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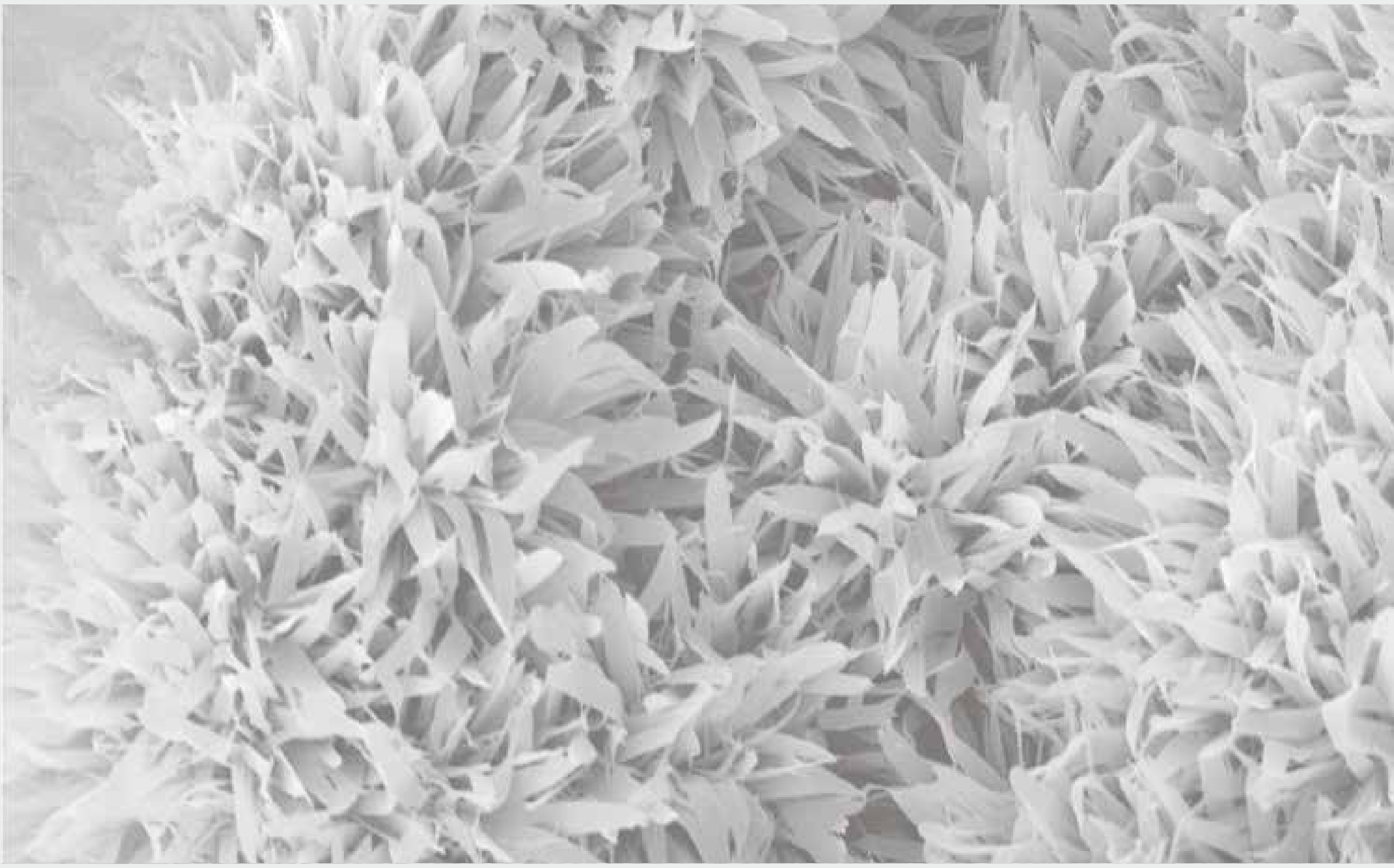
Deutsche Zementindustrie

Activity Report

2003 – 2005

Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie



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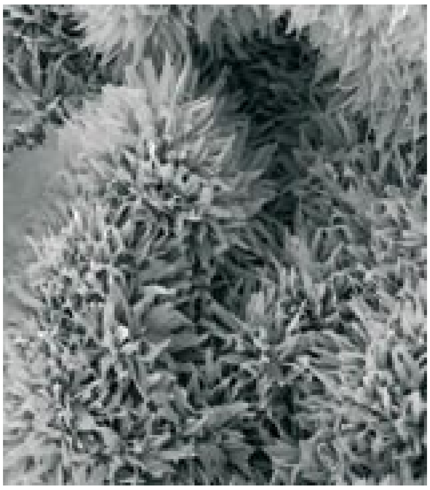
Activity Report 2003 – 2005

Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie
Postfach 30 10 63, D-40410 Düsseldorf
Tannenstraße 2, D-40476 Düsseldorf
Phone: (+49-211) 45 78-1
Fax: (+49-211) 45 78-296
info@vdz-online.de
www.vdz-online.de



The cover shows a picture taken by the Research Institute's scanning electron microscope.

The tobermorite, which was photographed at 1 000-fold magnification, is a natural mineral formed during cement hydration, but also in calcareous sandstone and silicate concrete. Its naturally-occurring manifestation is found in hollows of basalt, for example. Tobermorite is the "binder" in the hardened cement paste from which it derives its strength.

Chemically, tobermorite is a calcium silicate hydrate. Accounting for some 80%, the so-called CSH phases are a main constituent of hardened cement paste and substantially determine its properties.

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Contents

Verein Deutscher Zementwerke e.V. Forschungsinstitut der Zementindustrie

With the present Activity Report the German Cement Works Association (VDZ) has continued its proven tradition of regularly summarising the results of its industrial joint research of the past years. Covering the years from 2003 to 2005, the present report deals with all the relevant topics of cement manufacture and application.

The building materials industry worldwide is exposed to a climate of radical change. Rapid growth in the newly industrialised regions is opposed to a severe decline in sales in the mature markets. Against this backdrop, both the quality of concrete construction and that of the training of people handling cement-bound building materials is increasingly gaining importance. Industrial joint research is facing the challenge of supplying attractive, pioneering contributions to the advance of cement manufacture and application in spite of tight budgets. VDZ has faced up to this challenge. In view of the economic woes of the domestic cement industry, it has consistently re-oriented its work, now presenting itself as a competent partner in all questions arising in cement manufacture and concrete construction. Its research results are characterised by being tailored exactly to practical application and lending themselves to swift implementation. At the same time, VDZ offers an attractive range of services and consultancy. The Research Institute has a competent staff and state-of-the-art equipment that allow to carry out both standard investigations and highly demanding tasks.

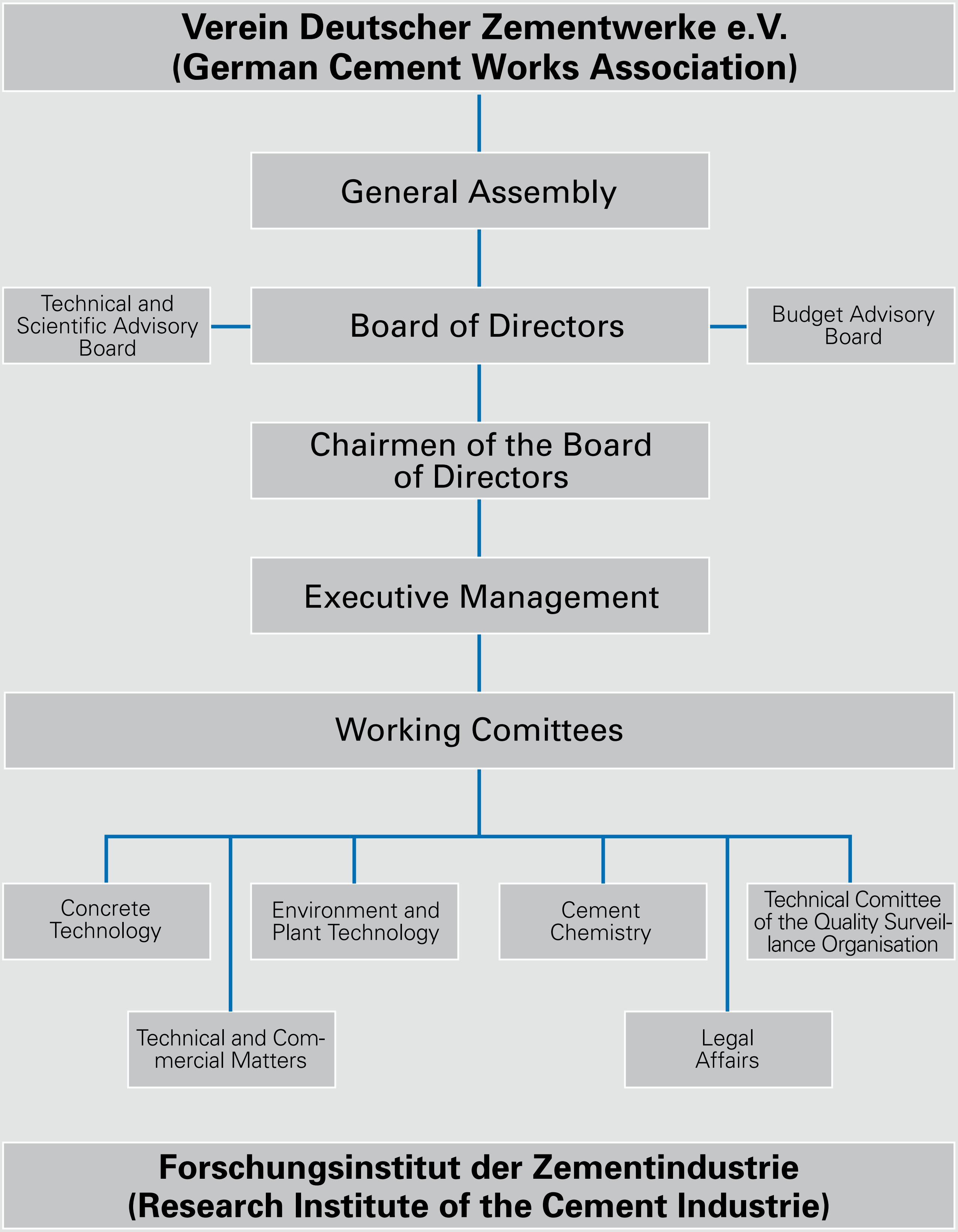
With its Research Institute, VDZ has adopted a consistently international orientation. Since the demand for attractive research does not make a stop at national boundaries, VDZ takes advantage of its international contacts to derive essential experience for its work. The member plants benefit from this practice as VDZ is involved in European developments that may have implications for the cement industry and for concrete construction. The most recent challenges that have arisen at EU level include draft legislation on emissions trading or on the maintenance of industrial health and safety while handling cement. The Research Institute's main fields of work have always comprised climate protection and the responsibility for employees and cement users. Extensive investigations on lowering fuel energy consumption and on the use of Portland-composite cements, for example, have contributed to a further significant reduction in the specific CO_2 emissions of the cement industry over the past few years. The results obtained from the Institute's work have shown that emission limits like those stipulated in the European Emissions Trading Directive will not have any effect on worldwide global warming prevention. Much rather, they will lead to cement production sites being relocated since domestic companies will not be able to purchase a sufficient number of CO_2 certificates.

