DIN 1045-2 has been supplemented by a corresponding section for the moisture classes of the “Alkali Guidelines” (see section on “Alkali-Silica Reaction“). Since the customer must state the moisture class for every definition of a concrete, consequently, the ready-mixed concrete delivery specification must also contain the moisture class. In future, every ready-mixed concrete delivery ticket must include the moisture classes that are possible for the respective concrete (WO, WF, WA or WS). In the past, this was necessary only in the “core application area“ of the Alkali Guidelines (e.g. North Germany).

- *Consideration of fibres according to European standard EN 14889-1/2.*
  Fibres for concrete (steel fibres and polymer fibres) have now been standardised throughout Europe. Use in concrete according to EN 206-1/DIN 1045-2 will be allowed with the A2 change. Fibres according to this standard may be added to the concrete; however, their load-bearing effect may not be considered. Further national technical approvals are required here; for instance, in the same way as steel fibres are to be considered in a DAfStb guideline. With the A2 change general information is provided for handling and adding fibres based on the regulations for additions. Polymer fibres and steel fibres formed into bundles in a metering package (paper bags) require national technical approval proving that they mix evenly throughout the concrete.

- *Stating the sulphate content of the groundwater in exposure class XA when the concrete is specified and ordered.*
  Another footnote has been included in Table 2 of DIN 1045-2. Accordingly, in exposure class XA and with sulphate concentrations above 600 mg/l in the groundwater, the customer must state the sulphate content when specifying the concrete. The ready-mixed concrete manufacturer can then choose a suitable cement with a high sulphate resistance (HS-cement), take account of the regulations for the use of fly ash and identify the concretes in the delivery documents accordingly.

- *Adapting the procedure to determine strength development in a concrete in case of a proof age for compressive strength other than 28 days. The regulations from the DAfStb guideline for “Massive concrete construction components“ have been adopted*
  If in special applications the compressive strength of a concrete is determined after more than 28 days, for these concretes the calculation of strength development (see DIN 1045-2, Tab. 12, r-value) must be adapted. Strength development should then be determined from the ratio of average compressive strength after two days and the average compressive strength at the time the compressive strength is determined. That means that it is not the strength after 28 days that is used for the calculation, but rather the value after 56 or 91 days. This procedure corresponds with the regulation that was already introduced in the DAfStb guideline for “Massive concrete construction components”.

- *Integration of the A1 changes to DIN 1045-2 from 2005.*
  The A1 changes already published in 2005 have been adopted and integrated into the A2 changes.

The following points were implemented in another change (A3 change):

- The previous standards DIN V 20000-100 (application regulations for concrete admixtures), DIN V 20000-103 (application regulations for aggregates) and DIN V 20000-104 (application regulations for lightweight aggregates) have been adopted;
- Supplementary definitions from the Technical Construction Regulations (e.g. for pigments) and the list of construction rules were integrated into the A3 change;
- Application regulations for cements according to DIN EN 197-1, German version of EN 197-1:2001+A1:2004+A2 (SR cements) +A3 (fly ash) have been adopted.

As an application regulation for the SR cements the following comment has been added at the appropriate places: "Until DIN EN 197-1/A2 is available, the definitions in DIN 1164-10 must be complied with for HS cements. As soon as E DIN EN 197-1/A2 can be used, the requirements for HS cements are deemed to be fulfilled if a cement with high sulphate resistance according to E DIN EN 197-1/A2 (CEM I-SR 3 or lower, CEM III/B-SR, CEM III/C-SR) is used."

Cements containing fly ash used to manufacture concrete according to DIN 1045-2 may contain only fly ash with up to 5% loss on ignition.

A consolidated version of DIN 1045-2 was published in August 2008. This now contains the A2 and A3 changes to DIN 1045-2:2001-07 and the requirements from DIN V 20000-100, DIN V 20000-103, DIN V 20000-104, DIN V 20000-106 and DIN V 20000-107. The changes to DIN 1045-2:2001-07, resulting from DIN 1045-2/A2:2007-06, E DIN 1045-2/A3:2008-01 and the results of the consultations regarding objections to E DIN 1045-2/A3 are marked with vertical lines beside the text. In addition, changes were made to the standard references to take account of the current status of the reference documents; however, these are not marked. An updated version of DAfStb booklet 526 will be published some time in 2009.

DAfStb Guideline "Massive concrete construction components"

The reason for the revision of the guideline was the new issue of DIN 1045, Parts 1 to 3, in August 2008. Use of the k-value concept for fly ash also in exposure classes XF2 and XF4 for frost attack with de-icing agents (see above) as described in DIN 1045-2:2008-08 was transfered to concrete compositions for massive construction components.

Fire protection

In terms of fire protection, a distinction is generally made between preventive and defensive fire protection. Defensive fire protection applies only when a fire has already started and essentially covers the fire brigade's work in extinguishing the fire. In contrast, preventive fire protection is used to prevent or limit the start or spread of fires. In addition to technical fire protection, which in particular includes fire alarm systems and automatic fire extinguishing systems, structural fire protection is one of the crucial pillars for the necessary level of safety in the area of preventive fire protection. Structural fire measures are permanent and offer the required level of protection without having to be triggered by operational or mechanical processes, which always harbour a risk of failure. Defensive fire protection depends on the deployment of the fire brigade, where there is also a risk of failure.

Concrete structural elements are a relatively simple way of fulfilling fire protection requirements and usually involve no major additional expenditure. The non-flammable construction material, concrete, can be used to build structural elements with a high resistance to fire and with a correspondingly stable shielding effect. This means that in the event of a fire, concrete structures retain their stability for a long time and that fires can be restricted to confined areas. These fire protection properties of concrete and concrete building members contribute to safety for human life, which has top priority in statutory fire protection requirements. However, saving the building itself or the contents of the building are also important in terms of protecting assets. Even if legislation has made protection of property the personal responsibility of the building owner and users, saving assets is in the interest of both private individuals and the general public. Furthermore, structural fire protection measures also protect the environment if effective fire limitation reduces smoke and gas emissions as well as the amount of extinguishing water that is needed and when the extinguishing water, which is generally contaminated, can be retained.

National regulations (Germany)

DIN 4102 "Fire behaviour of building materials and building components"

VDZ participated in the development of the A2 change to DIN 4102-4 "Synopsis and application of classified building materials, components and special components" and the A1 change to DIN 4102-22 "Application standard for DIN 4102-4 based on the design of partial safety factors". Both parts of the standards and a consolidated version, containing both parts are to be published in the second quarter of 2009 as a "yellow print".

In addition to a new section dealing with the fire behaviour of construction components made from high strength concrete, one of the main changes compared to the last version of the standard is the revision of a design table for reinforced concrete columns made with normal-weight concrete. The underlying conditions for the use of this revised table exclude its application for cantilever columns. However, since the fire design of cantilever columns is very important in practice (e.g. for factory buildings), the Institute for Construction Materials, Concrete Structures and Fire Protection at Braunschweig University in Germany was commissioned to develop a simplified calculation method to verify the fire resistance class F90 for cantilever columns. This research project, which was supported by VDZ, was completed in November 2008 and the method can thus be included in the revised DIN 4102.

DIN 18230-1 "Structural fire protection in industrial buildings – Part 1: Analytically required fire resistance time"

DIN 18230-1 defines a calculation process with which the technical fire protection design of supporting components in industrial buildings can be carried out. It is based on the proof that the construction components meet the required fire resistance time. The yellow print of a new version of DIN 18230-1 was published in 2008. One important change compared to the 1998 version is the introduction of the term "level" in industrial buildings: while by definition floors are separated from each other in terms of technical fire protection and each forms a separate fire compartment, levels can also have open spaces or can be made up from partial sections. The area of a fire compartment is then calculated from its floor area and the total area of the levels above it. According to the new DIN, platforms or scaffolds without the required fire resistance time are no longer counted as part of the calculated area and the fire load of these areas is added to the next calculable area below. This represents a tightening of the regulations.

Other important changes in the new standard are the consideration of facility protection systems (e.g. self-activating fire extinguishing systems) for the reduction of fire loads and new definitions for the consideration of openings in the calculation of heat dissipation.

European cooperation

The European associations for precast concrete (BIBM, Bureau International du Béton Manufacturé), ready-mixed concrete (ERMCO, European Ready Mixed Concrete Organi-sation) and the cement industry with the participation of representatives from 14 nations are working together in the European Concrete Platform working group “Fire Safety with Concrete” to promote concrete construction under fire protection aspects. Within the scope of this cooperation, developments in the field of international standardisation regarding fire safety are also being monitored.

A brochure developed by the working group at the start of 2007 entitled “Comprehensive fire protection and safety with concrete” was also published in 2008 in German as “Umfassender Brandschutz mit Beton” (**Fig. 42**). This brochure is aimed at architects, building owners, authorities, insurance companies and the general public. The idea behind it is to show how concrete can be used to implement comprehensive fire protection; in other words, protection of human life, property and the environment.

International developments in the field of fire protection

The traditional load-bearing design for fire cases is carried out using standard tables in which the minimum dimensions or protective cladding for individual building members are defined so that they achieve the required fire resistance class. These tables are based on standard fires that map a standardised temperature rise over a certain period, such as the temperature-time curve in accordance with DIN 4102 Part 2. For concrete construction components, high fire resistance times of more than 120 minutes without cladding or intuprescent coatings must be achieved if the building members and their concrete cover are properly dimensioned.

Fire Safety Engineering (FSE) methods have been developed over the last ten to fifteen years. Their goal is to enable a realistic, holistic estimate of the effects of a fire on a building or part of a building. In other words, the aim is no longer to base assessments simply on individual building members or standard fires. In a typical design using fire safety engineering methods, the first thing to do is define protection goals. The top priority is to protect human life and health; but property protection targets can also be defined. Fires are modelled with consideration of the actual existing fire loads and the geometry of the fire compartments under consideration, while the thermal and mechanical effects on the surrounding construction components are also determined. For example, the assessments take account of automatic fire detection and active fire fighting via automatic fire extinguishing systems or by the fire brigade. Computer programmes are used to simulate the effects of a fire or the behaviour of groups of people trying to escape from a burning building. In many cases the requirements for fire protection in the individual construction components are reduced when applying FSE.

Fig. V-42: Brochure “Comprehensive fire protection and safety with concrete”

The Eurocodes, the harmonised European standards for the design of building structures, also include Fire Safety Engineering methods. The ten Eurocodes consist of 58 parts, all of which were published by the end of 2007. Eurocode 2, consisting of four parts, regulates the design and construction of reinforced and pre-stressed concrete structures. At present, the participating member states are compiling the National Annexes, in which national choices for specific parameters or processes are specified. Guidance Paper L from the European Commission envisages complete implementation of the Eurocodes by 2010.