VDZ can look back on a tradition of more than 125 years. This long, successful work constitutes the foundation for today's industrial joint research and for the fact that both VDZ and its Research Institute form an integral part of the cement industry. Proceeding from this basis, VDZ has oriented its work in such a way as to continue making its contribution to competitive, environmentally compatible cement manufacture and high-grade concrete construction in the future by offering attractive research.

VEREIN
DEUTSCHER ZEMENTWERKE E.V.

The Research Institute of the Cement Industry in Düsseldorf

Düsseldorf, in May 2005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(German Cement Works Association)
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Board of Directors
Budget Advisory Board
Chairmen of the Board of Directors
Executive Management
Working Comittees
Concrete Technology
Environment and Plant Technology
Cement Chemistry
Technical Comittee of the Quality Surveillance Organisation
Technical and Commercial Matters
Legal Affairs
Forschungsinstitut der Zementindustrie
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Prof. Dr.-Ing. G. Thielen (up to 31. 07. 2004)

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Dr. M. Schneider (Chairman)
Prof. Dr.-Ing. G. Thielen (up to 31. 07. 2004)

The German Cement Works Association

The German Cement Works Association (VDZ) is located in Düsseldorf and is the technical/scientific association for the German cement industry. It continues the tradition of the Association of German Cement Manufacturers formed on January 24, 1877. As a result of differences of opinion between the Portland cement industry and the slag cement industry regarding the question of intergrinding granulated blastfurnace 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 Blastfurnace 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. (VDZ).

Object of the Association

VDZ has no political, profit-motivated or entrepreneurial aims. It is recognised by the tax authorities as a non-profit organisation. Some of the statutory functions are performed as part of entrepreneurial business activities, which are compatible with the non-profit status. The object of the Association is to promote technology and science – including research and development – in the field of the production and application of hydraulic binders. The statutory functions of the Association include, in particular, the development of hydraulic binders, including additives, the testing, monitoring and certifying of cements and cement-type binders for the purposes of the Construction Products Act as well as quality markings under private law, and the promotion of measures for quality assurance, environmental protection and safety at work. The members receive advice and support under the terms of the Association's charter. The transfer of scientific findings and of those obtained during practical plant operation is promoted by means of 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, since 1995, been administering the "Gerd Wischers Foundation", a science foundation of the German cement industry without legal capacity. The training and development programme for the member works' employees serves the same purpose.

VDZ membership

Any natural or legal person who manufactures cements or cement-type binders in the Federal Republic of Germany, which 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.

There are currently 27 German cement companies, with 50 cement works, as full members of the VDZ, and 29 foreign cement companies as associate members.

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 testing laboratory, inspection body and certification body.

The annual General Meetings provided for in the statutes took place during the period under review on May 22, 2003 in Baden-Baden and on May 13, 2004 in Weimar.

The General Assembly elects the chairman and his deputies (Executive Board), and the members of the Board of Directors, each for a three-year term. The composition of the Board must relate to the structure of the cement industry in terms of regional distribution, company size, and the main types of cement produced. The Board currently in office was elected on May 16, 2002.

The Board of Directors is responsible in principle for the 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.

Committees, working groups and commissions

Two advisory boards provide support and advice to the Board of Directors: the Technical and Scientific Advisory Board occupies itself with coordinating the tasks of the committees and with planning, implementing and evaluating research, while the Budget Advisory Board is in charge of financial matters concerning VDZ and its Research Institute. The Executive Board, the chairmen of VDZ's committees and commissions, the Executive Management and the Research Institute Directorate are members of the Technical and Scientific Advisory Board. The members of the Budget Advisory Board are elected by the Board of Directors. The chairman of BDZ's Budget Committee is an ex officio member of the VDZ Budget Advisory Board.

For certain specialist areas the Board of Directors can establish committees in which specialists from the member works and from the Research Institute are jointly involved. There are currently six such committees (see organisation chart on page 6), with the Legal affairs committee serving as a joint committee of both VDZ and the Federal German Cement Industry Association (BDZ).

At the recommendation of the committees the Board can set up working groups, which can also include specialists from non-members, to deal with specific questions. Moreover, the Board sets up 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. In the period under review, one VDZ commission and two joint VDZ/BDZ commissions were active.

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 quality surveillance carried out by the German Cement Works Association's surveillance organisation as testing laboratory, inspection body and certification body (PÜZ body). It currently consists of 10 members, each elected by the VDZ Board for a three-year term. 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 technical committee meets at least twice a year. There was a total of four meetings in the period under review.

The main function is to assess and evaluate the results of the third party inspection carried out by VDZ's quality surveillance organisation. This entails inspecting, assessing and evaluating the factory production control and implementing audit testing of cement samples. The technical committee discussed the results of inspection and certification and made recommendations on the execution of the surveillance.

Over the past years, the technical committee primarily dealt with questions arising in connection with the transition from "quality surveillance", which formerly bore a distinctly national mark, to harmonised Europe-wide quality assurance concepts. This particularly included the finalisation of harmonised European standards and the associated operating procedures as well as the introduction of a quality assurance system and its accreditation under private law for VDZ's quality surveillance organisation beyond the scope stipulated by law. Given the re-orientation of the Research Institute, the questions discussed during the period under review chiefly related to the consistent professionalisation of certification services and the extension of entrepreneurial business activities.

Further topics of discussion included the evaluation of the proceeding regarding direct dispatch, the conformity evaluation in case of non-continuous dispatch, and in case of individual exceedance of limit values, as well as the inspection of low-chromate cements, trends in laboratory organisation, the implementation of proficiency testing, and the dealing with markings under private law.

Certification advisory board FIZ-Zert

The Certification advisory board acts as a steering committee of FIZ-Zert, the certification centre for management systems established in 1998. In conjunction with the accreditation of VDZ's quality surveillance organisation under private law, it further acts as an advisory board for product certification. It consists of at least five members from the interested parties, all of whom have a voting right.

Concrete technology committee

Working groups: Fire resistance, Transport engineering, Cement and admixtures

The Concrete technology committee deals with questions of research and development in the fields of concrete technology and concrete application. Apart from intense discussions on current national and European standardisation activities, the committee attends to the Institute's numerous research projects. The Concrete technology committee's objective is to co-ordinate practical requirements in the application of cement in mortar and concrete with research and standardisation in this field.

Apart from the subject of the standardisation of cement and concrete, which is still topical, the focal subjects during the period under review included the alkali-silica reaction in concrete, sulphate resistance and thaumasite formation, and further issues dealing with the durability of concrete.

Following the introduction of the new generation of concrete standards in the year 2001, the active application of this standard gave rise to a couple of questions, some of which had not been conclusively clarified in part. A major issue was the extension of the k-value concept for fly ash in concrete to all CEM II cements, provided that their use is permissible in all exposure classes. Special cements were excluded to simplify the standard. The compilation of the guidelines by the German Committee of Reinforced Concrete (DafStb) for "Massive concrete components" and "Water-impermeable concrete structures", for example, was attended during the period under review.

Regarding the major topic of "Sulphate resistance and thaumasite formation", the imposition of unjustified disadvantages on the use of certain cement types in concrete with a high resistance to sulphate attack was prevented successfully. Corroborated by the research results gathered by the Institute, a cross-industry compromise which will ensure damage-free construction also in the future was adopted.

Given some occurrences of damage in concrete road pavings, the issue of "alkali-silica reaction in concrete" has taken centre-stage again. The committee intensively supported the research the Institute carried out on methods for performance testing.

The "Fire resistance" working group observes the German and European standardisation processes in the field of fire protection. In the wake of the adaptation of the dimensioning rules relevant for fire protection to the future European rules of the Eurocode, the regulations relevant for solid constructions are basically designed so as to remain effective for the next 8 to 10 years. Technical and economic arguments corroborating the advantage of concrete components on effective property protection in the case of fire have been gathered.

The major topics which the "Transport engineering" working group dealt with were "Surface properties of concrete road pavings", "Utilisation of CEM II cements in concrete for road paving", "Ballastless track", and "Continuously reinforced concrete pavements". An argumentation paper aimed at improving the chances of CEM II and CEM III cements being applied in road construction is currently being elaborated.

In the wake of the shift which the cement industry's economic interests underwent in the "Concrete admixtures" business unit, the tasks of the "Cement and admixtures" working group have changed. The working group did not convene in the period under review. It will, however, observe and discuss the Institute's research projects dealing with questions about the mode of action of concrete admixtures and about the interaction of cement and admixtures.

Cement chemistry committee

Working groups: Analytical chemistry, Performance of cement constituents

During the period under review, the activities of the Cement chemistry committee concentrated on the topics of "Chromate reduction", "Alkali-silica reaction", "Effects of the use of meat and bone meal on clinker quality and cement properties" and "Performance of fly ashes and limestone meals". Since January 17, 2005, the requirements laid down in the European Chromate Directive 2003/53/EC, which was transposed into German law in the spring of 2004, have had to be met by all manufacturers of cement and cementitious preparations. This directive stipulates a harmonised test method for chromate determination, and that cement manufacturers adopt a specified procedure to comply with the directive. The committee intensely scrutinised the draft of the European test standard on chromate determination (prEN 196-10) and the storage stability of chromate-reduced silo cements.

Apart from the well-known alkali-sensitive aggregates, there are aggregates of low reactivity that do not trigger a harmful alkali-silica reaction unless the conditions prevailing are unfavourable, e.g. in road construction when alkali is supplied via a de-icing agent. The Research Institute has been conducting several research projects dealing with alkali-silica reaction. From the committee's point of view, the determination and evaluation of the actually effective alkali content of the cements is of particular importance in these research activities.

The use of meat and bone meal as a secondary fuel can lead to a higher input of phosphate into the clinker. Investigations by the Research Institute, which were carried out in close co-ordination with the German cement industry, showed that phosphate actively engages in the reactions taking place during the clinker burning process and even changes cement properties. They also revealed, however, that phosphate contents of up to 1 wt.-% are compatible with the product, if the other clinker and cement parameters, such as the lime saturation factor, are fine-tuned with the phosphate incorporation.

The "Analytical chemistry" working group completed numerous projects during the period under review. These included the report entitled "Presentation of the state of the art in trace element determination" for the "Trace elements" working group, or the evaluation of interlaboratory trials performed on reference cements. Certified reference materials for determining the main and secondary constituents are now available and can be obtained from the Research Institute. Furthermore, new interlaboratory trials on Rietveld refinement were started. Their results are expected to be available in the early summer of 2005.

During the period under review, the "Performance of cement constituents" working group looked into the fundamental reaction mechanisms of hard coal fly ashes and their behaviour during application, as well as the behaviour of limestone meal as a cement constituent. It turned out that the iron content of fly ashes, for example, can have a significant influence on the physical properties. As a consequence, the considerable fluctuations in the water demand of a fly ash and the ensuing concrete technology effects were eliminated by setting a higher and more constant iron content. As regards the behaviour of limestone meals, the focus of work has been placed on the question about the active contribution to the hydration of cement constituents made by limestone meal, and about the factors determining this contribution.