Fig. V-43 shows the various different possibilities of fire design according to the Eurocodes. Fire Safety Engineering methods are included here under the heading “Ad-

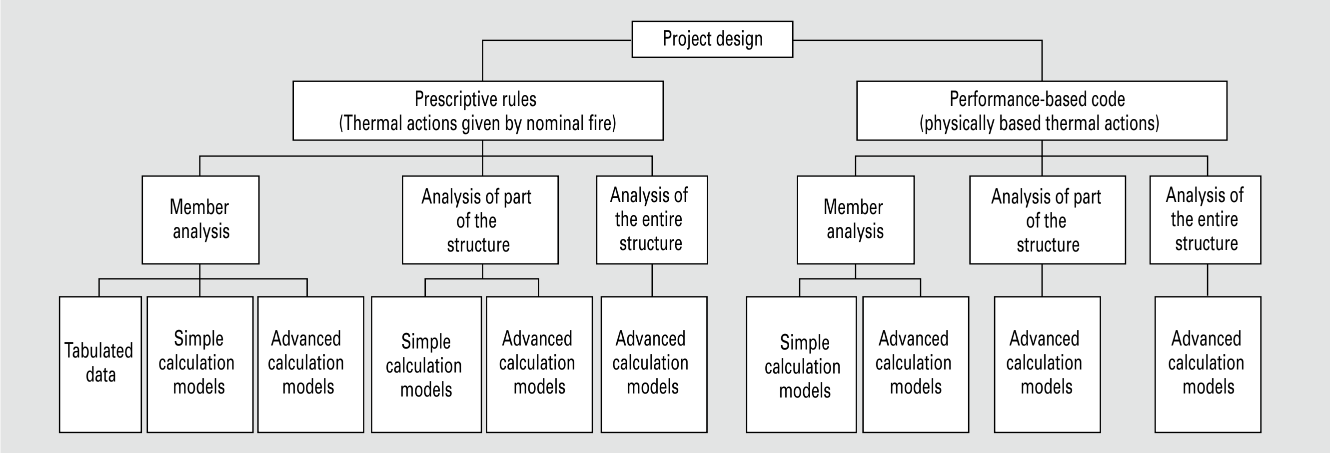


Fig. V-43: Design procedure (Eurocode-Brandschutzteile, excerpt)

Fig. V-44: AVR experimental reactor with material lock (left) and construction site tent to fill the reactor chamber (right)

vanced Calculation Models". The decision as to whether use of advanced calculation models is permitted in a member state is regulated in the National Annexes. Many member states allow use only with restrictions. For example, it is defined that use is limited to experts with adequate experience. The concrete and cement industries welcome these restrictions, as improper use of FSE can easily result in faulty assumptions in the calculations, which, in turn, can lead to requirements being wrongly defined.

Within the scope of the European cooperation at the European Concrete Platform (ECP) level, the European Cement Research Academy (ECRA) has taken over an important role and will now actively support further work on the Eurocodes concerning concrete and fire protection in the corresponding standardisation committees. In addition, the National Annexes to Euro-code 2, Parts 1-2, which regulates fire safety designs of concrete structures, will be assessed and compared to encourage more harmonisation in Europe.

Consultancy and expert advisory services ■

Demand for concrete technology consultancy and expert advisory services rendered by the Research Institute of the Cement Industry has increased considerably over the past years. This principally applies to the following key areas:

- Development of optimised concrete and mortar mixes for the respective clients' area of application,
- Structural analyses and assessments,
- Development of repair concepts,
- Clarifying issues related to alkali-silica reactions and assessing aggregates (see section on Alkali-Silica Reaction)
- Chemical attacks on concrete.

Experts in all areas of concrete engineering who are represented on the corresponding national and international committees and who have extensive experience from laboratory and practical work find efficient solutions to what are sometimes very complex problems. The interdisciplinary cooperation with experts in the fields of mineralogy, chemistry, physics and applied technology in the other departments of the Research Institute is a particular advantage in this connection.

Below we would like to present a project concerned with developing optimised concrete and mortar mixes in which the concrete engineering support of the Research Institute was requested. In particular, the Institute's extensive experience in research work and the development of self-compacting concrete as well as experience in the area of special concretes helped it develop efficient solution proposals.

Filling the experimental reactor of AVR GmbH

The experimental nuclear power plant of Arbeitsgemeinschaft Versuchsreaktor GmbH (AVR) was designed in the 1950s although it only started supplying electricity to the grid at the end of 1967. The plant was decommissioned on 31 December 1988 after 21 years of operation. The experimental nuclear power plant is a graphite moderated high-temperature helium gas-cooled reactor (HTGR) with an output of 15 MW. In accordance with the nuclear law approvals, since 1994 work has been carried out to decommission the plant, to defuel the core of the reactor, dismantle parts of the plant and to set up a material lock (**Fig. V-44**). To completely dismantle the plant AVR plans to fill the reactor chamber with lightweight concrete (LC) in order to fix the internal components in the reactor chamber for dismantling. The reactor chamber filled with LC is to be removed from the reactor building in one piece so that it can be transported to an interim storage area on Jülich Research Centre's grounds. There the reactor chamber is to be stored safely until it has been conditioned suitably for storage in its permanent repository.

Requirements for the LC

The concrete engineering development of the LC was carried out by Schlumberger Oilfield Services GmbH, Vechta (SLB) with the support of the Research Institute. Apart from fixing the internal components in the reactor chamber, increased safety to exclude the chance of a major incident was absolutely vital and included binding dust-like radioactive graphite. The LC had to fulfil the following main requirements:

- Low bulk density as the most important requirement for the LC. To limit the maximum weight of the reactor chamber the LC had to have a bulk density of $\rho \approx 0.7$ kg/dm^3 in an installed, hardened and conserved condition.
- Compressive strength of at least 2 N/mm^2 to fix the internal components and to guarantee safety against a major incident,
- Workability and pumping capacity over a period of several hours,
- Ability to fill small cavities,
- Chemically "inert" behaviour towards graphite, carbon brick and steel,
- Fixing powdered graphite,
- Low hydration heat,
- Radiological resistance,
- Long life

The fresh and hardened properties of LC were investigated and documented in many laboratory experiments at the Research Institute and in experiments carried out under practical conditions at SLB's premises. The bulk density of the fresh and hardened concrete at atmospheric pressure was, as planned, approx. 0.7 kg/dm^3. Under the influence of increased pressure, such as can occur during pumping or due to the hydrostatic pressure head of the reactor chamber, the bulk density increased to a maximum of 0.8 kg/dm^3. The compressive strength of the sealed LC was approx. 4 N/mm² after six months. The flowability of the LC was assessed on the basis of rheological investigations. The laboratory results showed that the LC flowed sufficiently well and was easily pumped up to temperatures of 30 °C and for about six hours. Under practical conditions with temperatures of approximately 20 °C, the LC flowed and could be pumped for roughly 11 hours. The LC exhibited no corrosion-promoting effects on steel.

Filling the reactor chamber

To ensure the quality of the LC, the Research Institute drafted a monitoring concept defining measures for third-party inspection of the constituents, of the properties of the fresh concrete while the reactor chamber was being filled and of the hardened concrete properties after the chamber had been filled. Within the scope of this third-party inspection concept, the Research Institute inspected the quality and uniformity of the constituents before the filling process commenced. The suitability of the constituents for manufacturing LC for the filling was investigated on the basis of chemical-mineralogical analyses and performance tests. The portioning of the constituents before the filling was also monitored. During the filling the following fresh concrete properties were monitored:

- Bulk density of the fresh concrete,
- Temperature of the fresh concrete,
- pH-value,
- Shearing resistance,
- Sedimentation stability.

Fig. V-45: View of four of the eight mixing tanks, some of the silos containing constituents and the mobile crane inside the construction site tent

A total of 20 batches of LC each approx. 25 m³ were mixed (**Fig. V-45**). All batches fulfilled the requirements defined in the third-party inspection concept and the client's requirements. The filling of about 500 m³ LC into the reactor chamber was completed in roughly 10 hours.

Besides providing concrete technology consultancy and expert advisory services, the Research Institute can also carry out virtually all concrete technology investigations and tests under the terms of contract investigations. Customary standardised testing is accredited according to EN ISO 17025. In order to be braced for any future questions arising, the pool of testing equipment is continually extended.

VI

Environmental compatibility of cement and concrete

Water sampling tower of the drinking water barrage Frauenau

Environmental criteria for cementitious building materials ■

In industrial nations cementitious building materials play an extremely important role as regards construction of reliable and durable building components and buildings. Accordingly, environmentally compatible manufacture and use of cement is also very important. The cement industry was and is conscious of its responsibility towards the environment and for many years has been working towards assessing and improving the environmental compatibility of cementitious building materials in all phases of their lives. This includes cement manufacture and processing, the use of mortar and concrete as well as disposal.

The clinker burning process is a material conversion process that is characterised by the strong alkaline reaction of the kiln feed, high kiln feed temperatures of approx. 1 450 °C, and intensive contact between the solids and the kiln gas, which reaches temperatures of up to 2 000 °C. Thus, the rotary kilns in the cement industry present excellent conditions for the reliable and environmentally compatible utilisation of many residual materials. However, on principle the German cement industry uses only residual materials that do not have any adverse effect on emissions, the homogeneity and the structural properties of the cement as well as its environmental compatibility.

Extensive investigations carried out by the Research Institute corroborate that the utilisation of alternative materials common in the German cement industry today does not significantly change trace element contents in the product. Overall, the trace element content of German cements is within the same order of magnitude as the contents of natural rocks, soils or clays. This applies regardless of whether or not alternative materials are used in cement manufacture.

Use of alternative materials

Given its process-specific conditions, the clinker burning process is very well suited for energetic and material recycling of numerous alternative materials. In 2008, about 54 % of fuel energy consumption in the German cement industry was covered by alternative fuels. The most important fuels are processed fractions of industrial and commercial waste, used tyres, waste oil, bone meal and animal fats as well as scrap wood.

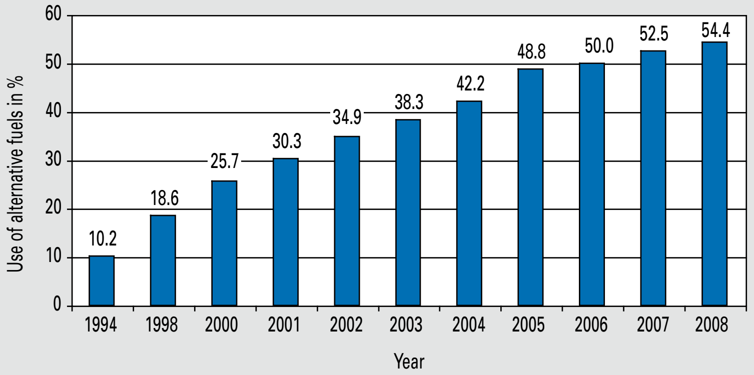


Fig. VI-1: Trends in the use of alternative fuels in the German cement industry

Fig. VI-1 summarises the trend in the use of alternative fuels in the German cement industry. Energy recovery contributes towards CO_2 reduction without generating production-specific residual materials. The high temperature in the rotary kilns ensures that organic substances are almost completely converted to carbon dioxide and water. The emission concentrations of organic compounds, such as dioxins, furans, etc., are therefore very low. This applies regardless of the fuels that are used.

Depending on their chemical composition secondary raw materials can replace raw material components and are also suitable as corrective materials for the raw mix. Depending on their main constituents, they can be divided into calcium, silicon, iron, aluminium, sulphur or fluorine agents. In clinker production, fly ash, used foundry sand, lime residues and waste from the iron and steel industries are primarily utilised. The materials chiefly used in cement grinding are granulated blastfurnace slag as well as gypsum from flue gas desulphurisation.

Trace elements in cement

Like all building materials derived from natural raw materials, cement contains small quantities of trace elements. The trace element content in the clinker is substantially influenced by the trace element contents of the raw materials used in clinker production, which may differ considerably depending on the geochemical composition of the raw material source.