Environment and plant technology committee

Working groups: Environmentally compatible quarrying, Operational performance of precalciners, Refractory materials, Safety at work, NO_x abatement, Trace elements, Training courses advisory board

The VDZ Board decided in late 2002 to merge the "Environment" and "Process engineering" committees, thus taking account of the current economic situation of the cement industry. The new committee will attend to the working groups previously assigned to the "Environment" and "Process engineering" committees.

In the period under review the committee focused its activities on questions regarding the utilisation of secondary fuels and raw materials, and the implementation of the 17th Federal Ambient Pollution Protection Regulation (17. BImSchV) and its implications on plant operation. The further subjects discussed and debated during meetings were the operational experience with dust removal techniques, crystalline silica emissions, sewage sluge utilisation, and CO_2 emissions trading.

The newly established committee held its first general meeting as a specialist conference on cement process engineering. The 100 participants in the internal VDZ meeting professed great interest in operating experiences gained with bypass systems on the one hand and with the use of meat and bone meal and sewage sludge on the other hand.

After the "SO_2 reduction/recirculating systems" working group had performed its tasks by completing the code of practice, the "Environmentally compatible quarry operation" working group commenced work in the autumn of 2003. Proceeding from the work of the VDZ/BDZ Commission "Securing of raw material supplies", the working group has the task to establish a guidance paper on environmentally compatible quarrying. This manual is to summarise the technical possibilities of environmentally compatible quarrying. Its target group comprises both engineers and the employees in charge of securing raw material supplies at the cement works.

The "Operational performance of precalcining systems" working group completed its task by compiling a code of practice, which summarises operating experiences with new precalcining systems regarding emission behaviour, use of secondary fuels, service life of the refractory lining, as well as influence on clinker properties and energy consumption.

The know-how the cement works possess on the use of refractory materials decreased over the past years. The "Environment and process engineering" committee therefore proposed to have the findings on the subject of "Refractory materials" compiled by a working group. To that end, the previous work performed in this field is to be updated and summarised. The working group is to deal with the following topics: diagnosis of the condition of refractory materials, de-lining techniques, installation techniques, safety aspects, choice, heating-up programmes, influence of varying conditions of use on the service life, anchoring technique, repair in hot state and corrosion problems.

The permanent functions of the "Safety at work" working group include the analysis of accidents in member works, the establishment of accident statistics, the determination and recommendation of measures for improving safety at work, and the preparation of safety data sheets and checklists. The seminars on safety at work for industrial foremen were continued with new topics on an ongoing basis in cooperation with the Quarry Employers' Liability Insurance Association.

In taking care of the training courses the committee is supported by a Training courses advisory board. During the period under review, the 21st industrial foremen's course "lime/cement" and the 10th and 11th production controllers training course "cement" were successfully concluded. Furthermore, the compilation of model training notes, which deal with typical training subjects for cement work employees and are intended to support the works' in-house training, was continued. By the end of the period under review, 31 of the scheduled total of 46 model training notes had been completed and made available to the member works.

The "NO_x abatement" working group intensely studied questions regarding the effectiveness of the SNCR process under consideration of different reducing agents and operating conditions. The working group further devoted its attention to combining the process of staged combustion in the calciner with the SNCR process, and to the SCR project conducted at a German cement works. In addition to that, it drew up a cost estimate both for the SNCR and the SCR processes.

The "Trace elements" working group has largely completed its tasks. The various technical reports (sampling, production process and cement application) are presently being finalised. These comprehensive reports pertaining to the topic of "Trace elements" will soon be made available to the VDZ member works via the intranet.

Harmonisation committee for technical and commercial matters

The Harmonisation committee, which is a joint VDZ/BDZ body, has been dealing with questions having both technical and commercial aspects. During the period under review the committee was particularly concerned with the regulations governing CO_2 emissions trading, the manufacture of low-chromate cements and products, and the trends regarding CEM II cements and blastfurnace slag production.

Against the backdrop of the commitment to CO_2 reduction by the year 2012 which the European Union made in the Kyoto Protocol, an emissions trading system for CO_2 emissions permits was introduced at European level and corresponding rules were specified. The composition and implementation of the legal specifications on the trading of greenhouse gas emissions subsequently passed in Germany and the national allocation plans were discussed in joint meetings of the Harmonisation committee and the VDZ "Emissions trading" commission. From the cement industry's perspective, the most crucial issue was the demand that the allocation of CO_2 emissions permits for CO_2 resulting from calcination (process CO_2) and for CO_2 resulting from secondary fuel utilisation should be free of charge and in keeping with requirements (see also report on the "Emissions trading" commission).

Intensive discussions in the Harmonisation committee focused on the transposition into German law of EU directive 2003/53/EC, which regulates the putting into circulation and the use of cements and cementitious preparations containing chromate. They resulted in the resolution to supply, in addition to bagged cements, also silo cements in chromate-reduced quality, i.e. with a maximum water-soluble chromium(VI) content of 2 ppm relative to dry mass.

The introduction of the European cement standard EN 197-1 has considerably extended the scope for the manufacture of cements containing two or more main constituents. In strength class 32,5, CEM II cements already account for a larger share than CEM I cements. Given the reduction of the clinker proportion it entails, the increased use of CEM II cements contributes to lowering CO_2 emissions. In this context, the committee also debated the trends to be observed with materials that can be used to replace clinker in cement manufacture, such as ground blastfurnace slag or fly ash. With blastfurnace slag, a rise in output by the year 2006 is emerging. In case of a stagnation in domestic cement dispatch, this may result in an excessive blastfurnace slag supply in Germany.

As a consequence of restructuring measures implemented at VDZ's and BDZ's association level, questions previously discussed and co-ordinated in the Harmonisation committee can in the future increasingly be dealt with in other bodies, most particularly in meetings of the Board. For that reason, the Harmonisation committee was dissolved at the end of 2004.

Legal affairs committee

The Legal affairs committee is a joint VDZ/BDZ body. It is concerned with all legal aspects of the production and use of cement. However, the members also discuss other legal issues, which may e.g. relate to environmental, antitrust and corporate legislation.

The introduction of emissions trading in Europe topped the agenda of several meetings. The main focus was placed on the companies' legal protection with respect to authorities and on the possibilities of influencing the composition of the German emissions trading system. In this context, the committee's specialist knowledge enabled it to provide support to the member works in a number of individual questions.

Furthermore, the committee attentively followed trends in legislation on environmental protection at national and European level as well as the numerous projects aimed at new legislation in this field, and discussed their consequences for the cement industry.

The scheduled 7th amendment of the Law against Restraint of Competition (GWB) was one of the major issues discussed in the domain of antitrust legislation. Pursuant to this law, the entrepreneurs themselves will be responsible for verifying whether their conduct and their co-operations are in compliance with antritrust legislation in the future. Entrepreneurs can only counter the danger of failing to notice or misjudging facts relevant to competition by instituting a risk management system comprising the systematic monitoring and evaluation of any risks regarding antitrust legislation.

The consequences for chromate reduction ensuing from the amendment of the Prohibition of Chemicals Ordinance and the Hazardous Substances Ordinance have an immediate impact on cement manufacture. In this context, the committee primarily had to identify the regulation which applies to chromate reduction, in particular when reduction takes place during the manufacture of ready-mixed concrete, for example.

VDZ Alkali-silica reaction commission

The commission intensely studied the occurrences of damage in concrete road pavements. The Research Institute had found out that part of the damage was attributable to a harmful alkali-silica reaction (ASR) in some cases. The commission developed strategies aimed at preventing this damage and elaborated recommendations on lowering the effective alkali content of cements for road paving. It further recommended that the use of aggregates known to be reactive for road pavement construction should be subject to the presentation of an expertise, or be refrained from in the first place (see also Chapter V, section on road engineering). The commission further attends the Institute's research on extending the range of cements with low effective alkali content and on the application of additives that may contribute to preventing a harmful ASR.

VDZ/BDZ "Emissions trading" commission

The "Emissions trading" commission was established to succeed the "CO_2 abatement" commission in 2003 to take account of the increasing importance of CO_2 emissions trading for the cement industry. The commission is tasked with attending the introduction and implementation of CO_2 emissions trading in Germany. Discussing the results of the CO_2 monitoring carried out annually constitutes a further main focus of its work.

Since mid-2003, the commission has intensely discussed the implementation in Germany of the EU directive on introducing an EU-wide CO_2 emissions trading system. Attention initially focused on the formulation and the quantitative definition of the national allocation plan (NAP) for the first trading period of 2005/2007. Presentation of the NAP to the EU Commission by the federal government was followed by transposition into national law. The details of the Greenhouse Gas Emissions Trading Act and of the allocation law 2007 were intensely discussed, and various initiatives of the cement industry aimed at the Federal Ministry for the Environment (BMU) and the Federal Ministry for Economic Affairs and Labour (BMWA) were coordinated.

In order to provide member works with realtime information, workshops on the subjects of "CO_2 data collection" and "Filing applications using the RISA software" were held. In addition to that, a specialist conference was held at the Research Institute at which some of the lectures were held by external experts.

The commission discussed the results of the monitoring surveys conducted in the years from 2000 to 2004. These results have shown that the cement industry is well on its way towards fulfilling its updated voluntary agreement on climate protection. A joint monitoring report covering the years from 2000 to 2003 was established and can be downloaded from the Research Institute's website.

VDZ/BDZ Commission on "Environmentally compatible use of secondary materials"

The use of suitable wastes in German cement works has increased continually over the past years. In the year 2004, about 40% of the fuel energy requirement was met by such alternative materials. The quantities of waste actually utilised and the emissions of the rotary kiln plants operated in Germany are recorded and published once a year under the overall control of the Secondary materials commission. This measure allowed to achieve a high degree of transparency also towards the parties interested in waste utilisation in industrial plants and in cement works in particular. The use of suitable substitute fuels will continue to play an important role in the German cement industry.

Apart from technical aspects, especially decisions in the fields of politics and waste legislation determine whether certain materials may be utilised in a cement works. Against this backdrop, a decision by the European Court of Justice (EUCJ) dating from February 2003 which pertained to the permissibility of shipping waste of high calorific value from Germany to Belgian cement works was of particular importance for the cement industry. The Secondary materials commission scrupulously analysed the verdict by the EUCJ. From the cement industry's point of view, the criteria listed by the EUCJ as being characteristic of utilization measures are of particular interest. Accordingly, properties such as the calorific value or the pollutant content of waste must not play any role in delimiting utilisation from disposal. In spite of these clear statements made by the European Court of Justice, however, German waste legislation (Waste Management and Recycling Act) has not been amended. In Germany, the minimum calorific value of 11 MJ/kg laid down as a permissibility threshold for utilisation continues to apply.

Another important subject on which the Secondary materials commissions focused its attention during the period under review was the use of sewage sludge in cement works. It has been known from other European countries, especially from Switzerland, that cement works provide an excellent means of simultaneously utilising both the material and thermal content of sewage sludge. In the past, such use of sewage sludge at German cement works was politically undesirable; instead, large quantities of sewage sludge, in particular municipal sludge, were put to agricultural use. In this area, a change in political opinion is becoming apparent, which is attributable to various reasons. In the meantime, several German cement works carried out trials on the use of sewage sludge, some of which were conducted over a fairly long period. The Secondary materials commission subsequently discussed them intensely. In addition to that, a long-term trial on the utilisation of sewage sludge was conducted at a cement works in Baden-Württemberg in co-operation with the Ministry for the Environment. This measuring programme attended by a public authority allowed to demonstrate that the use of sewage sludge neither had adverse effects on the emission scenario, nor did it have any negative impacts on product quality.

The Secondary materials commission was further concerned with the strategic aspects of the implementation of the German Municipal Waste Specifications and the secondary fuel quantities expected to accrue in the future. Changes are expected to occur in this domain from the middle of 2005, since a landfilling ban for untreated wastes will take effect from June 1, 2005. The Federal Ministry for the Environment has repeatedly confirmed its resolve to stick to this date. As a consequence, waste management will undergo drastic changes from mid-2005 at the latest. The plants for domestic waste incineration will presumably be charged to capacity by domestic and municipal waste that must be delivered to the public waste management authorities. Various surveys predict that the waste produced will then exceed the thermal treatment capacities available by 5 to 7 million t. The German cement industry is forearmed for this situation: the corresponding licensing procedures for increased secondary fuel utilisation have already been completed in many works and are currently being conducted in others.

One prerequisite for an actual increase in the use of secondary fuels is compliance with quality parameters, which the Secondary materials commission studied thoroughly. As regards the requirement for higher capacities for thermal content utilisation from mid-2005, it has to be pointed out, however, that the 60% regulation for dust and NO_x limit values laid down in the amended Federal Ambient Pollution Protection Regulation (17th BImSchV) may prove an obstacle to a further increase in the use of substitute fuels, too. The Secondary materials commission devoted its attention to this issue as well.

The amended Federal Ambient Pollution Protection Regulation (17th BImSchV), which has to be implemented by December 28, 2005 at the latest, comprises stringent requirements. Most particularly, it specifies the same emissions of trace elements, dioxins and furans for co-incineration plants and for waste incineration plants. The rotary kilns of the German cement industry in which waste is utilised meet these requirements, which are the most stringent worldwide. This is one of the reasons why the environmentally compatible and harmless utilisation of waste-derived fuels in cement rotary kilns has become an accepted fact in environmental policy discussions by now. However, a growing number of scientific studies dealing with the potential effects of waste utilisation on the product quality of the cement works have been drawn up in the recent past. The cement industry attended such studies through the Secondary materials commission. Accordingly, the kind and extent of waste utilisation in the German cement industry do not compromise product quality in the least. With regard to trace elements in particular, which have always played a major role in environmental policy discussions, primary raw materials have been found to be the principal path of introduction into the cement.

In spite of these unambiguous scientific findings, at least the political discussion on waste utilisation can be assumed to increasingly focus on the question about the potential effects on cementitious binders to be expected. For that reason, the Secondary materials commission considers the ecological positioning of cement and concrete to be one of the subjects of main emphasis in the future. It must further be pointed out that waste management policies are influenced by international trends to an ever increasing extent. The Secondary materials commission will continue its activities in this domain as well. At the same time, German positions are argued in international working groups, such as CEMBUREAU or the World Business Council for Sustainable Development, via the Secondary materials commission. This helps to ensure that the high technical level that waste utilisation has by now reached in German cement works in particular is taken into account at international level as well.

Cooperation with other organisations ■

The committees, working groups and the Research Institute are cooperating with other institutions at national and international level in numerous fields. These institutions include public authorities, universities, material testing institutes and numerous professional associations, standards committees and organisations of related industries. In many cases, VDZ is represented on these organisations' bodies by individual employees of the Research Institute. This cooperation again achieved very good results on many issues in the period under review.

Federal German Association of the Cement Industry (BDZ)

The Federal German Association of the Cement Industry (BDZ) is the professional organisation of the German cement industry. Its functions include the representation of economic interests, public relations work, and carefully directed information on questions about concrete construction that are relevant under market aspects. VDZ and BDZ have coordinated their activities for many years. For the first time, the cooperation of the two organisations has been highlighted by the institution of a joint VDZ and BDZ management in the summer of 2004. In this way it can be ensured that members are optimally integrated into the work of both organisations. On the one hand, the joint appearance of VDZ and BDZ ensures that topical research results obtained from VDZ's work are made available to all interested parties quickly and appropriately. If necessary, on the other hand, the Federal Association can fall back on this sound technical and scientific foundation in its economic policy work. The cement industry thus possesses both attractive and modern institutions for promoting cement manufacture and concrete construction, and a powerful representation of economic interests at the two locations of Düsseldorf and Berlin.

Furthermore, the "Concrete circle" maintained by VDZ is a platform that also representatives of BDZ and of the regional sales promotion organisations take advantage of in order to boost concrete construction throughout Germany. In this way, the findings of the Institute's non-profit research activities can be applied under practical conditions efficiently and promptly.

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

AiF, of which VDZ is a founding member, promotes industrial joint research with funds provided by the Federal Ministry for Economic Affairs and Labour (BMWA). This research especially benefits medium-sized companies and presupposes the provision of own research funds that at least match the grants. VDZ is represented by the chief executive in the scientific council of AiF and by several employees in various expert committees. In the period under review covering the years from 2003 to 2005, VDZ was again able to bankroll research projects largely by funds provided by AiF. The assistance of AiF and the BMWA is gratefully acknowledged.

Cement production and environmental protection

There was again intensive cooperation during the period under review both with the Federation of German Industries (BDI) and the German Building Materials Association (BBS) and its member associations. Both the employees of the Research Institute and of VDZ member companies are working on committees and steering bodies of these associations, where they jointly discuss questions concerning all the industries involved. These include e.g. questions of emission reduction, emissions trading, and policies regarding chemicals. Given the wide range of technical fields it covers, VDZ has further traditionally been cooperating 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 Steel Institute 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).

Cooperation with the Federal German Association of the Lime Industry primarily focuses on finding joint solutions regarding the training and development for foremen in the field of lime and cement. There was also intensive cooperation with the lime industry association in the domains of safety at work, securing of raw material supplies, CO_2 emissions and emissions trading.

During the period under review, VDZ again took part in intensive specialist debates with the ministries responsible at state and federal level. These included the Federal Environmental Agency, various environmental authorities at state level, and the German Centre for Emissions Trading (DEHSt), to name but a few.

Institute staff members are involved in the bodies of the German Institute for Standardisation (DIN). In this context, especially the standards committees for "Construction" (NABau), "Water" (NAW) and "Materials testing" (NMP) as well as "Fundamentals of environmental protection" (NAGUS) must be mentioned.

Use of cement

VDZ is represented on the board and the steering committees of the German Committee for Reinforced Concrete (DAfStb), in numerous bodies of the German Institute for Building Technology (DIBt), and on the advisory board and various working committees of the Standards Committees for Construction and Materials Testing. In addition to that, it is strongly involved in the work of the Road and Transport Research Association. Prof. Thielen, who was VDZ's managing director of many years' standing, will continue to advocate concrete construction as chairman of the Construction Standards Committee (NABau) and as deputy spokesman and chairman of the Research Advisory Board of the German Committee for Reinforced Concrete (DAfStb) even now that he is retired.

There has traditionally been close, trusting cooperation with the technical and scientific cement consumer associations. These include 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). Close professional contact has further been maintained with the Association of German Concrete Engineers (VDB) and the German Industry Association for Construction Chemicals. The contact committee with the BTB, which is concerned with questions on the use of cements in ready-mixed concrete, again tried to find a common basis for questions relevant to both institutions in the period under review. An intensive exchange on reducing alkali-silica reaction in concrete was maintained with the gravel and sand industry and aggregate manufacturers.

The joint concrete working group (GAK)

The joint concrete working group (GAK) regards as its tasks, among other functions, the intensive attending of standardisation and also the initiation, attending and, in case of need, financial sponsoring of joint research projects. 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) – supported by the head of the concrete information department of the Federal German Association of the Cement Industry (BDZ) – are represented. Chairmanship of the GAK, which rotates annually, was passed from DBV to VDZ in 2005. At present, the GAK is intensely debating whether the precast components industry is to be admitted to the joint working group.

The expert production and processing of fair-faced concrete constitutes a joint research project of paramount importance. Several university institutes and the Research Institute of the Cement Industry (FIZ) are taking part in this research, which deals both with the composition of fair-faced concrete and its processing. The sulphate resistance of concrete is a further topic. After a status report sponsored by the associations was completed and the specifications previously laid down in DIN 1045 were maintained, two institutes are now carrying out practical tests in cooperation with FIZ as part of the work of the DAfStb. The investigations are sponsored and closely attended by the associations.

Concrete admixtures coordination committee

The Concrete admixtures coordination committee was revived after several German manufacturers of admixtures had been taken over by larger international companies. The German Industry Association for Construction Chemicals is currently chairing the committee, in which experts from the cement and admixtures industries are represented. Chairmanship will rotate every year.

The coordination committee thoroughly discusses questions relating to the interaction of cement and admixtures. At present, two topics are studied in depth: these are the efficiency of curing agents and the air content of the concrete when super-plasticisers are used. The air content was recently observed to drop below 0.5% when a super-plasticiser had been added. It is to be clarified whether this may possibly impair the freeze-thaw resistance of the concrete. In addition to that, the coordination committee intends to work out joint positions the associations adopt on industrial safety and environmental precautions.

Furthermore, a workshop for interested parties from both associations' member works, in which certain technical subjects are to be discussed, is scheduled to be held in due course.

Universities

Promoting university activity in the fields of construction research and structural engineering has always been a priority for VDZ, which again provided funds for research at university institutes in the period under review. Together with the Federal Association of the German Lime Industry, VDZ has 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 23 national cement associations perform supranational cooperation. VDZ has contributed its technical and scientific expertise to this joint work for many years. Experience VDZ has gathered in national research work, for example, helps develop the cement industry's positions in the realm of European legislation. In the period under review, issues relating to environmental protection and CO_2 reduction were given top priority. The Europe-wide trade in emission certificates at the beginning of 2005 created tremendous challenges for the cement industry. On the basis of this example, the joint work performed in CEMBUREAU highlighted that Europe still has a long way to go to achieve harmonisation. The potential impact of cement processing on human health is one of the further major issues of joint European work. The cement industry has always expended great efforts to safeguard its own employees and cement users. In the dispute about the European directive on the chromate reduction of cementitious products, however, the cement industry did not prevail with its demand for solutions that are both technically reasonable and economically efficient.

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) as well as that of CEN/TC 229 for precast concrete elements and of CEN/TC 178 for prefabricated road construction products. Standardisation work covering different types of building materials is increasingly gaining in importance, too. For example, a draft mandate of the Commission provides that any potential, environmentally relevant release from building materials be given equal treatment for all building products in standardisation work in the future. Work on the standardisation of cements with special properties resulted in a harmonised standard for cements with low heat of hydration being elaborated in the period under review as well. The same applies to the test standards for determining the heat of hydration. Whether a standard for cements with high sulphate resistance will be adopted is still unclear. As there is no conclusive performance test, the different national experiences have so far precluded a uniform course of action. CEN/TC 104 successfully continued its work on the fly ash standard EN 405 in the period under review. Thus, a harmonised European fly ash standard also covering the fly ashes generated by co-incinerating waste in coal-fired power stations is now available. CEN/TC 229 conclusively discussed most of the European product standards for precast concrete elements, which are available for practical application now. Completing the European standards for concrete paving blocks, slabs and kerbstones, which have replaced the previous national standards in Germany as DIN EN standards, CEN/TC 178 has performed its task. FIZ employees were involved in the work of the three CEN/TC groups.