During the clinker burning process the physical/chemical properties of the trace elements determine the evaporation and condensation behaviour. Non-volatile elements, such as arsenic, beryllium, chromium, copper, nickel, vanadium and zinc, as well as low-volatile elements, like lead and cadmium, are almost completely discharged from the kiln system with the clinker. The highly volatile element thallium is retained in the preheater which results in an internal recirculation system being formed. In the exhaust purification systems, at temperatures below approx. 120 °C the highly volatile element mercury can condense on dust particles and be separated with these particles.

If natural feed materials are replaced by suitable alternative fuels or raw materials, their trace element content is an important assessment criterion. It must be remembered that alternative materials replace only a corresponding amount of primary materials, which also contain trace elements. With the amount of alternative materials used these days in the German cement industry, minor increases or decreases of trace element content in the cements can occur. However, these changes are normally covered by the natural variations in the concentrations of the primary feed materials.

Back in 1995, the Research Institute first investigated around 100 Portland cements from the 1994 inspection period for 10 trace elements. In 1999 and 2002, all cements manufactured in Germany and inspected by the Research Institute from the test periods 1998 and 2001 were analysed as regards the elements referred to in the German Technical Instructions on Air Quality Control (TA Luft) and the 17th Federal Immission Control Ordinance (17. BImSchV) and also for beryllium and zinc. In order to expand and update this data base, during the period under review all cements from the 2005 test period were analysed again. **Fig. VI-2** shows the average values of trace element contents in the investigated standard cements for the four manufacturing periods. As the figure shows, trace element contents have not changed significantly, although the use of alternative fuels increased more than fivefold between 1994 and 2005 (see Fig. VI-1).

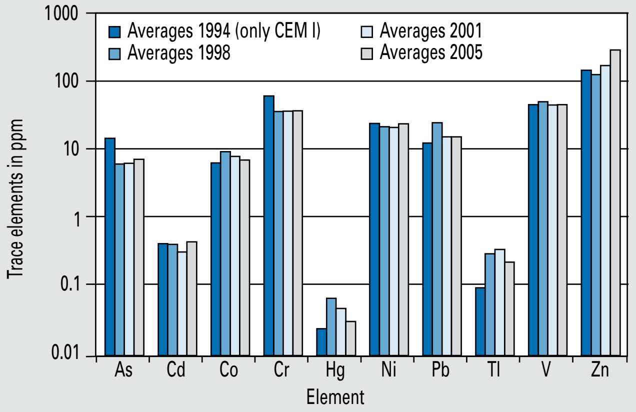


Fig. VI-2: Comparison of the average trace element content in German standard cements

Release of trace elements

Like all building materials that come from natural raw material sources, cementitious building materials contain small concentrations of trace elements that are input via the cement, the aggregate and any concrete additions. Experience has shown that the trace element content of the mixing water and concrete admixtures is negligible and can be ignored in the overall consideration. However, to assess the environmental compatibility of a building material it is not the content of potentially unsafe substances that is decisive but rather the proportion that can be released to the environmental media, water, soil or air during the manufacture, use and, possibly, demolition or recycling of the respective materials.

Cement undergoes a series of complex chemical reactions immediately upon its first contact with the mixing water, during which calcium sulphate and a small proportion of the tricalcium aluminate (C_3A), for example, are dissolved and the first reaction products such as calcium hydroxide and trisulphate (ettringite) are formed. After a few minutes the cement paste suspension has a pH of 12.7 to 12.9. As a result of this high alkalinity, numerous metal ions, such as cadmium, mercury, manganese, cobalt and nickel, which might possibly be dissolved once the cement comes in contact with the mixing water, are immediately precipitated again as insoluble hydroxides. Trace elements, such as arsenic or molybdenum, which form oxyanions, are precipitated as insoluble calcium compounds. Other trace elements are absorbed on the cement phases formed or incorporated in their crystal lattice as hydration progresses further.

The leaching behaviour of environmentally relevant constituents from hardened concrete has been well researched and numerous reliable scientific results are available. On the whole, the investigations have shown that it is not the detectable quantity of trace elements in a cementitious building material that is decisive for any release but only the small amount that is dissolved in the pore water of the hardened cement paste.

Besides the chemical interactions of the trace elements with the hydration products, another factor is that during the hardening of cementitious building materials a solid, largely water impermeable structure forms. For instance, the rate of diffusion of a substance in a correctly manufactured concrete can be reduced by a factor of up to 5 000 compared to free diffusion in water. Therefore, leaching of substances dissolved in the pore water of hardened mortar or concrete is possible only via diffusion processes in the liquid-filled pores. Because of the low concentrations of constituents in the pore water, the rate of diffusion is very low and the released volumes are reduced very quickly. On the whole, it can be said that cementitious building materials have no negative effect on the environment under common conditions of use.

During the period under review the research project started many years ago by a European consortium, "**E**nvironmental **Cri**teria for **Cem**ent Based Products (ECRICEM)", was completed. The research partners were:

- the Energy Research Centre for the Netherlands (ECN),
- the Holcim Group Support Ltd,
- Holcim Belgium,
- NORCEM, HEIDELBERGCEMENT Group,
- and the German Cement Works Association (VDZ).

Initially, the main focus of the research work was to determine the release behaviour of cementitious building materials that were manufactured with cements available worldwide (Portland cement and cements containing several main constituents) with high contents of trace elements. The results of the investigations substantiated the environmentally favourable performance of cementitious building materials. They also demonstrated that in general all the cements that were investigated – regardless of the cement type – have similar release characteristics. For example, the bandwidth of leaching results in the trough procedure for many elements was only a factor of 2.5 above or below the average.

Table VI-1 contains average values of leached trace elements in relation to the respective total content in the mortars that were investigated, which were manufactured with twenty different cements containing several main constituents. The following three leaching methods were used:

- The Dutch availability test (NEN 7341) on ground samples with a particle size < 125 µm and pH values of 4 and 7 and leaching times of three hours for each pH value as a digestion process.
- A batch procedure on crushed samples with a particle size < 2 mm and a pH value of 8 and a leaching time of 48 hours.
- A trough procedure (based on the Dutch diffusion test NEN 7345) on mortar prisms (16 x 4 x 4 cm^3) with no artificial pH adjustment over a total leaching time of 64 days – as the basis for calculating the quantity of leached substances over 100 years.

Table VI-1 shows that the released quantities of trace elements differ by orders of magnitude in the three methods. But it must be remembered that in the last-mentioned trough procedure the leached quantities of elements relate to a period of 100 years. The results show that the release of trace elements from cementitious building materials has no environmental relevance under common conditions of use. It is also clear that test procedures in which specifically manufactured, largely dense mortars

Table VI-1: Average quantity of leached trace elements in relation to the respective total content for three different leaching processes

Element	Quantity of leached trace elements as a % of total content		
	Availability test Particle size < 125 µm pH = 4 and 7	Batch procedure Particle size < 2 mm pH = 8	Trough procedure $^{*)}$ mortar prisms 16 x 4 x 4 cm^3
Arsenic (As)	2.0	0.60	0.01
Barium (Ba)	14	4.2	0.10
Cadmium (Cd)	8.7	0.94	0.16
Cobalt (Co)	90	2.0	0.02
Chromium (Cr)	5.1	2.5	0.04
Copper (Cu)	8.1	0.03	0.02
Mercury (Hg)	10	4.8	< 0.02
Manganese (Mn)	10	0.74	0.0003
Molybdenum (Mo)	70	3.2	0.05
Nickel (Ni)	20	2.1	0.02
Lead (Pb)	2.9	0.60	0.01
Antimony (Sb)	8.6	1.3	0.04
Vanadium (V)	1.0	0.43	0.006
Zinc (Zn)	15	0.05	0.02
Tin (Sn)	2.9	1.1	0.15

$^{*)}$ extrapolated to 100 years standing time

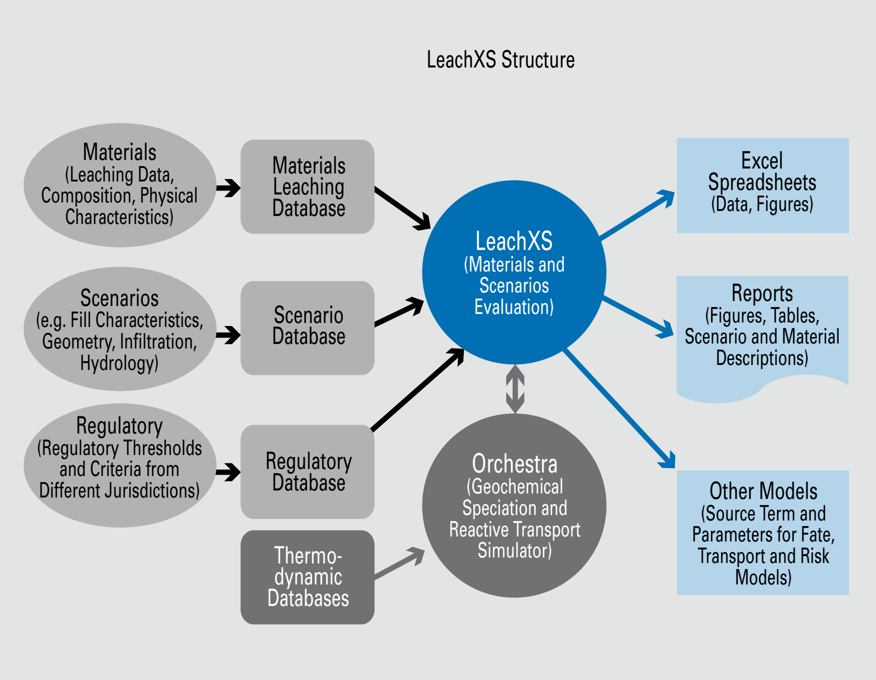


Fig. VI-3: Diagram of the LeachXS expert system

or concrete structures are destroyed again during the investigation are not suitable for a practical assessment of cementitious building materials.

After the experimental work was completed in 2004, intensive work was carried out on modelling chemical reactions in cementitious building materials. The LeachXS expert system was used for the model calculations (**Fig. VI-3**). To assess the long-term leaching behaviour of cementitious building materials it is vital to have an understanding of the "controlling" factors that determine the solubility of a trace element in the pore water and thus also the diffusion-controlled release. For example, one specific trace element cannot be considered on its own, but only in interaction with the other components in the pore water and with the cement hydrate phases. Consideration of these interactions, such as the formation of hardly soluble compounds, like lead chromate that can have a major effect on the release of the respective elements, is possible only with model calculations.

Effects such as carbonation, the formation of protective carbonate layers, etc. on the release of trace elements from concrete in contact with surface water, groundwater or the soil are also very difficult to simulate in laboratory experiments. In this case mechanistic model calculations can be used to provide at least an estimate of how these effects influence leaching of trace elements. Based on the results of experiments, for example with long-term leaching tests in a tank leaching test (**Fig. VI-4**), and corresponding model calculations, it is possible to determine the "source term" for the leaching.

On the whole, it can be said that the results of the ECRICEM projects offer a scientifically sound basis for the imminent European standardisation work to embed Essential Requirement No. 3 "Hygiene, Health and Environment" in the harmonised European product standards (see European Construction Products Directive).

REACH ■

The new European Regulation 1907/2006, generally know as the REACH Regulation (**R**egistration, **E**valuation, **A**uthorisation and Restriction of **CH**emicals), has been in force since 1 June 2007 (for the time schedule see **Fig. VI-5**). The associated annexes IV and V "Exemptions from registration obligations" were only passed in October 2008. Since then, it has been official that cement clinker is exempted from the REACH registration obligations. This applies not only to Portland cement clinker, but also to calcium aluminate and calcium sulphoaluminate clinker. Also exempted are natural substances like limestones and pozzolans as long as they are not chemically modified. All other manufactured and imported substances must be registered over the next few years. Extended registration deadlines can only be made use of if the substances have been preregistered. This was possible between 1 June 2008 and 1 December 2008. Of the substances normally used in cement manufacture, hard coal fly ashes, blastfurnace slags, calcium sulphates and chromate reducers, among others, have been preregistered. Cement manufacturers may also have to register these substances if they manufacture or import them.

The bypass and kiln dusts that occur in cement works are covered by the REACH Regulation if they are declared as a product and not as waste. Because of the variable composition with high proportions of alkali salts and free lime, it may not be possible to classify all dusts as clinker dust. Separate registration is then necessary so that the dusts can continue to be marketed as a product or in products. This is why these dusts have been preregistered as flue dust, Portland cement under the EC number 270-659-9. The VDZ acts as a third party representative for many cement works during the pre-SIEF phase (**S**ubstance **I**nformation **E**xchange **F**orum). Together with other registrants, it is being clarified which dusts accrue and under which conditions these can be registered together.

The REACH Regulation demands a hazardous substance classification for every substance, and therefore also for Portland cement clinker, by the end of 2010, which must be submitted to the new European Chemicals Agency (ECHA).

The complex subject of the REACH Regulation and the many different requirements for cement manufacturers resulting from the regulation have been discussed over the last three years by the REACH Working Group within the VDZ – incorporated into the work of Working Group 4 of the CEMBUREAU.

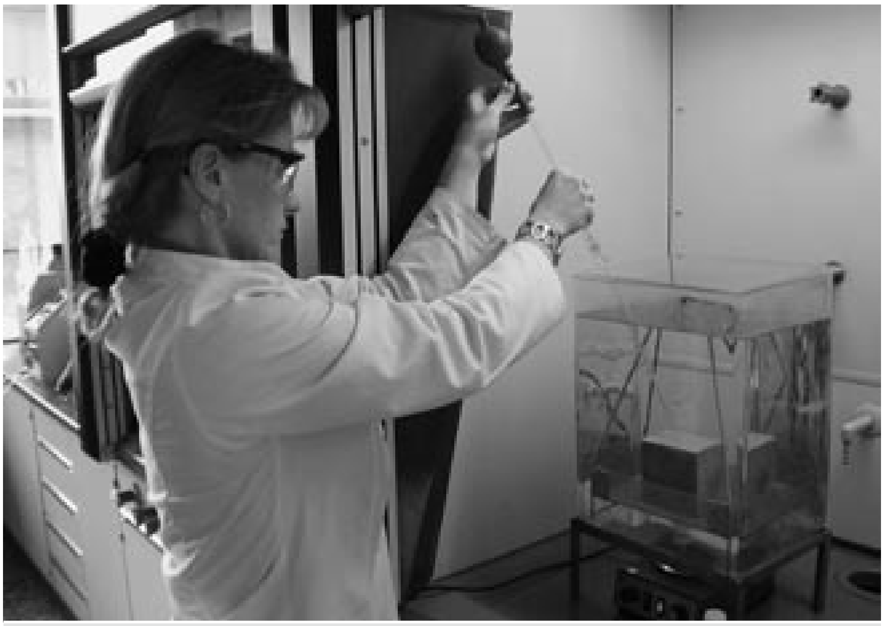


Fig. VI-4: Leaching of a concrete sample (dimensions 10 x 10 x 10 cm^3) in a long-term tank leaching test

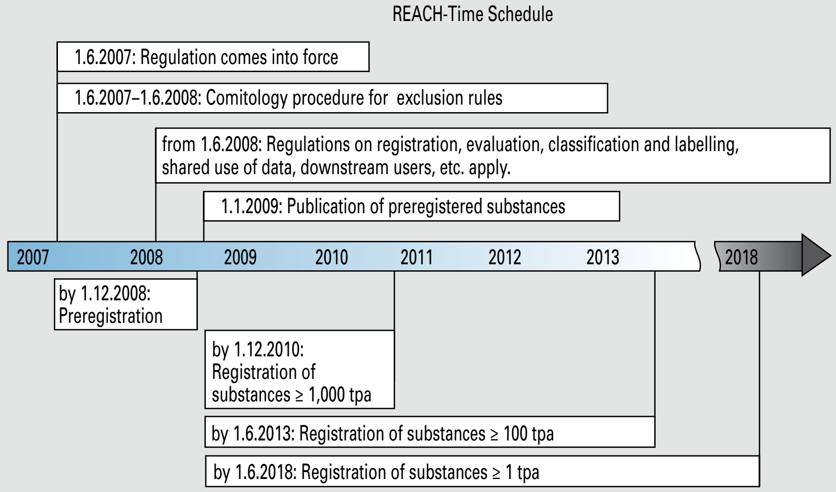


Figure VI-5: Commencement and implementation deadlines for the REACH Regulation

European Construction Products Directive ■

The European **C**onstruction **P**roducts **Di**rective (CPD) demands that only construction products that are suitable for their intended use may be traded in the Single European Market. In addition to the requirements traditionally embedded in construction law, such as stability, fire protection and safety in use, it specifically refers to hygiene, health and the environment (Essential Requirement No. 3). Currently, the Construction Products Directive is being revised and, in future, is to be transferred into a legally binding regulation called the **C**onstruction **P**roducts **R**egulation (CPR).

While the CPD concentrates solely on the usage phase of a building as regards “Essential Requirement No. 3”, the draft CPR envisages consideration of the entire life cycle; in other words, beginning with the construction, through the usage phase to demolition. The draft CPR also includes the new

1. Definition of the construction product(s) according to one or more hENs

2. Definition of the intended use (contact with soil, groundwater, surface water or indoor air) and selection of the relevant release scenarios from the corresponding hEN

3. List of mandated RDSs related to the relevant release scenarios and the Member States to which the construction product will be supplied
(The EU Commission will mandate the RDSs and they will be listed by CEN in the relevant hENs)

4. Identification and elaboration of mandated RDSs and sets of RDS classes in the corresponding hEN

Conformity assessment where the classification is based on using the	
WT procedure Step 1: Initial type assessment Step 2: Dossier preparation and assessment	WFT/FT procedure Step 1: Initial type assessment Step 2: Initial type testing
Conformity evaluation	
Step 3: Factory production control to show conformity to the conditions for the WT procedure	Step 3: Factory production control, including, where needed, further testing

Fig. VI-6: General procedure for classification of construction products to the WT or WFT/FT procedures

"Essential Requirement No. 7: Sustainable use of natural resources". This new requirement will ensure recyclability and durability of buildings as well as the use of environmentally compatible secondary materials in the construction of buildings.

Mandate M/366 and CEN/TC 351

To implement "Essential Requirement No. 3", at the start of 2005 the European Commission issued mandate M/366 "Development of horizontal standardised assessment methods for harmonised approaches relating to dangerous substances under the Construction Products Directive – emissions to indoor air, soil, surface water and groundwater". This mandate is based on the existing CPD; in other words, only the usage phase of a product is considered. It is not yet clear what effects the coming CPR will have on the activities of CEN/TC 351 described below.

The mandate envisages the development of horizontal test and assessment methods by the European Committee for Standardisation (CEN), while the specific requirements for construction products will still be defined nationally by the individual Member States.

A multi-stage attestation procedure is embedded in the mandate that is intended to ensure that testing is required only where it is really necessary for the respective construction product. In detail, the following attestation procedures are planned:

- Attestation without testing, referred to as the WT procedure
- Attestation without further testing, referred to as the WFT procedure
- Attestation with further testing, referred to as the FT procedure

It is still unclear just how these attestation options are to be implemented later, as the EU Commission and the responsible CEN/TC 351 (see next section) each have different ideas about this. According to the EU Commission, the decision as regards classifying construction products to the WT procedure, for example, is to be taken in agreement with the Member States, represented by the "Standing Committee on Construction (SCC)". This would mean that for the WT procedure the most stringent requirements would have to be complied with throughout Europe, which could lead to a situation where only very few construction products could be considered for the WT procedure. At present, intensive discussions are being carried out between the Commission and the CEN representatives to find a practical solution.

Standardisation work in CEN/TC 351

In 2006 the Technical Committee CEN/TC 351 "Assessment of release of dangerous substances from construction products" was formed to develop the test and assessment procedures required under mandate M/366. In accordance with the different intended conditions of use for the construction products, the two following working groups were established:

- Working Group 1: Release into soil and ground/surface water
- Working Group 2: Emissions from construction products into indoor air

To prepare for the actual standardisation, work was commenced on developing six Technical Reports (CEN/TR) on the subjects of barriers to trade, horizontal test methods and their use, WT, WFT/FT procedures, sampling, content and radioactivity. In the period under review, the reports on barriers to trade and WT, WFT/FT procedures were completed and published as prCEN/TR 15855:2008 (E) and prCEN/TR 15858:2008 (E).

The Technical Report on WT, WFT/FT procedures, which was compiled with substantial support from the Research Institute of the Cement Industry, envisages the general procedure presented in **Figure VI-6** for the classification of construction products to the WT or WFT/FT procedures. These procedures apply to the release of regulated dangerous substances into soil, surface water and groundwater and also to emissions of regulated dangerous substances into indoor air.

A condition of classification to the WT procedure is that the existing long-term experience or available test results have shown that the product contains no significant quantities of regulated dangerous substances or releases them only in insignificant amounts that are below the limit values of all EU Member States. In addition, existing knowledge about the constituents, raw materials, the production process, etc. of the respective products are to be included in the assessment.

The WFT procedure, without regular testing, is envisaged for specific products or product groups on the basis of an initial type assessment. In this assessment, the constituents, raw materials, and the release behaviour of the products will be evaluated to see if there is a significant release of regulated substances. If substances could be released, an initial type testing with harmonised European test methods must be carried out to prove that the released quantities of regulated dangerous substances are below the limit values of all Member States of the EU.

If it is not possible to classify a product to the WT or WFT procedure, it is planned that specific products will subjected to further testing according to the assessment criteria defined in their technical specifications (routine tests). If the results of the further tests show that the specific product fulfils the assessment criteria for a WFT procedure, it is planned that the manufacturer can initiate a reclassification to the WFT procedure.

As regards the necessary harmonised European test methods, for the areas of soil and ground/surface water – indoor air has a subordinate significance for purely inorganic, cementitious construction materials – it is planned that a tank leaching process (monolithic materials) and a column process (granular materials) will be developed. The first drafts for these test methods, based on existing methods used in the Netherlands and Germany, have already been proposed. When these drafts have been suitably reworked, it is envisaged to start with the necessary validation tests at the end of this year, so that the work on the test methods can be completed in 2010.

Effects on cement and cementitious construction products

The standardisation work in CEN/TC 351 as regards the test methods is progressing well; however, it will be a few years before the entire concept, such as the WT, WFT/FT procedures can be fully implemented. The Research Institute is represented in the respective important committees and contributes the favourable experiences with cement and concrete that it has gathered over many years for components that are in contact with soil, surface water and groundwater as well as drinking water to the standardization work. The cement industry believes that the scientifically-backed results of the investigations that are available form the basis for the continued use of cement according to EN 197-1 to manufacture construction products and building components that come into contact with the soil and surface water or groundwater without having to be tested (WT procedure).