The European umbrella association of building material manufacturers (CEPMC) is an important platform for the cement industry, too, as it allows to perceive European developments early on. Especially as far as the environmental impact of building materials is concerned, all manufacturers of building materials pursue joint interests. The experiences gained at VDZ find their way into the work of CEPMC. In this way, Research Institute employees are immediately involved in activities at European level. The German Building Materials Association (BBS) is also working on the establishment of German positions for the discussion in Brussels. VDZ is supporting these efforts.

VDZ is still involved in scientific projects in which supranational cooperation allows to achieve synergies. These particularly include cooperation in the NIST consortium, which has been intensively studying the computer-aided modelling of cement hydration for many years. The work performed has been very successful so far and shows that essential properties of the hardened cement paste can be predicted reliably. These include strength development and porosity, which constitute two substantial features of mortar and concrete.

VDZ has taken an active role in the European research and training consortium NANOCEM since the latter was founded. NANOCEM consists of 30 partner organisations, which include universities, national research institutes and industrial partners. More than 120 researchers cooperate in NANOCEM. The aim they pursue is to enhance knowledge about the nanostructures and microstructures of the hardened cement paste in order to gain better understanding of macroscopic properties of cement-bound building materials.

In addition to the cooperation with the international organisations mentioned above, the VDZ and its Research Institute maintain contacts with other European and international organisations. VDZ's cooperation with the National Council of Building Materials (NCB) in India was started during the period under review. The main focus is placed on an exchange about technical and scientific questions regarding the manufacture and application of cement. This particularly includes questions about the conservation of natural resources and emission reduction. The cooperation agreed upon with the China Building Materials Industries Association (CBMIA) is to provide the basis for an exchange of experience about all the relevant issues of modern cement manufacture. VDZ additionally maintains contacts with the International Standards Organisation (ISO), the Fédération Internationale du Béton (fib), the International Association of Testing and Research Laboratories (RILEM), the International Institute of Flame Research (EFRF), the American Concrete Institute (ACI) and the American Society for Testing and Materials (ASTM). Further contacts are kept with the U.S. Portland Cement Association (PCA) and numerous research institutions worldwide.

European Cement Research Academy

Following its foundation in the year 2003, the European Cement Research Academy (ecra) can now look back on 2 years of successful activities. Back then, VDZ had taken the initiative in establishing this European research platform, in which more than 30 individual or associated companies are now involved. Reports on topical questions of cement manufacture and concrete construction were presented in various seminars and workshops. As a consequence of their cooperation in ecra, VDZ and its member works are strongly involved in an international exchange of experience within the cement industry. A newsletter published 4 to 5 times per year purposefully deals with individual questions of environmental protection or process engineering.

The undisputed highlight of the year 2004 was the first international conference on innovation and future developments in cement manufacture and concrete construction. On this occasion, international experts convened in Amsterdam to report on questions relating to the preservation of natural resources, CO_2 reduction, and cutting-edge developments, some of which were even visionary. For example, the latest models of cement hydration were presented. Furthermore, a paper on so-called "Contour crafting" presented an outlook on the possible future automation of construction technology.

ecra is headed by a Technical Advisory Board on which leading German and European cement manufacturers are represented. These include the companies Buzzi, Cemex, CRH, Dyckerhoff, HeidelbergCement, Italcementi, Schwenk and Titan Cement.

Dissemination of findings

The results of the work of the committees, working groups and commissions and of the research activity of the Institute are disclosed to the members and to a wider specialist audience in numerous publications, colloquia, seminars, lectures and conferences. Most of the publications compiled are available to the VDZ members and the specialist public in electronic form on VDZ's internet pages, or can be ordered online via these pages.

Publications

The proceedings of the 5th VDZ Congress "Process engineering of cement manufacture" held in Düsseldorf in September 2002 were completed and published in the period under review. Comprising 68 papers from 6 technical fields and more than 500 pages, the proceedings offer a wide range of publications tailored to practical needs. Particular focus was placed on comminution and combustion techniques, but the utilisation of secondary materials, information management at the plant, and sustainability in connection with cement manufacture are not missed out either. In order to satisfy the needs of international readers, the proceedings were published in English.

The "Environmental data of the German cement industry", which is a comprehensive, continually updated documentation of the German cement industry's environmental data, has been extrapolated on the basis of the data surveyed in the years 2002 and 2003; thus, the 6th issue already is available. The CO_2 monitoring report has been continued as well; its 7th issue, which covers the period from 2000 to 2003, appeared in February 2005.

The "VDZ-Mitteilungen" (VDZ Newsletters), which are published three times a year, again furnished realtime information on the activities of VDZ and its Research Institute. During the period under review, numerous articles dealt with the developments in the field of EU-wide CO_2 emissions trading. The compilation of the German national allocation plan, the conversion into German law of the EU directive and the subsequent phase of applications for allocation of certificates being filed caused vast need for information and thus met with particularly great interest among readers. As usual, this was complemented by reports on current own research projects and information on the results of other research institutions.

During the period under review, two new volumes appeared in the cement industry publication series containing primarily dissertations and theses. In 2003, volume 64 appeared entitled "Production of durable cement-bound surfaces in the drinking water domain: corrosion analysis and fundamental technical requirements" by P. Boos. It was followed in 2004 by volume 65 entitled "About the influence of long-term set retarding admixtures on phosphonic acid basis on the hydration of individual clinker phases, Portland cement clinkers and Portland cements" by J. Rickert.

The safety codes of practice No. 94 to 99 and the safety checklists No. 74 to 79 were compiled by the "Safety at work" working group and issued as supplements to the VDZ bulletins. Moreover the "Operational performance of precalcining systems" and "SO_2 reduction/recirculating systems" working groups each compiled a code of practice summarising the results of their

Participants in the specialist conference on cement process engineering on February 19, 2004, taking a break in the Research Institute's foyer

The audience in the Research Institute's lecture hall during the specialist conference on emissions trading held on April 6, 2004

work. Both codes of practice can be downloaded from VDZ's Internet pages. The VDZ training notes, which were revised thoroughly and extended significantly in the period under review, are now available both in printed form and on CD-ROM.

Numerous articles have been published in the leading professional journals. These are primarily the journal "Cement International", which is also an organ of VDZ, in the field of cement chemistry and process engineering, and the journal "beton" for the field of concrete technology. The Institute's publications in the journal "beton" are summarised periodically in the form of "Concrete Technology Reports". The 29th issue of these "Concrete Technology Reports", which covers the years from 2001 to 2003, appeared in the spring of 2004.

Conferences

The VDZ committees regularly stage colloquia and specialist conferences to inform on their current projects. The "Concrete cycle", which has been organised for more than 30 years now and for which the Institute invites concrete engineers from the cement and ready-mixed concrete industries and the building trade, took place on March 23, 2004 and on March 15, 2005 in the period under review. In addition to the specialist conference on "Cement process engineering" held after the usual 2-year interval on February 19, 2004, a specialist conference on "Emissions trading" took place on April 6, 2004 and met with great interest due to its enormous topicality. Several workshops on subjects like "CO_2 data survey" and "Use of the RISA software to file applications for the allocation of CO_2 emissions certificates" were held to take account of the enormous need for information in the area of emissions trading.

Training and development programme

Training, development and knowledge transfer are some of VDZ's most important functions. "Lime/cement" industrial foremen's courses have been organised jointly with the Federal German Association of the Lime Industry for 47 years now. These courses, which are subdivided into a theoretical and a practical training part, last 18 months and end with an examination at the Chamber of Industry and Commerce in Düsseldorf. The 21st course ended in March 2005. Apart from the training and development of foremen, VDZ's training programme also provides carefully directed training for control room operators. The training of control room operators as production controllers consists of a practical part carried out at the plants, and a theoretical part, which is performed by the Research Institute and lasts seven weeks. In 2003 and 2004, the 10th and 11th training course were completed, and the 12th training course began in April 2005. This training primarily focuses on lessons in the subjects combustion, environmental and preparatory processing techniques, as well as work with the SIMULEX kiln and mill simulation programme.

To train employees in the field of production, a total of 31 training notes dealing with various subjects of the cement manufacturing process have been compiled so far. These are available both in printed form and on CD-ROM for use at the computer.

As in the preceding years, VDZ again offered a range of one-day or several-day seminars and workshops in the period under review. These related to the areas of cement production, quality assurance, environmental protection, concrete constituents, concrete manufacture and the performance of concrete.

Cement Industry Science Foundation

The "Gerd Wischers Foundation" founded on June 2, 1995, has the objective to foster the training and development of junior scientific staff, especially in the cement industry. The foundation has assets of EUR 1 533 875 (DM 3 000 000). The inter-est income accruing on this amount allows to award four or five scholarships at a time. During the period under review, two dissertations treating the subjects of "Working mechanisms of admixtures reducing shrinkage" and "Influence of the grinding system on the properties of Portland cements and blastfurnace slag meals", respectively, were sponsored. One research project currently underway deals with the working mechanisms of super-plasticisers on the basis of polycarboxylate ether (PCE). In addition to that, one half-year scholarship for the completion of a diploma thesis and a further short-term scholarship for finishing a research project on the "Influence of the composition of the pore solution on the sorption behaviour of superplasticisers" were awarded.

The Research Institute of the Cement Industry ■

VDZ maintains the Research Institute of the Cement Industry (FIZ) to carry out its functions. The 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 even sophisticated fundamental investigations. The Research Institute can also act on behalf of third parties, e.g. by performing tasks under public law as an officially notified emission monitoring body or as an officially accredited testing laboratory. Moreover, the Research Institute has increasingly offered expert's advisory and consultancy services in technical matters, in line with the object of the association.

The Institute is made up of five departments, which report directly to the Institute's management. The general services include the units of administration, information and data processing comprising the DP centre, library, documentation and publishing, as well as mechanical and electronic workshops. The Research Institute's laboratories are accredited, and the Institute also possesses a certified quality and environmental management system. The organisational chart on page 18 shows the areas of responsibility of the various departments and the Certification body for management systems, FIZ-Zert.

Workforce

At the time of reporting, the Research Institute has 132 employees, 43 of whom have higher education, such as a university or technical college degree. The Institute is currently providing a total of three training places in different fields. During the period under review, three trainees successfully completed their apprenticeship as chemical laboratory assistant at the Institute.

Institute's premises

The Institute's main building was constructed in 1955/56 in the north of Düsseldorf. The Institute was expanded in the 1960s to accommodate its growing workforce. A seven-storey extension was planned, of which the four bottom storeys were completed in 1964/65 and the remaining storeys in 1992/94. The closer entwining of VDZ and its fellow association BDZ (Federal German Cement Industry Association) implemented in 2004 necessitated the provision of office space for the employees of the BDZ office previously located in Cologne. The 7th floor of the Institute in Düsseldorf was put to that use. It had been fitted out as recently as in 1999/2000 with the objective of creating additional conference rooms, training rooms and offices. A rebuilding measure carried out in the ground floor of the Institute in the summer of 2004 allowed to also accommodate BDZ's in-house printshop.