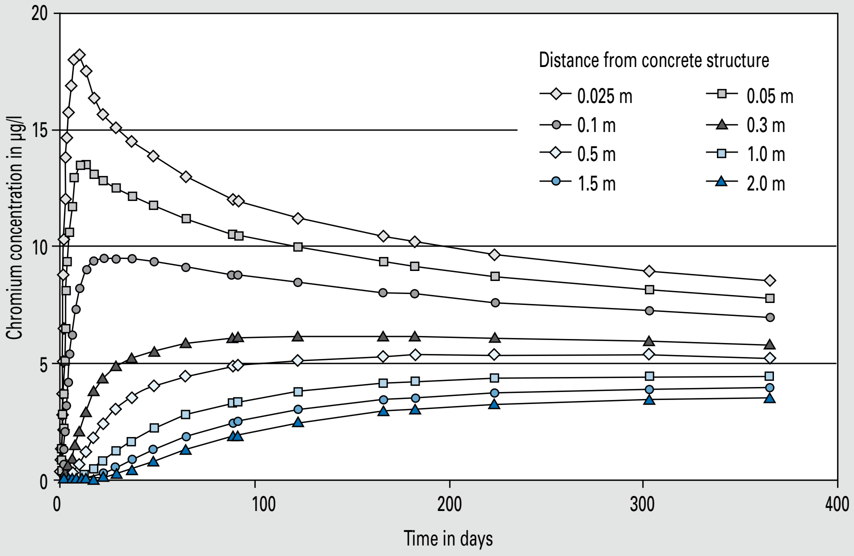


Fig. VI-7: Calculated chromate concentrations at different distances from a concrete structure (Source: DIBt Guideline, Part II, May 2008)

DIBt Guideline "Assessment of the effects of construction products on the soil and groundwater" ■

In Germany, standardised construction products and products approved by the building supervision authorities meet all environmental protection requirements. In the case of new, unknown construction products that require building inspectorate approval, however, potential hazards to the soil and the groundwater have to be taken into account as well. In Germany, the German Institute of Structural Engineering (DIBt) drafted the guideline on "Assessment of the effects of construction products on soil and groundwater" to summarise the scientific, technical and legal fundamentals in one fact sheet. This general concept, which applies to all construction products that come into contact with soil or groundwater, was first published in the version of November 2000. In order to take the material-specific properties of the different construction products into account in an appropriate manner, the general assessment principles for different construction products were specified by the corresponding DIBt project groups in Part II.

The corresponding DIBt project group developed an assessment model for concrete and concrete constituents that allows the results of laboratory investigations (DAfStb Guideline: Determination of the release of inorganic substances through leaching from cementitious construction materials) to be transferred to the actual groundwater impact in the immediate vicinity of a structure. The evaluation model is based on the combination of a diffusion model for leaching from the building material and a geological flow and transport model for the dispersion of the substance in the soil and the groundwater. This combination allows the concentration of a substance in the groundwater in terms of time and space to be calculated. **Figure VI-7** shows an example of the calculated chromium concentrations at different distances from the concrete structure. The substance concentration in the groundwater forecast on the basis of the assessment model has to comply with the corresponding limit values (insignificance threshold). Investigations that the Research Institute carried out on concretes made specifically from cements from German cement works with high contents of trace elements showed that they all meet these requirements. However, the values were, for example, only slightly below the insignificance levels for chrom-ium where the cement contained high levels of chromium.

In 2004, a subcommittee of the German Working Group of the Federal States on Water Issues (LAWA) revised and in some cases drastically lowered the insignificance levels laid down in the DIBt guideline of November 2000. In addition, new levels were set for other parameters, such as barium, boron, thallium and vanadium. The Conference of Ministers for the Environment gave the go-ahead for the publica-

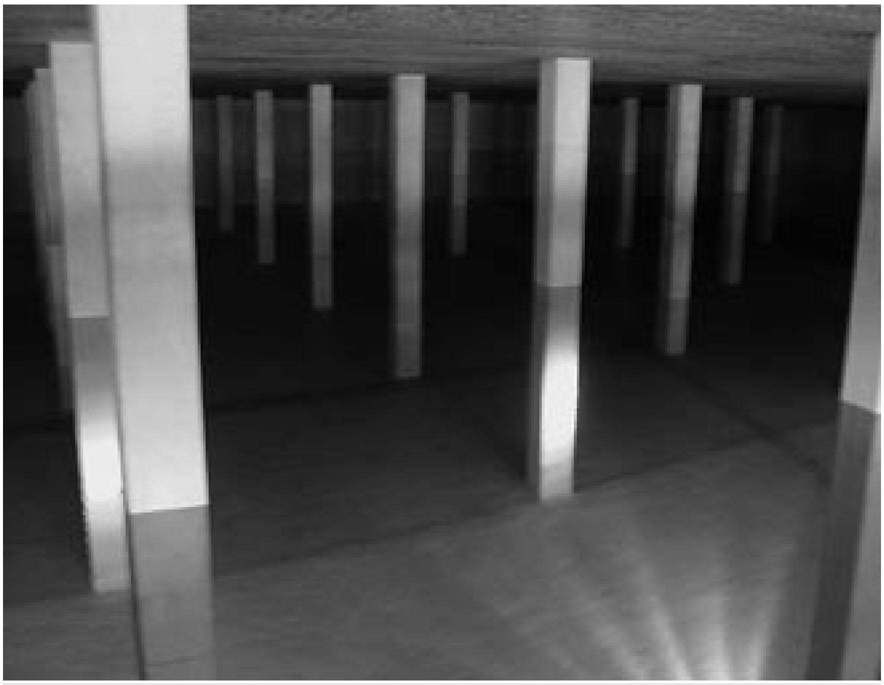


Fig. VI-8: Inside view of a concrete drinking water vessel.

tion of the revised and supplemented insignificance levels, which led to a situation where even concretes manufactured with conventional cements did not meet some of the parameters. However, LAWA was not willing to change these levels – with the exception of vanadium, which was suspended until 31 December 2008 after pressure from the affected building industry. They did, however, agree to a change in the underlying conditions of the DIBt assessment approach. For example, the distance from the structure for which the assessment is made was increased from the original 0.30 metres to 2.0 metres. This change somewhat cushions the effects of the tightened requirements. However, the suspension of the insignificance level for vanadium was not extended after the end of 2008, which could lead to severe restrictions for some construction materials. It can be assumed that concretes manufactured using commercial cements will, in some cases, not comply with the levels for vanadium.

The DIBt guideline also serves to argue a common German position in the European discussion on the implementation of Essential Requirement No. 3 of the European Construction Products Directive on “Hygiene, health and the environment”. The DIBt had agreed not to initiate the notification procedure until a version agreed to by the industry was available. Violating this agreement, the procedure was initiated at short notice in early 2006. As the submitted “Principles for assessing the effects of construction products on the soil and groundwater” refer to the new LAWA insignificance levels, the industry unanimously rejected this procedure. In spite of this, the notification procedure was concluded in 2008. The final version of the principles Part I and Part II (concrete and concrete constituents) can be found on the Internet via the European Commission’s **T**echnical **R**egulations **I**nformation **S**ystem (TRIS).

The new insignificance levels and parameters and the associated considerable reduction in permissible release rates are still emphatically rejected by the affected construction industry. This applies especially to levels that are below the limit values of the German drinking water regulations. From the industry’s point of view LAWA did not furnish evidence that such precautions, which could represent considerable limitations for building practice, are necessary. On top of this, the new insignificance levels, which were previously only recommendations by LAWA for downstream authorities, are now included, for example, in § 48 of the new draft water management law and would for this reason legally enforceable. The German Building Materials Association (Bundesverband Baustoffe - Steine und Erden e.V.) commissioned expert legal advice on § 48, which came to the conclusion: “It is not the insignificance level itself that is unconstitutional because it is based on an ideal and utopian purity requirement for groundwater; however, an emission limit that drastically overweights the degree of groundwater protection that is actually achievable and implementable is unconstitutional”.

Cementitious materials in the drinking water area ■

European Acceptance Scheme (EAS) for construction products in contact with drinking water

Due to the fact that it is extremely important to ensure a supply of clean drinking water, strict hygiene demands are made regarding all materials that come into contact with drinking water. The European Drinking Water Directive defines minimum requirements for all Member States. Because of this, it was also self-evident to harmonise the requirements for materials that come into contact with drinking water throughout Europe. To this end, from 1999 to 2004 drinking water hygiene experts authorised by the Member States worked in the **R**egulators **G**roup for **C**onstruction **P**roducts in Contact with **D**rinking **W**ater (RG-CPDW) to establish a uniform **E**uropean **A**cceptance **S**cheme (EAS). The EAS was intended to apply to all materials that come into contact with drinking water and ensure that the existing consumer protection level was maintained and that it would be possible to continue using all the tried and tested materials with no restrictions.

The work of the RG-CPDW was stopped in 2004 after the EU Commission decided that there was no legal basis for the group to exist. Because of this, the regulators group was changed into an experts group that has no regulatory or decision-making competence but only an advisory function for the Commission. It was further stated that the European Construction Products Directive only covers construction products that correspond to a harmonised technical specification and that the requirements to be placed on these products are left to the individual Member States’ discretion. Thus, it is only possible to harmonise the test methods for construction products in contact with drinking water.

Cementitious materials have been used safely in all areas of drinking water supply for many years (**Fig. VI-8**). Therefore, CEN/TC 104 “Concrete and related products” compiled an **A**pproved **C**onstituent **L**ist (ACL) for constituents that could be used without testing to manufacture concrete that came into contact with drinking water. This ACL contains a list of constituents, such as cements, aggregates, concrete additions, concrete admixtures, etc., that are traditionally used in the drinking water area and which are approved for this purpose in at least one of the EU's Member States. The aim of this ACL concept is to reduce the scope of testing required for building products in contact with drinking water to the extent that is actually necessary.

The EU Commission approved the concept of the ACL. It was then summarised in a Commission paper together with similar lists for plastics (positive list) and metals (composition list) and submitted to the Standing Committee on Construction (SCC) for information. It is not yet foreseeable what status will be conferred on the ACL and the other lists in the future or which committee will decide on these lists. Currently, in the “4 Member States Group” drinking water regulators from France, Great Britain, the Netherlands and Germany are discussing how the work on the EAS can be continued.

The Research Institute’s point of view is that the ACL concept should be continued, as it is a good basis for future work in the field of drinking water. This concept might also serve as a model to develop criteria for WT procedure classification in the work of CEN/TC 351 – Emission of regulated dangerous substances in indoor air, soil, surface water and groundwater.

DVGW worksheet W 347

Worksheet W 347 “Hygiene requirements applying to cementitious materials in the drinking water sector – testing and evaluation”, issued by the German Technical and Scientific Association for Gas and Water (DVGW) was presented and discussed in detail in the last Activity Report. The worksheet defines the hygiene requirements for cementitious materials that come into direct or indirect contact with drinking water or untreated water that is used to recover drinking water. In the May 2006 version of Worksheet W 347, changes were made to take account of the state of the art and the relevant European testing methods. In the period under review there have been no significant changes to the worksheet. However, the inclusion of new substances in the positive list has been discussed. It is planned that in future this list will be discussed each year by the DVGW Project Group 3.4.12 “W 347” and that the extended list will be published on the Internet. The project group is also intensively following the European activities in the drinking water sector. Since the European work is likely to go on for some time yet, in the coming years the May 2006 version of Worksheet W 347 will continue to provide a solid basis for assessing the hygiene properties of cementitious materials in the drinking water sector.

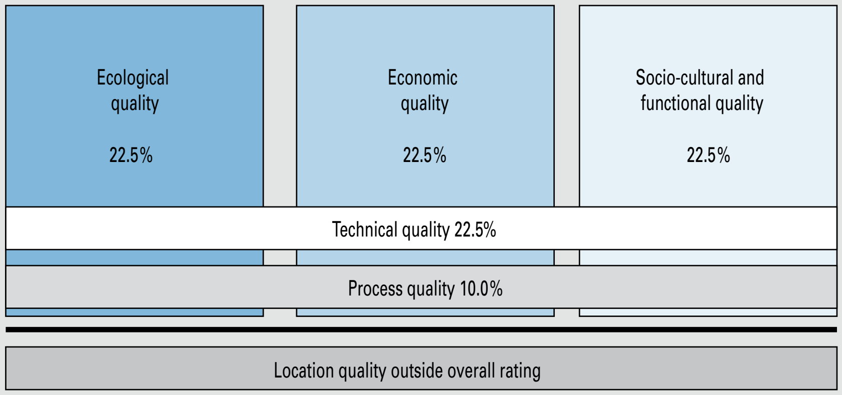


Fig. VI-9: Structure of the assessment system for the German Sustainable Building Certification with a breakdown of the qualities in the overall score

Sustainable building with concrete ■

In sustainable development the needs of the current generation are satisfied without jeopardising the future generations’ chances of living. The building industry follows this guiding principle when functional structures are built at low cost and with a low impact on the environment and when they are used durably.

German Sustainable Building Certification

In Germany, a Sustainable Building Certification was developed by the Federal Ministry for Transport, Building and Urban Development (BMVBS) in collaboration with the German Sustainable Building Council (DGNB). This will allow sustainability to be measured in the building industry in future. In principle, the assessment is based on the life cycle of the building – from the manufacture of the building material and construction of the building through its use stage to the demolition stage. The fundamental criteria were discussed with the participation of the German Building Materials Association (Bundesverband Baustoffe - Steine und Erden e.V.) and the VDZ at the BMVBS's Sustainable Building Round Table.

Ecological, economic and social criteria were considered equally in the overall consideration (**Fig. VI-9**). One ecological criterion is, for example, the contribution of the building to the greenhouse effect on the basis of its construction and use. The key economic yardsticks are the life cycle costs which, in addition to the costs of construction, also include running and maintenance costs. The socio-cultural criteria take account of the effects that the structure has on the health and comfort of its users, among other things. In addition to these three dimensions of sustainability, the technical quality of the building involves, for example, an assessment of fire and noise protection. Although only to a lesser extent, process quality is also considered with criteria such as integral planning. At the end of this process, the structure has an overall score made up from the partial scores for ecological, economic and socio-cultural aspects, which also assesses the technical and design performance. The quality of the location of the structure is also taken into account, but this aspect is not included in the overall score. The certificate is awarded in gold, silver and bronze to provide a visual illustration of the assessment.

DGNB wants the buildings to be assessed by suitably trained auditors. Initially, the certification is limited to newly constructed office and administrative buildings. The practicability of the system has been tested in some pilot projects. DGNB plans to establish the German Sustainable Building Certification outside Germany and thus compete with certificates that are already established there.

Fig. VI-10: New carbon-hydrogen analyser with autosampler

Fig. VI-11: The new ion chromatograph

Standardisation regarding sustainable building

The European Committee for Standardisation (CEN), wants to build on the work of the ISO to establish clear guidelines for implementing sustainability in the European building industry. The general principles to describe buildings in the light of sustainability are to be described in the first of four framework documents. The three other parts will deal with the ecological, economic and social aspects. For the ecological dimension, the rules for calculating the environmental impact of a building and for drafting an environmental declaration for construction products will also be explained. Through its work in the DIN Mirror Committee, the VDZ ensures that the procedures established in Germany and accordingly regarded as practical are also incorporated into the European standards.

Sustainable concrete construction

Given its performance capacity, its wide range of applications and the large quantities of building materials used, concrete construction assumes a pre-eminent position in the building sector. This is why the development of rules and technical recommendations is of particular importance. The German Committee for Structural Concrete (DAfStb) is preparing the guideline “Basis of Sustainable Construction with Concrete (GrunaBau)”. To develop this guideline DAfStb has initiated a joint project which is funded by the German Federal Ministry for Education and Research (BMBF) and in which, under the auspices of the Research Institute, the potential for the use of alternative materials in cement and concrete manufacture will be investigated.

Ecological building material profiles

Information about the environmental effects associated with the manufacture of building materials is needed in the DAfStb project so that it can be used to calculate the sustainability indicators for a building. BMVBS also bases its sustainability assessments on suitable data. Ecological building material profiles summarise the environmental impacts related to the manufacture of a building material and provide these profiles for such calculations.

The updated building material profile for cement presents the contribution towards greenhouse potential and the contributions towards other environmental impacts for a cement that has been averaged for all the cements produced in Germany, and is based on the average proportions of cement clinker and other main constituents in 2006. The profile also takes account of the environmental impacts of upstream supply chains, for example the electricity used to produce the material. Considerable improvements have been made compared to the first calculation of the building material profile for cement ten years ago (see Table V-1). For instance, the specific contribution to the greenhouse effect has been reduced by 23 % and consumption of non-renewable energies has fallen by 38 %; contribution to other environmental impacts has also been drastically reduced. The reductions reflect the fact that in Germany more cement is produced with several main constituents but also the increased use of alternative fuels has a positive effect on many key values. The indicators determined for cement are also used as a basis for the building material profiles of cementitious building materials, such as concrete, and also for the ecological profiles of buildings constructed with these materials.

Measuring and testing methods ■

The Research Institute has had efficient analysis techniques to determine main, minor and trace elements at its disposal for many years. While in the past these techniques were used mainly in research projects and to clarify analytical issues, the Institute is now increasingly in demand as a service provider for these analysis tasks. As external customers need reliable investigation results quickly, the increased share of contract services demands analysis techniques that ensure high quality as well as rapid order processing. The Research Institute therefore strives to maintain state-of-the-art analysis equipment. For example, during the period under review the Institute acquired a high-performance carbon-hydrogen analyser and another ion chromatograph.

Focus on fuel analysis

For the cement industry, the steady increase in the use of alternative fuels has made reliable analysis of the carbon and hydrogen content in the fuels more important. In particular, this concerns determination of the biogenic carbon content according to the selective dissolution method and the determination of calorific values. The newly acquired carbon-hydrogen analyser is equipped with an autosampler for 50 samples (**Fig. VI-10**). This allows the carbon and hydrogen content of many different samples to be determined within a very short time. The standard deviations of repeatability are very low in spite of small sample weights of about 30 mg. The analyser also has very good long-term stability and only needs to be calibrated just once a year.

Due to the increase in fuel analyses, the number of fluorine, chlorine, bromine, iodine and sulphur determinations has also increased. The Institute thus acquired another ion chromatograph (**Fig. VI-11**) with autosampler. This allows parallel measurement of anions and cations. Both devices can cover all measurement tasks, which means that any downtime in one measuring system can be compensated for by the other. The new analysis devices have shortened testing times and increased sample throughput.

VII

Responsibility for employees

Safety at maintenance according to regulations

Safety at work ■

Results of the safety activities

Improving safety at work in the cement plants is one of VDZ's constitutional functions. Efforts at plant level and at the Research Institute are therefore a priority for the association. VDZ's Environment and Plant Technology Committee develops and initiates measures to improve safety at work and is effectively supported in its work by VDZ's "Safety At Work" working group. The common goal of all these efforts is to promote an awareness for safety among employees at cement works, to inform them regularly about ways of improving workplace safety and to encourage them to continuously review safety in the workplace.

The workplace safety measures carried out in the works and the cooperation with VDZ and its Research Institute have greatly contributed to the fact that accident frequency (based on reportable accidents according to the definition of the Quarry Employers' Liability Insurance Association – StBG) has fallen continuously in German cement works since 1969 and is now at less than a third of its original level. In 1984, accident frequency among all employees was already at a very low level of about 20 accidents per million hours worked. In the current reporting period accident frequency is about 13.50.

The economic importance of workplace safety can best be described by the time employees are unable to work as a result of workplace accidents taken as a percentage of total working hours. While in 1969 the average time lost due to reportable workplace accidents was roughly 0.8 %, by 2008 this had fallen to just 0.3 %.

VDZ accident statistics

The Research Institute has recorded and statistically analysed the number of reportable workplace and commuting accidents in German members' works each year since 1965. The most important results and key figures from the accident statistics in 2007 and 2008 are aggregated in **Table VII-1**. To compare and characterise the trend in accident statistics the first column of the table contains the corresponding figures from 1969, the first year in which accidents in the cement industry were statistically analysed. To take account of the changing personnel structure in the works, from 1993 onwards the figures include not only industrial workers but the entire workforce as a basis for calculating accident statistics. In the assessment of the statistics for 2008 it must be considered that the underlying conditions for the workplace safety competition were made more stringent than in the previous years. Now, a works is deemed to be accident free only if employees are able to work on the day following an accident – in other words, they are also not permitted to lose working time due to non-reportable accidents – however, the day on which the accident occurs is not counted. Under these new underlying conditions for the competition the main assessment criterion is now also calculated in a different manner: from 2008, the accident frequency rate takes account of all industrial accidents where employees are unable to work in relation to one million hours worked.

In 2007, the workforce rose slightly compared to the previous year (+ 0.4 %), but in 2008 dropped again to the 2006 level. The number of hours followed a trend in the opposite direction: despite the increased workforce in 2007 the hours worked fell by approx. 1 %. However, with the reduction in the workforce in 2008, the number of hours worked increased by about 0.4 %. For this reason, the number of hours worked per employee per annum fell from about 1 654 in 2006 to 1 631 in 2007 and then increased again in 2008 to 1 644. As Table VII-1 shows, during the reporting period production rose from roughly 34.4 million metric tonnes in 2007 to 34.7 million mt in 2008. However, production-related working expenditure was about the same in both years (0.24 h/t). The number of reportable industrial accidents – 121 in 2006 – dropped to 110 in 2007 and in 2008 had fallen further to just 109. During the period under review the total number of industrial accidents also pleasingly declined: while in 2006, 270 industrial accidents were reported for the workforce, in 2007 this number had fallen to 249 and in 2008 was just 176. Accordingly, this was also reflected in the average accident frequency trend. However, when these quotients of the number of industrial accidents per 1 million hours worked are assessed, it must be remembered that from the 2008 reporting year the total number of industrial accidents where employees were unable to work are also counted while up until 2007 only reportable industrial accidents according to the StBG definition (in other words, industrial accidents where more than 3 working days are lost) were included in the statistics. To better illustrate the trend in these values, Table VII-1 includes

Table VII-1: Accident statistics for the workforce in VDZ member companies in 1969, 2007 and 2008

Year	1969	2007	2008
Number of works covered	98	48	47
Cement production in millions of metric tonnes	34.3	34.4	34.7
Plant headcount			
Number of employees	15 190	4 997	4 975
Hours worked	31 339 177	8 148 904	8 178 699
Production-related working hours in h/t	0.91	0.24	0.24
Reportable industrial accidents	1 376	110	109
Total industrial accidents (including non-reportable industrial accidents)	1 541	249	176
Accident rate (definition before 2007) (reportable accidents per 1 million hours worked)	43.90	13.50	13.33
Accident rate (definition from 2008) (total industrial accidents per 1 million hours worked)	49.17	30.56	21.52
Calendar days lost as a result of reportable industrial accidents	31 935	3 573	3 363
Working days lost per employee	2.10	0.72	0.68
Calendar days lost per industrial accident	23.20	32.48	30.85
"100-men" rate (old definition) (reportable accidents per 100 employees)	9.10	2.20	2.19
"100-men" rate (new definition) (total industrial accidents per 100 employees)	10.15	4.98	3.54

accident frequency rates based on the old and the new definitions. It is especially clear that the accident frequency rate according to the new definition fell dramatically from 2007 to 2008; this can be attributed to the drop in non-reportable accidents in this period.