It is of great importance to the Research Institute to always adapt the efficiency of its laboratories to the latest technological and scientific developments. The expensive measures taken in the years from 2001 to 2003 to install a centrally controlled air conditioning system in the laboratories and specimen storage chambers, and to separate especially sensitive laboratories from the laboratories for wet-chemistry analysis, have proven their worth. This also applies to the installation of separate storage facilities for hazardous materials. No major building measures were necessary during the period under review; only the installation and renovation work coming up as part of routine maintenance had to be carried out.

Overall, the Research Institute has now about 40 000 m^2 of interior space. Given a total floor space of some 8 400 m^2, the main building accounts for 3 445 m^2 and the seven-storey extension for 2 915 m^2. The remaining 2 040 m^2 comprise the single-storey laboratories and the basement as well as a residential building for FIZ employees.

Laboratory information and management system (LIMS)

A laboratory information and management system (LIMS), which was restricted to the cement chemistry department during the initial phase, was taken into operation in early 2000. The system allows to achieve a high degree of transparency for the processes taking place in the units it connects. At the same time, it ensures that all the people participating in a project can easily access the data they require. In the period under review, the cement chemistry department investigated some 8 000 samples annually, which involved an average of approx. 10 tests per sample. After the successful introduction of the LIMS in the chemistry laboratory unit, the system was extended and completely revised in terms of performance.

Following this revision, the LIMS was introduced in the Concrete technology, Environment and plant technology, and Environmental measuring departments as well in January 2005. The system now allows to input all the laboratory results obtained in the departments it connects. In this way, the laboratory investigations carried out at the FIZ as part of project administration shall be rendered significantly more efficient and transparent. This applies to the interdisciplinary use of the LIMS and the allocation of cost centres to the projects with the associated orders and samples in particular.

The high degree of availability of the system – nearly at every workstation – allows all the employees involved in a project to call up the information relevant to them, input results and compile reports at any time. The project management can always get an overview of the current status of work. To call up detailed results that have been compiled for special evaluation purposes and may even derive from different projects, a special report generator individually extending the call-up features comprised in the LIMS is available.

Data processing/Internet

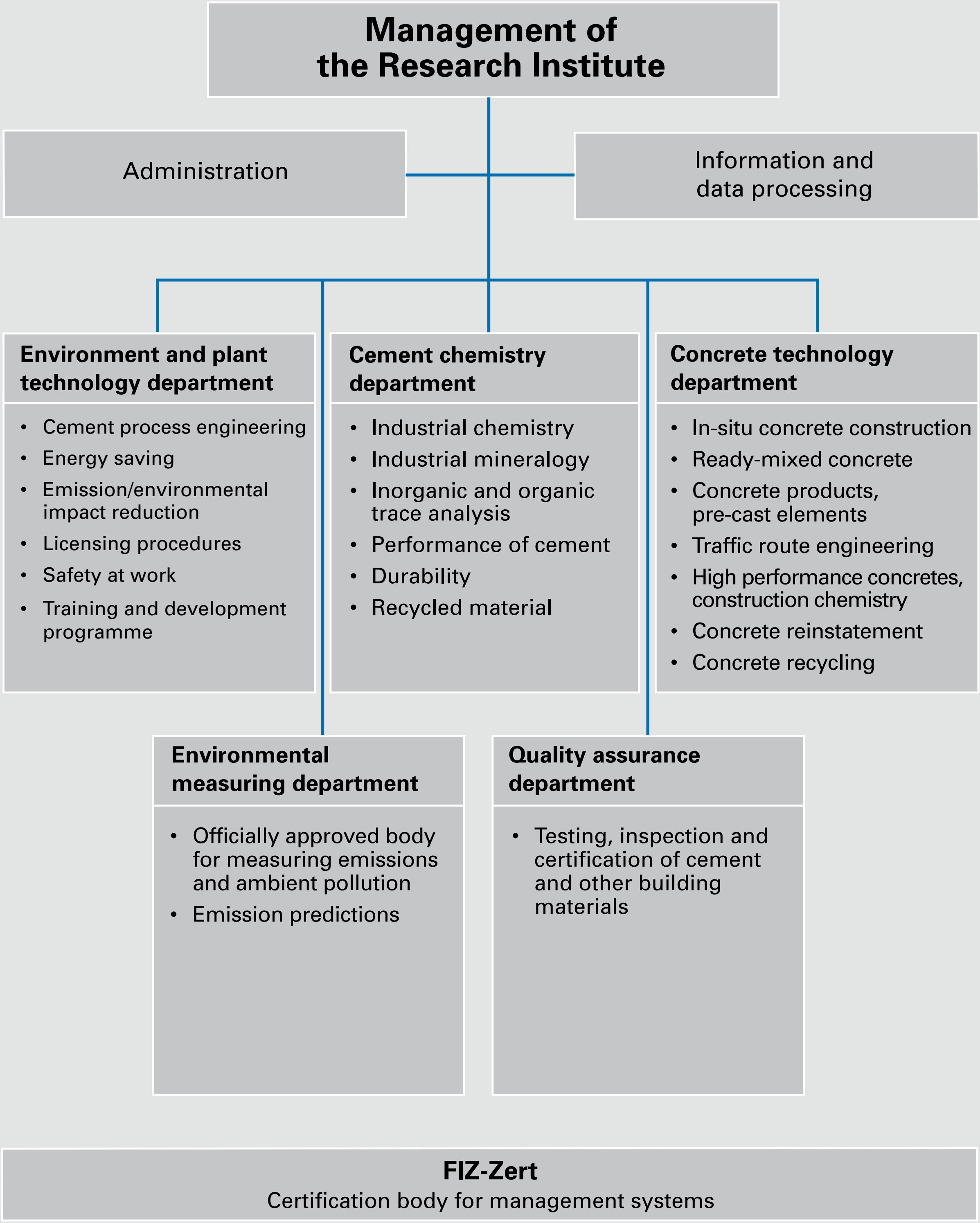
The Research Institute has a thoroughly homogeneous IT infrastructure. All relevant parts of the building are networked. The Microsoft Windows operating systems (Windows 2000 and XP, respectively, on the client side, and Windows 2003 on the servers) have been used successfully since 2003. The applications used on the client side are primarily from Microsoft. Specialised software and individual developments mainly used in the systems for measurement data acquisition complete this spectrum.

The merger of BDZ (located in Cologne) and VDZ in Düsseldorf, which was performed at the end of 2004, entails enormous cost benefits in terms of IT and the administration of the two networks, the consolidation of which is being pushed ahead with at full stretch. BDZ's branches located in Berlin and Erkrath are connected directly via the Internet, which allows these branches to be administered directly from Düsseldorf, too. All in all, 13 servers and 140 IT workstations are administered.

Networking throughout the association, i.e. beyond the branch located in Düsseldorf, ensures that all employees can avail themselves of all relevant information directly from their workstations. This particularly includes the internal literature database, numerous reference books available in digital form from a central source, and of course also the Internet/intranet. The interdisciplinary application of the Laboratory Information Management System LIMS has been successful. VDZ is present on the Internet at www.vdz-online.de. The information offered on the homepage, which is scheduled to be revised completely in the year 2005, is rounded off by an extranet accessible to registered users only.

Information centre – library

The information centre provides the employees of the Research Institute with a comprehensive collection of literature,



Management of the Research Institute

Administration

Information and data processing

Environment and plant technology department

- Cement process engineering
- Energy saving
- Emission/environmental impact reduction
- Licensing procedures
- Safety at work
- Training and development programme

Cement chemistry department

- Industrial chemistry
- Industrial mineralogy
- Inorganic and organic trace analysis
- Performance of cement
- Durability
- Recycled material

Concrete technology department

- In-situ concrete construction
- Ready-mixed concrete
- Concrete products, pre-cast elements
- Traffic route engineering
- High performance concretes, construction chemistry
- Concrete reinstatement
- Concrete recycling

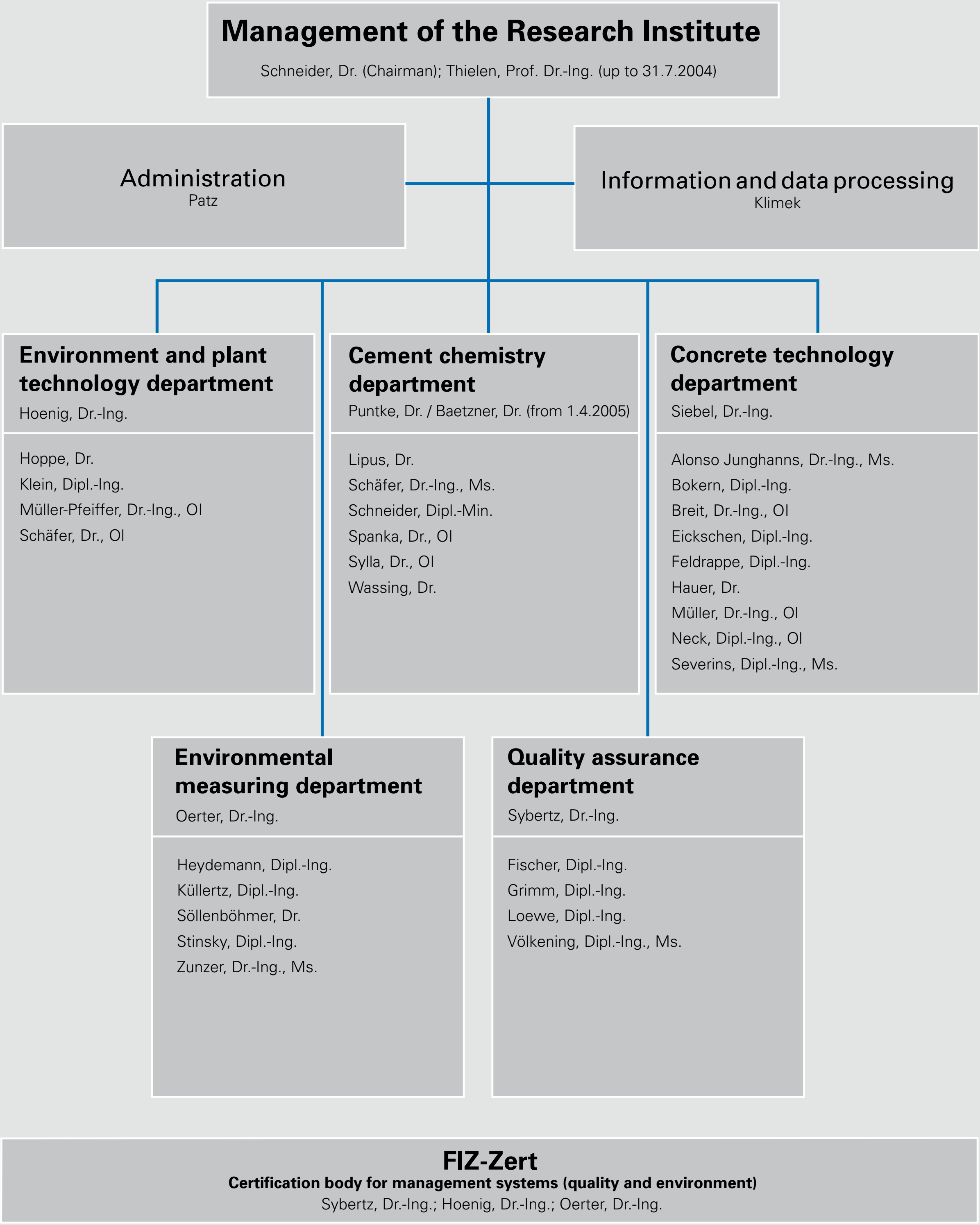
Environmental measuring department

- Officially approved body for measuring emissions and ambient pollution
- Emission predictions

Quality assurance department

- Testing, inspection and certification of cement and other building materials

FIZ-Zert
Certification body for management systems



Management of the Research Institute

Schneider, Dr. (Chairman); Thielen, Prof. Dr.-Ing. (up to 31.7.2004)

Administration
Patz

Information and data processing
Klimek

Environment and plant technology department

Hoenig, Dr.-Ing.