The new definition for accident frequency from 2008 has a major effect on VDZ's workplace safety competition. Since the accident frequency rate is the basis for the ranking in this competition, the number of works awarded a prize fell considerably from 2008. The only works able to achieve first place in this competition are those that report no days lost as a result of industrial accidents. The large decline in the number of winners in the workplace safety competition between 2007 and 2008 is easily explained by the above. Based on the new definition, in 2008 two works reported no accidents; in 2007 (according to the old rules) ten works were accident free (**Fig. VII-1** and **Table VII-2**).

The average number of calendar days lost due to reportable industrial accidents fell by approximately 5 %, from 32.48 in 2007 to 30.85 in 2008. The economic significance of industrial accidents can also be assessed on the basis of the annual loss in productivity. This key figure shows the number of calendar days lost due to reportable industrial accidents in relation to the number of employees in the plant. The average annual loss in productivity dropped from 0.72 in 2007 to 0.68 in 2008. The "100-men rate", the number of industrial accidents per 100 employees in the plant, dropped further between 2007 and 2008. Based on the new definition (i.e. total industrial accidents per 100 employees), the value fell by approx. 40 %, from 4.98 in 2007 to 3.54 in 2008. To provide a better comparison with the previous year's figures, Table VII-1 shows the "100-men rate" according to the old and new definitions.

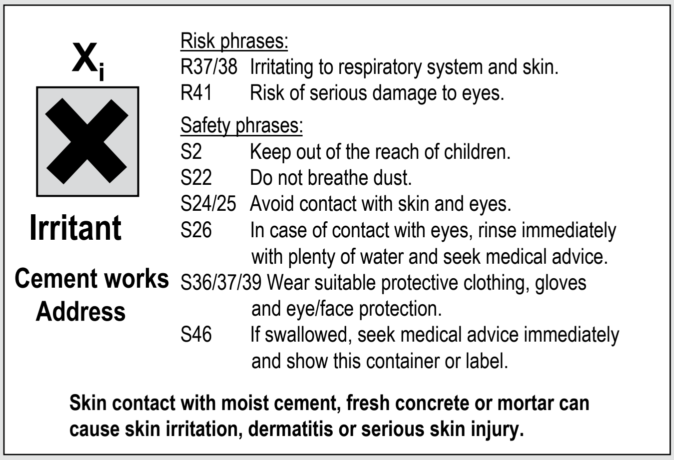
Promoting safety at work

Over the last two years, five safety codes of practice (Nos. 106 to 110) describing typical and particularly noteworthy workplace accidents as well as five safety checklists (Nos. 86 to 90) to review measures and improve workplace safety in various areas of the works have been published. For the last 30 years, awards have been given to the clinker producing members' works with the lowest accident frequency rates. The award consists of a plaque and the VDZ safety symbol with the inscription "Safe working – VDZ". The plaque recognises the efforts by plant management and the workforce to

Fig. VII-1: Presentation of the awards to the winners of the 2007 VDZ industrial safety competition

Table VII-2: Winners of the VDZ industrial safety competition for clinker-producing works in 2007 and 2008

	2007	2008
1st place	CEMEX WestZement GmbH Beckum-Kollenbach works Accident rate: 0.0	Schwenk Zement KG Allmendingen works Accident rate: 0.0
	CEMEX OstZement GmbH Rüdersdorf works Accident rate: 0.0	Schwenk Zement KG Mergelstetten works Accident rate: 0.0
	Dyckerhoff AG Geseke works Accident rate: 0.0	
	Dyckerhoff AG Göllheim works Accident rate: 0.0	
	HeidelbergCement AG Ennigerloh-Nord works Accident rate: 0.0	
	HeidelbergCement AG Lengfurt works Accident rate: 0.0	
	Holcim (Deutschland) AG Höver works Accident rate: 0.0	
	Lafarge Zement Karsdorf GmbH Karsdorf works Accident rate: 0.0	
	Schwenk Zement KG Mergelstetten works Accident rate: 0.0	
	Teutonia Zementwerk AG Accident rate: 0.0	
2nd place	Südbayerische Portland-Zementwerk Gebr. Wiesböck & Co. GmbH Accident rate: 2.70	Holcim (Süddeutschland) GmbH Dotternhausen works Accident rate: 4.02
3rd place	Dyckerhoff AG Lengerich works Accident rate: 3.42	Holcim (Deutschland) AG Höver works Accident rate: 4.08



X_i

Irritant

Cement works
Address

Risk phrases:
R37/38 Irritating to respiratory system and skin.
R41 Risk of serious damage to eyes.

Safety phrases:
S2 Keep out of the reach of children.
S22 Do not breathe dust.
S24/25 Avoid contact with skin and eyes.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37/39 Wear suitable protective clothing, gloves and eye/face protection.
S46 If swallowed, seek medical advice immediately and show this container or label.

Skin contact with moist cement, fresh concrete or mortar can cause skin irritation, dermatitis or serious skin injury.

Fig. VII-2: New labelling of bagged cement

ensure workplace safety. The award is also intended to motivate employees and to raise safety awareness in the works.

Since the potential risks in clinker-producing works are quite different from those for employees in works without clinker production, there is a limit as to how far a standard measure can be applied to assess safety standards at all works. In order to also provide motivation to improve safety at work in grinding plants, a special workplace safety competition was introduced for this group of plants in 1995. The grinding plants with the lowest accident frequency rates are awarded with a corresponding certificate.

Safety seminars

The pattern of accident statistics for recent years clearly shows that safety at work improved markedly as a consequence of the substantial efforts made at plant level with the support of the working group and the Research Institute. However, to continually improve safety at work there must be no slackening in the efforts made by all employees; in fact they must be further intensified. The key factor is employee motivation to correctly apply plant safety rules and to actively implement them. This is primarily the responsibility of the works management – works managers, plant managers and especially foremen and assistant foremen. The industrial foreman is in constant contact with his team, and as a role model he has the greatest influence on improving safety at work. In the light of this, VDZ has offered intensive training courses for practising foremen and assistant foremen on the recommendation of the “Safety at Work” working group. The aim of the seminars is to improve knowledge of safe working practices, especially in high-risk areas, to highlight significant accidents and convey suggestions for direct action to improve safety at work. The seminars are provided jointly by the Quarry Employers’ Liability Insurance Association (StBG) and VDZ. They are arranged jointly by VDZ’s Safety at Work working group and the StBG, last approximately two days and are organised and conducted off-site in groups of 15 to 20 participants by StBG seminar leaders. The seminars have been offered on a regular basis since 1993. The speakers are qualified StBG staff. The course content is updated regularly and is thus suited to the participant’s current working environment.

Safety data sheets

The REACH Regulation demands a hazardous substance classification for every substance, and therefore also for Portland cement clinker, by the end of 2010, which must be submitted to the new European Chemicals Agency (ECHA). So that this takes place throughout Europe in a standard manner, the substances are being classified by a group of experts in CEMBUREAU with the intensive participation of VDZ based on the current statutory regulations and the latest scientific findings. On this basis, sample safety data sheets (SDS) were drafted for Portland cement clinker and for Portland cement. These take account of the changes in structure and content demanded in the REACH regulation. The sample safety data sheets have been translated into German and have been provided to cement producers as VDZ sample safety data sheets. There are only a few substantial changes compared to the 2005 version. A new addition is the hazard warning R37 “Irritating to respiratory systems”. Apart from that, many points are formulated in more detail. In spite of the intended harmonisation, the VDZ version differs from the CEMBUREAU version in one important point. The hazard warning R43 “May cause sensitisation by skin contact” is not mentioned for low-chromate and chromate-reduced cements, as this would be in contradiction to the requirements of the German workplace safety authorities. However, this difference does not exist in the sample safety data sheets for cements containing chromate or for cement clinker.

Besides the new features in the safety data sheets, agreement has been reached throughout Europe regarding the use of an additional warning in the labelling of bagged products, the sentence “Skin contact with moist cement, fresh concrete or mortar can cause skin irritation, dermatitis or serious skin injury”. This is intended more to warn private users of potential risks (**Fig. VII-2**).

VDZ training and development ■

Training courses for industrial foreman

VDZ offers training courses and seminars to promote advanced training among cement works employees. It has been conducting training courses for industrial foremen in collaboration with the Düsseldorf Chamber of Industry and Commerce since 1958. By 1965, eight training courses had been held and a total of 274 industrial foremen had successfully completed the "cement" course. The specialist "lime/cement" industrial foremen's course that the VDZ has been running jointly with the Federal German Association of the Lime Industry since 1965 is unique in German-speaking countries. 563 people had successfully taken part in 23 industrial foremen training courses on "lime/cement" as at March 2009 (**Fig. VII-2** and **Table VII-3**). Thus, VDZ can look back on 51 years of successfully training industrial foremen.

In a total of 28 subjects taught over 946 hours the future foremen learn the theoretical fundamentals for their subsequent work in the cement and lime works. During the 7-month residential course in the new training facility in Hilden, the foremen are also taught the basic subjects of mathematics, physics, chemistry and the fundamentals of materials science. In alternation with two four and six-month correspondence courses in their own works, the foremen are subsequently trained in specific areas such as quarrying technology, process technology, firing engineering, environmental engineering, mechanical and energy engineering. Other focuses of the training are management, workplace safety and behaviour in the works. For example, technical situations are discussed and handled in detail, such as, "How would I behave in case of an accident or how do I handle conflicts among co-workers?" The recognised advanced training is completed with the foremen obtaining a trainer aptitude certificate (German trainer aptitude regulations, AEVO). When the foremen have passed this examination, they are also able to train employees.

Fig. VII-3: "Lime/Cement" industrial foremen after completion of the final examination in March 2009

Table VII-3: Number of graduates from the industrial foreman training courses

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	1987/1989	22	3	25
	13	1989/1991	20	10	30
	14	1991/1993	20	10	30
	15	1992/1994	24	6	30
	16	1993/1995	26	3	29
	17	1995/1997	24	2	26
	18	1997/1999	21	2	23
	19	1999/2001	21	2	23
	20	2001/2003	13	2	15
	21	2003/2005	13	0	13
	22	2005/2007	11	1	12
	23	2007/2009	15	2	17
Grand total			684	153	837

The new training facility in Hilden certainly helped make the last 23rd foreman training course a success. The trainee foremen, trainers and managers were all very impressed by the accommodation, the training rooms and the food. Over the last two years, trainee foremen were accommodated for a total of 7 months in the new residential facility. Apart from full board, beverages during the breaks and accommodation in single ensuite rooms, the facility also offers many leisure activities (**Fig. VII-4**).

Production controller course

In response to the increased level of qualifications necessary for control room operators, in 1990 VDZ decided to organise training courses for production controllers. These advanced training courses are designed to provide control room operators with up-to-date knowledge of process engineering and environmental technol-

Fig. VII-4: New training facility in Hilden

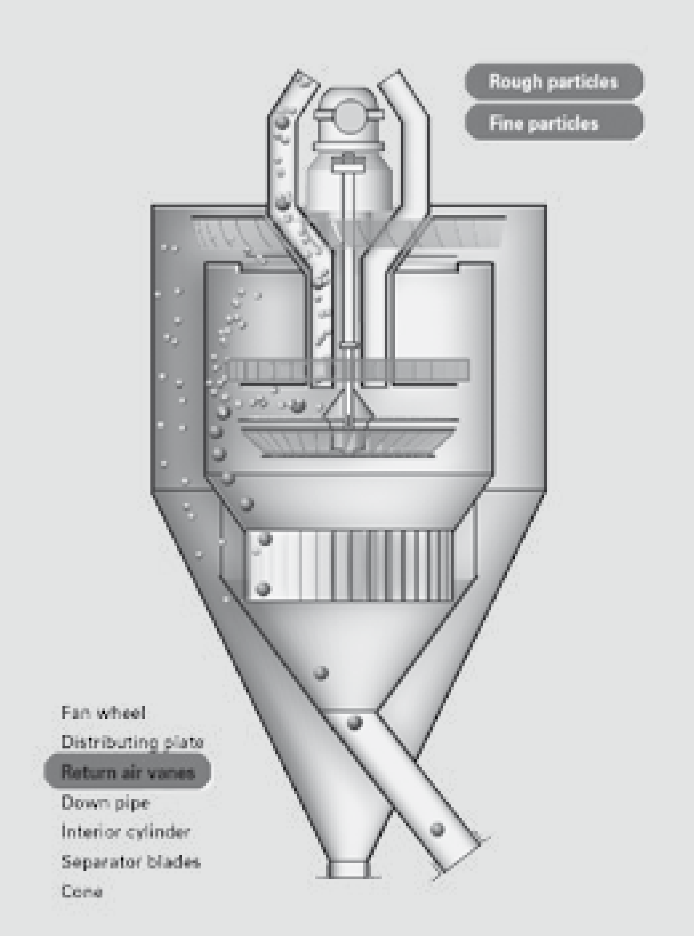


Fig. VII-5: Animation "Recirculating air classifier"

ogy in the areas of cement manufacturing and measuring and control technology in cement works. The aim is to make it easier for the control room operators to adapt to changes in production control resulting from automation and new developments in order to ensure reliable and effective operation of the cement plants. The complete programme includes a theoretical part offered by VDZ within the scope of a residential training course in the Hilden training facility and a practical part in the cement works. During the seven weeks of the theoretical part, the participants are given in-depth training in subjects such as materials science, firing technology, environmental engineering, process engineering, instrumentation technology and the basic subjects of mathematics, chemistry and physics. Apart from the many hours of training, the course also focuses on exchanging practical experience.

320 "cement" production controllers had taken part in 15 advanced training courses by 2009. In September 2008 the first production controller course in the new training facility in Hilden was successfully completed. The very good underlying conditions offered by the new training facility certainly helped make this course a success. Trainers and trainees are also very impressed by the learning conditions, the accommodation and the full board.

The next course will be held in the Düsseldorf-Hilden training facility from April to September 2011.

Training certificates - multimedia

Over the last years, VDZ and the VDZ working group "Training certificates" have compiled 47 training certificates for advanced training of industrial-technical employees and have successfully introduced these in the cement industry's works. As a result of the ongoing developments in electronically aided forms of learning, known as e-learning, in 2007 the VDZ Training Courses Advisory Board decided to optimise the training certificates for use in such application scenarios and to provide the cement works with the option of using the training certificates within the scope of e-learning modules.

The possibility of implementing a corresponding solution was given in 2008 by the German Federal Ministry for Education and Research (BMBF) within the scope of a funded project for the use of electronically-aided forms of learning in vocational training. In the "Vocational training for sustainable development in the German cement industry" project, which VDZ is carrying out together with SustainConsult, visaplan and selected pilot works, an investigation is being conducted to see the extent to which Internet-based forms of learning are suitable for industrial-technical employees, using the cement industry as an example. The project is initially scheduled to last two years and should be completed at the end of 2009.

Within the scope of the project, the existing 47 training certificates were revised in terms of the teaching methods, the content and the use of media on the basis of trials carried out in the works. In particular, the project partners developed innovative visualisations and animations that helped the trainees to better understand the subjects and the connections (**Fig. VII-5**). The training certificates were also extended with questions, tests and tasks to be submitted, so that the success of the learning can be controlled individually.

VDZ provides the revised training certificates on the Internet platform http://www.elearning-vdz.de where they can be used by the cement industry and associated industries. The technologies used also allow individual subjects to be aggregated and the works to add specific topics and tasks. It is also possible to order the training certificates in printed or electronic format.

Professional training seminars

In addition to the existing industrial foremen's and production controllers' training courses and the safety at work seminars, VDZ offered a series of one-day and extended seminars on chemical analysis, immission control and environmental engineering, process engineering for cement production, monitoring cement quality and the fundamentals of concrete engineering and concrete processing for the first time in 1998 as part of its further education programme. The programme is intended as an introduction for junior staff in VDZ's member companies, as well as an advanced training programme for longer-serving employees. The current seminar programme for 2009 was announced to the member works in the form of a brochure and also via the VDZ website www.vdz-online.de

According to the 5th Ordinance to the Federal Immission Control Act (5th BImSchV), immission control officers must take part in an advanced training course every 2 years. While the basic courses for immission control officers cover all areas of environmental protection, focal points can be dealt with in the advanced training courses. To date, VDZ has organised eight of these advanced training courses specially designed to handle the requirements of the cement industry. Besides the latest developments in environmental law in Germany and Europe, they have focused on emissions of organic compounds and trace elements as well as reducing CO_2 emissions in the clinker burning process. The seminar is recognised as an advanced training course in terms of the 5th BImSchV by the Ministry for the Environment and Nature Conservation, Agriculture and Consumer protection of the state of North-Rhine Westphalia and is organised every two years to focus on current topics.

The seminar "Introduction to Environmental Technology" is also held every two years, alternating with the advanced training course for immission control officers. The seminar was cancelled in 2007 due to a lack of demand but will be held in 2009. Those taking part in the seminar will be introduced to all sub-areas of environmental protection and environmental engineering. The subjects dealt with include environmental law, emission measuring technology, reducing gas, dust and heavy metal emissions, noise and vibration, ecological recycling of waste and production-integrated environmental protection. The presentations are supplemented with practical demonstrations of emission and immission measuring technology. The seminar is recognised as a basic training course for future immission control officers.

The aim of the four-day seminar for "young plant engineers" is to provide a comprehensive overview of all areas of cement production through to the use of cement in concrete. Accordingly, the seminar deals intensively with process engineering subjects, chemical-mineralogical issues, environmental legislation, environmental measuring technology, quality assurance and concrete engineering. The seminar is offered every two years. The seminar was well attended in 2008, with more than 20 people taking part. The next seminar will be held in 2010.

Practice-related advanced vocational training was extended in 2005 with the first seminar on "From practical application – for practical application". The target groups for the seminar, which was held in 2008 and will be organised next time in 2010, are practicing industrial foremen and production controllers. The participants are given in-depth training into modern developments in process engineering and cement production. Building on this basis, the participants are shown how to train production employees on the basis of training certificates.

Four seminars are offered on the subject of "cement quality monitoring" every year. These seminars are aimed at laboratory managers and responsible staff in the works' laboratories. In a one-day seminar on "X-ray fluorescence (XFA)" the participants gain in-depth knowledge of XF analysis techniques. The two-day seminar "Technical mineralogy" explains how to determine the chemical-mineralogical properties of cement constituents, clinker, cement and concrete using microscopic and X-ray diffractometric analysis methods and how to assess the results. Practical demonstrations are given and the technical fundamentals of the analysis systems are explained. The two-day seminar "Testing according to DIN EN 196" introduces the physical and chemical tests for cements and cement-type binders, raw materials and constituents that are defined in the standard. Particular importance is attached to compliance with the work methods stipulated in the standard and to the detection and avoidance of error sources. The focus of a further one-day seminar is the determination of the blast furnace slag content in cements based on a combined microscopic-chemical method. This seminar is supplemented by a one-day seminar called "Determination of the blast furnace slag content – overview of methods". Participants are given an overview of potential methods for determining the blast furnace slag content in cement.

In the area of cement applications a two-day seminar is offered on "Fundamental principles of concrete engineering/durability of concrete and reinforced concrete elements". The first part of the seminar introduces the participants to the fundamentals of concrete technology and concrete engineering. Special attention is paid to the effects of the new standards DIN 1045 and DIN EN 206-1. Practical demonstrations in the concrete laboratory help illustrate the theoretical presentations. The seminar also deals with practical building issues, such as processing concrete at the building site and in the concrete works as well as transport, pumping, laying and compacting of concrete. The second part of the seminar handles the durability of concrete and reinforced concrete elements. One of the aims of this part is to assess deformation, transport and damage mechanisms with consideration of exposure and resistance. Proceeding from the explanations given regarding elastic and plastic deformation of concrete, load-free deformation caused by shrinkage and hydration heat is discussed, as are the possibilities for reducing crack formation in structural elements. As part of the topic of "concrete corrosion", resistance to frost and de-icing salt, resistance to acid and sulphate attack as well as to harmful alkali-silica reactions are discussed. The concept of exposure classes (e.g. frost XF1 to XF4) specified in the standards and its effects on the concrete composition to be chosen are explained and the test methods for assessing the resistance of concrete are demonstrated in practical presentations.

The Research Institute offered seven seminars in 2007 and nine in 2008. Another seven seminars are scheduled for 2009.

Publications

Schriftenreihe der Zementindustrie (Publication series of the cement industry)

Schneider, C.	*Zur Konstitution von Hüttensand, seiner quantitativen Bestimmung und seinem Festigkeitsbeitrag im Zement.* Düsseldorf: Verl. Bau und Technik, 2009 (Schriftenreihe der Zementindustrie 72)

Merkblätter und Prüflisten (Codes of practice and checklists)

Sicherheits-Merkblätter (Safety codes of practice)

Nr. 106	Empfohlene Unterweisungen für Zementwerksmitarbeiter
Nr. 107	Unbeleuchteten Keller betreten – Fußverbrennung
Nr. 108	Tödlicher Unfall bei Wartungsarbeiten an einem Kettenförderer
Nr. 109	Schwere Verletzungen durch Absturz von Brückenkran

Sicherheits-Prüflisten (Safety checklists)

Nr. 86	Unterweisung
Nr. 87	Heißmehlaustritt in Kellerbereichen
Nr. 88	Arbeiten in Kippstellen, Silos, Bunkern
Nr. 89	Arbeiten in Höhen auf Schutzgerüsten

VDZ-Merkblätter (VDZ codes of practice)

Feuerfeste Materialien
Umweltverträgliche Rohstoffgewinnung

VDZ-Mitteilungen (VDZ Newsletter)

Nr. 133 (Mai 2007) – Nr. 138 (Dezember 2008)
Jedes Jahr werden drei Ausgaben mit Erscheinungstermin im Mai, September und Dezember publiziert.

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