Hoppe, Dr.
Klein, Dipl.-Ing.
Müller-Pfeiffer, Dr.-Ing., OI
Schäfer, Dr., OI

Cement chemistry department

Puntke, Dr. / Baetzner, Dr. (from 1.4.2005)

Lipus, Dr.
Schäfer, Dr.-Ing., Ms.
Schneider, Dipl.-Min.
Spanka, Dr., OI
Sylla, Dr., OI
Wassing, Dr.

Concrete technology department

Siebel, Dr.-Ing.

Alonso Junghanns, Dr.-Ing., Ms.
Bokern, Dipl.-Ing.
Breit, Dr.-Ing., OI
Eickschen, Dipl.-Ing.
Feldrappe, Dipl.-Ing.
Hauer, Dr.
Müller, Dr.-Ing., OI
Neck, Dipl.-Ing., OI
Severins, Dipl.-Ing., Ms.

Environmental measuring department

Oerter, Dr.-Ing.

Heydemann, Dipl.-Ing.
Küllertz, Dipl.-Ing.
Söllenböhmer, Dr.
Stinsky, Dipl.-Ing.
Zunzer, Dr.-Ing., Ms.

Quality assurance department

Sybertz, Dr.-Ing.

Fischer, Dipl.-Ing.
Grimm, Dipl.-Ing.
Loewe, Dipl.-Ing.
Völkening, Dipl.-Ing., Ms.

FIZ-Zert

Certification body for management systems (quality and environment)

Sybertz, Dr.-Ing.; Hoenig, Dr.-Ing.; Oerter, Dr.-Ing.

which, upon approval, can also be used by outsiders. The library has currently a stock of around 41 000 volumes. It includes approximately 13 150 monographs and 18 700 journals, 36 150 patents, 6 500 standards and numerous research reports, annual reports and special publications.

The library currently subscribes to 131 periodicals to provide current information. They are evaluated by the scientific staff of the organisation; important essays are included in VDZ's literature database, which currently comprises 46 000 documents. The entries consist of bibliographical information, which describes the respective medium by indicating features such as its author or its title (formal registration). In addition to that, the contents are referenced by means of the adapted CEMBUREAU thesaurus, which describes the contents of a medium by a few distinctive terms (registration by content). The ZKG system continues to be used for classifying and structuring the information centre's stock.

The subsequent recording of the card index covering the stock before 1985 was pushed ahead with further, allowing researches for fairly old media to be carried out already now. Since, however, complete recording is very time-consuming, it will constitute one of the information centre's crucial tasks for the next period to be reviewed. Apart from the subsequent registration of fairly old stock, BDZ's library will be incorporated in VDZ's literature stock in the wake of the merger of BZD and VDZ. It comprises some 500 volumes that have to be recorded formally and by content. In this way, they will be made accessible to the BDZ and VDZ staff in a structured manner. Furthermore, the collections on radon (about 1 000 documents), cracking frame (a temperature stress testing machine, about 200 documents), and high-strength concrete (about 630 documents) have been completely registered and incorporated in the VDZ literature database in digitalised form.

The library's objective is to procure the necessary information and make it available to FIZ staff promptly regardless of the specific medium. In this context, particular emphasis is placed on digital information, since it allows to considerably reduce access and processing time. For example, the circulation of journals within the Institute has been converted to digital tables of content fed to the intranet as PDF files, which has significantly reduced processing time.

In addition to stock administration and procurement of information, supporting the Institute's employees in their Internet use constitutes an essential task of the information centre. This field of activities includes the maintenance of link lists for structured access to sources required and also the tapping of new access channels for known services, such as the use of electronic delivery services to reduce delivery periods.

The library is also involved in issuing all the Research Institute's publications. It is further responsible for coordinating dispatch of VDZ publications and maintains an extensive exchange of literature with many research organisations at home and abroad. In this way the library also acquires the not readily available "grey literature" for its collection on concrete technology, cement chemistry, process engineering and environmental protection. Participation in inter-library loan programmes allows to obtain literature supplementing its own collection.

Accreditation/certification

During the period under review, the Institute intensified its efforts to carve out an increasingly market and service-oriented position for the Research Institute both at national and international level. This also implies a high degree of efficiency and transparency of processes within the Institute, and most particularly in the laboratories. For that reason, a lean, EDP-aided management system that ensures minimum administrative efforts was introduced some years ago. This system regularly undergoes external inspection pursuant to the four standards for conformity evaluation ISO 9001, ISO 14001, ISO 17025 and EN 45011 as part of accreditation inspections and certification audits.

The accreditation of the Research Institute's laboratories pursuant to ISO 17025 comprises a total of about 300 test features including some 520 feature-process combinations. The FIZ thus fully complies with the requirements that clients at home and abroad impose on correspondingly qualified monitoring centres and testing institutes. Accreditation under private law is gaining increasing importance as a qualification criterion also with regard to the activities performed within the statutory domain.

The next steps scheduled to be taken in the implementation of the LIMS (see also p. 17) include the incorporation of the quality assurance department, test equipment administration, and cost accounting with internal billing and quotation.

Services

The Research Institute can also provide services for third parties by rendering expert's advisory or consultancy services on specialist matter in line with the Association's object. This also includes the undertaking of public and private sector assignments, e.g. via the surveillance organisation's activities as a testing laboratory, inspection body and certification body, as environmental monitoring body, or as certification body for management systems (environment and quality). The services are rendered separate from the non-material activities of VDZ joint research. 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 on the basis of fixed per diem rates and billed. Fixed prices are charged if the services rendered constitute standardised activities.

Concrete technology

In addition to the research activities in the field of concrete technology, the FIZ employees have increasingly performed contract investigations and issued expert's statements. In the area of contract investigations, the main focus was placed on the following investigations, among others:

- Determination of heat of hydration development according to the Langavant method (DIN EN 196-9) using the differential calorimeter and the testing devices developed at the FIZ for more extensive mortar and concrete series
- Determination of the C value
- Determination of the air void parameters in hardened concrete (DIN EN 480-11)
- Determination of the resistance to freeze-thaw and freeze-thaw with de-icing salt
- Investigations on alkali-silica reaction (ASR)
- Testing of the reactivity of different aggregates
- Evaluation of concrete compositions with regard to the risk of a harmful ASR (performance test method)
- Determination of the mechanical parameters of concrete, mortar and lime floor and their deformation behaviour
- Determination of rheological parameters using hardened cement paste suspensions
- Investigations aimed at assessing the corrosion behaviour of admixtures (according to DIN V 18998)

- Determination of the penetration behaviour of water polluting substances (DAfStb guidelines)
- Determination of the total porosity, the pore volume distribution and the specific surface of solids by mercury intrusion (DIN 66133)
- Determination of chloride migration coefficients and carbonation behaviour for durability assessment
- Wear by grinding (DIN 52108)

Expert's advisory or consultancy activities were performed on the following topics, for example:

- Fresh concrete properties
- Deficiencies in concrete strength
- Durability of concrete
- Damage in drinking water tanks
- Coating of drinking water tanks
- Crack formation in concrete
- Surface properties of concrete
- Carbonation and corrosion of reinforcements
- Mortar properties
- Effect of saliferous, concrete-aggressing water on built volumes
- Adaptation of concrete mix formulations
- Development of self-compacting concrete for locally available constituents
- Incompatibility of concrete admixtures and cement
- Assessment of floor slabs subject to the specifications of the water resources law
- Assessments regarding crack grouting measures
- Impurities in factory-made dry mortars

Environmental monitoring body

The Research Institute's Environmental monitoring body, represented by the Environmental measuring department, has been a service centre available to the cement industry and other industries to assist them in fulfilling their legal environmental obligations for many years. The range of services covers all environmentally relevant domains. Due to official notification as an officially recognised, independent monitoring body in accordance with § 26 and § 28 BImSchG (Federal Ambient Pollution Protection Act), § 26 and § 28 of the 13th BImSchV (Federal Ambient Pollution Protection Regulation), § 10 of the 17th BImSchV and clause 3.2 (clause 5.3 since October 2002) of TA Luft (Technical Instructions on Air Pollution Control), the FIZ is also authorised to carry out measurements in the statutory domain. Thus, the independent measurements that may be invoked at court can also be referred to for controlling compliance with stipulations laid down in licence certificates.

Particular focus is placed on activities in the following areas:

- Planning and competent execution of emissions measurements pursuant to BImSchG at industrial plants
- Establishment of measuring plans with due consideration of the pertinent VDI guidelines
- Emissions measurements and sampling of airborne pollutants (e.g. nitrogen oxides, trace elements, dusts, organic hydrocarbons, PCDD/F etc.)
- Determination of noise emissions and ambient noise levels
- Elaboration of noise reduction concepts and plant-specific noise maps
- Determination of emissions and ambient pollution levels from blasting vibrations
- Control of the proper installation and function as well as the calibration of continuously operating measuring equipment
- Inspection of on-site measuring devices

The environmental monitoring body employs an interdisciplinary team of engineers, natural scientists and laboratory staff having many years of practical experience. The accreditation on the basis of the international standard DIN EN ISO/IEC 17025 (previously DIN EN 45001) successfully completed in the year 2002 created a sound basis enabling the measurement body to also acquire orders abroad. Given the ever-closer intertwining of the industrial sector and the harmonisation of environmental stipulations, the requirement for qualified measurements abroad has increased. Its long-time experience and its special understanding of cement manufacture render the environmental monitoring body an interesting partner for industry in this respect. This extension of international activities is not made at the expense of the quality of services rendered in Germany. Quite on the contrary, the environmental monitoring body has currently initiated an improvement campaign that is based on a detailed survey conducted among clients and is aimed at further enhancing the body's own quality and thus the clients' satisfaction.

Environment and plant technology

Apart from research activities in the fields of environmental protection and process engineering, the Research Institute, and more in particular its Environment and plant technology department, also offers services for cement companies. Among other areas, Environment and plant technology focuses on expert's advisory and consultancy services. The Research Institute has assisted the VDZ member works in carrying out licensing procedures for many years. This applies to the following tasks in particular:

- Management of licensing procedures
- Assistance in dealings with authorities, e.g. regarding new regulations of environmental legislation
- Expertise compilation (calculation of stack heights, emission predictions, environmental impact predictions, etc.)
- Execution of investigations on environmental compatibility

In the technology domain, the Environment and plant technology department can support the cement works by:

- Technical advice
- Optimising the operation of kiln and grinding systems
- Optimising fuel utilisation
- Reducing emissions (NO_x, SO_2, dust, mercury, etc.)
- Carrying out process measurements at kiln and grinding systems
- Carrying out investigations of recirculating systems
- Establishment of energy balances and implementation of measures to reduce energy consumption

In line with the Research Institute's increasingly European orientation, these services have been offered more and more at international level. In doing so, the FIZ can resort to many years of experience in international projects (e.g. EU research projects).

VDZ's quality surveillance organisation

The traditional functions of the German Cement Works Association include the testing, monitoring and certification of cement and cement-type binders for the fulfilment of the protection aims of the Federal State Building Codes and in accordance with the Construction Products Law. Accordingly, VDZ's quality surveillance organisation is recognised by the responsible construction supervision authorities as a testing laboratory, inspection body and certification body ("PÜZ-Stelle") in the ambit of standards as well as technical approvals for cement, hydraulic binders, concrete additions and admixtures, and certain preparations produced from these. Chapter IV gives a detailed account of the functions of VDZ's quality surveillance organisation for the period under review.

Certification body for management systems – FIZ-Zert

The Research Institute's certification centre for management systems has been accredited since June 1998 by the TGA (accreditation agency). Companies can enlist the services of FIZ-Zert regardless of their location, their membership in any association, and any other restrictions (see Chapter IV).

FIZ-Zert was originally established to certify quality management systems in accordance with DIN EN ISO 9001 with the aim of using possible synergies with the statutory product certification procedure. Since 2003, FIZ-Zert has been accredited for the certification of environmental management systems in accordance with ISO 14001 as well. In the year 2004, FIZ-Zert carried out verifications of CO_2 emissions pursuant to the Law on Trading Greenhouse Gas Emissions at a total of 28 cement works sites for the first time.

I

Process Technology of Cement Manufacture

Process engineering research aims primarily at optimising the energy consumption and use of manpower in cement manufacture as well as the quality and uniformity of the cement, and at reducing emissions without compromising economic efficiency. The optimisation of secondary fuel utilisation and the exploration of the impact of secondary fuel use on burner operation and environment were two of the major issues on which investigations focused in the past years. The share that secondary fuels account for in the overall energy consumption of the German cement industry has risen to approx. 38% (2003) by now. This means that many kilns are operated at high substitution rates topping 60% in some cases.

Since the BSE crisis in the year 2000, the German cement industry has utilised the thermal content of meat and bone meal on a large scale. The Research Institute has carried out extensive investigations on the effects of meat and bone meal utilisation on product quality as well as kiln operation and emissions. From an operational point of view, especially the effects on chlorine cycles and the behaviour of phosphate in the kiln plant were of tantamount importance. As far as emissions are concerned, the interest chiefly centred on possible effects on NO_x emissions.

The work performed by a VDZ working group which intensively studied the impact of pre-calcining technology and secondary fuel utilisation on the wear and stability of refractory materials also relates to secondary fuel utilisation. This work has been continued and extended to include the entire kiln in the meantime.

The endeavours to simulate the clinker burning process in a computer model and to make use of simulation calculations to optimise kiln systems and investigate scientific questions, respectively, were continued in the period under review. The process model for the entire clinker burning process available at the Research Institute was extended: It now also comprises the elements of the external cycle (conditioning tower, raw mill, dust filter) and the possibility to simulate chlorine and sulphur behaviour as well as alkali cycles. After the corresponding validation by experimental results, the model can now be employed to design or optimise bypass systems, for example.

Investigations in industrial and semi-industrial grinding and classifying plants were used mainly to examine the effects of separate grinding and mixing or intergrinding, respectively, on the particle size distribution of the cements obtained. The comparison of different grinding systems for cement manufacture represents a new subject of main emphasis in the field of mechanical process engineering. Interest focuses on the different product properties obtained in spite of identical particle size distributions, which may ultimately be attributable to different grinding techniques. Corresponding investigations at semi-industrial grinding and classifying plants are being carried out at the Research Institute and at various plant manufacturers.

Utilisation of used tyres in a cement works

Energy consumption ■

Kilns

In the period under review, the licensed kiln capacity of the German cement industry declined from 132 820 t/d (2002) to 130 020 t/d in 2004. The operating permit of one kiln plant expired. As a consequence, the total of kiln plants with operating permits decreased from 70 to 69. The kiln systems operated in Germany today are almost exclusively plants applying the dry or semi-dry processes, respectively. In addition to that, there are permits for 8 shaft kilns. The average kiln capacity for rotary kilns rose slightly from 2 106 to 2 112 t/d. **Tab. I-1** gives an overview on the status of the available kilns. Accordingly, plants with cyclone or grate preheaters, respectively, account for 99.1% of the total capacity. Reaching 88.3% (relative to capacity) in the year 2004, the proportion of cyclone preheater plants grew further. At 11, the number of pre-calcining systems remained unchanged. Of these systems, 8 are equipped with a tertiary air duct. Since their kiln capacity is higher by comparison, pre-calcining systems represent more than one quarter of the installed, licensed clinker capacity of the German cement works.

Tab. I-1: Number and capacity of the kilns with operating permits in Germany in the years from 2002 to 2004

		As at 01.01.2003			As at 01.01.2004			As at 01.01.2005		
		Number	Capacity		Number	Capacity		Number	Capacity	
			t/d	%		t/d	%		t/d	%
Kilns with cyclone preheaters		46	116 550	88.4	45	114 750	88.3	45	114 750	88.3
Kilns with grate preheaters		16	14 070	10.7	16	14 070	10.8	16	14 070	10.8
Shaft kilns		8	1 200	0.9	8	1 200	0.9	8	1 200	0.9
Total		70	131 820	100	69	130 020	100	69	130 020	100
Average kiln capacity in t/d	Rotary kilns		2 106			2 112			2 112	
	Shaft kilns		150			150			150	
Clinker production[1] (year) million t/a			(2002) 24.0			(2003) 25.2			(2004) [3]	
Utilisation[2] in %			56			61			[3]	

[1] according to CO_2 monitoring
[2] assumed availability 320 d/a
[3] not available y et

At 56%, utilisation was significantly lower in the year 2002 than the long-term average. It rose to 61% again in the year 2003, which was primarily attributable to increased clinker exports. Overall, these degrees of utilisation fall considerably short of the long-term average as well. The utilisation figures are based on an assumed availability of the kiln plants of 320 days per year.

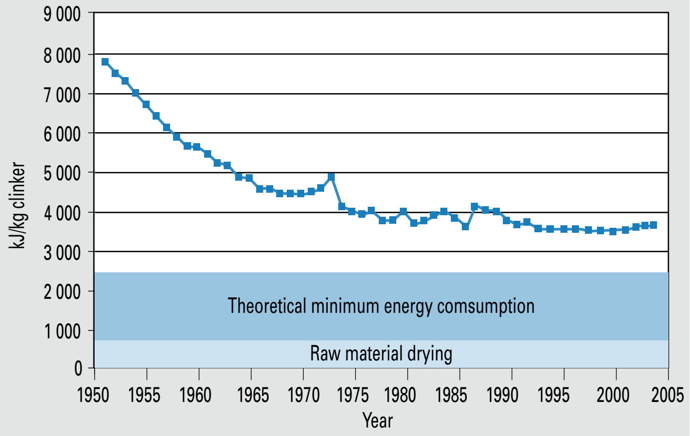


Fig I-1: Specific fuel energy consumption (up to 1987 old federal states, past 1987 whole Federal Republic)

Fuel energy consumption

The main use of fuel energy in cement manufacture is for burning the cement clinker. To a lesser extent, thermal energy is also used for drying other major cement constituents, such as blastfurnace slag. To manufacture cement clinker with its characteristic properties, the raw materials, principally limestone marl and clay, are burnt 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-1** shows the trend of the specific thermal energy consumption of the cement industry from 1950 to 2003. Form 1987 onwards, the new federal states are included in the values. As the diagram illustrates, the burning process in the German cement works is now optimised to such an extent that no noteworthy further reductions can be expected from process engineering measures.

By contrast, the German cement industry succeeded in significantly reducing its specific energy consumption relative to one ton of cement over the last years. It becomes apparent from the cement companies' data on energy consumption and output, which the Research Institute collects every year, that only a small proportion of this reduction was due to process engineering measures in the years under review. The stepped-up production of cements with several main constituents is of far greater importance. In this way, the German cement industry managed to lower its specific fuel energy consumption relative to the cement quantity produced from 3 510 kJ/kg cement to 2 740 kJ/kg cement over the past 16 years, as can be seen from **Tab. I-2**. The clinker proportion in the cement dropped from approx. 86% to 76% over the same period.

This development must be seen against the backdrop of the voluntary agreement on climate protection, to which the German cement industry committed itself in 1995 together with other branches of the German industrial community. In fulfilling this voluntary agreement the cement industry contributes to a reduction in climatically relevant CO_2 emissions. It is thus striving to lower its specific fuel energy consumption by 20% from 1987 to 2005.

In the past few years there has been a continuous change in the structure of the fuels used in the German cement industry. Since 1987 the total fuel usage has fallen from 119.9 to 91.3 million GJ/a in 2003, which is attributable to the slump in production, among other factors. In absolute terms, this corresponds to a reduction of 23.9%. As can be seen from **Fig. I-2**, the proportion of secondary fuels continued to rise in the period under review and now totals 38.3% (2003), as against 23.0% in 1999. The increasing use of secondary fuels entailed the substitution of hard coal and, to a smaller extent, petcoke and lignite during the period under review. The consumption of heavy fuel oil decreased from 5.9 million GJ/a in 1999 to 2.7 million GJ/a in 2003.

The break-down of secondary fuels for the years 2000 and 2003 demonstrates that traditional secondary fuels, i.e. used tires and waste oil, have lost in importance in comparison to other secondary fuels. **Tab. I-3** shows that the input of used tires remained nearly constant at just under 250 000 t/a, whereas the quantity of waste oil utilised decreased from 140 000 t/a in 2000 to 116 000 t/a in 2003. The use of fractions from industrial and commercial wastes increased substantially, from 372 000 t/a in 2000 to 626 000 t/a in 2003. Besides, a rise to 155 000 t/a in the utilisation of processed fractions from municipal wastes was recorded. The use of meat and bone meal and animal fat began in 2000 in the wake of the BSE crisis and was increased to 452 000 t/a by the year 2003. It is, however, predictable that these quantities will no longer be available on the same scale in the future.

Electrical power consumption

Electrical energy is consumed in cement manufacture primarily for raw material processing (about 35%), for burning and cooling the clinker (approx. 22%) and for cement grinding (approx. 38%). **Fig. I-3** shows the trend of electrical power consumption by German cement works in the period from 1950 to 2003. The long-term rise in electrical power consumption could be stopped after the German reunification. This was even followed by a slight reduction in the succeeding years, which reached a new low of 99.5 kWh/t in the year 2003.

Tab. I-2: Absolute and specific fuel energy consumption

Year	Fuel energy consumption	
	Absolute 10^6 GJ/a	Specific kJ/kg cement
1987	119.9	3 510
1990	109.5	3 200
1994	102.9	3 000
1995	102.8	3 000
1996	97.6	2 995
1997	99.3	2 975
1998	100.7	2 905
1999	102.3	2 800
2000	99.3	2 835
2001	89.8	2 790
2002	85.8	2 790
2003	91.3	2 740
2005[1]	--	2 800[2]

[1] target year of the voluntary agreement of 1995

[2] value in the target year predicted by the German cement industry under the terms of its voluntary agreement

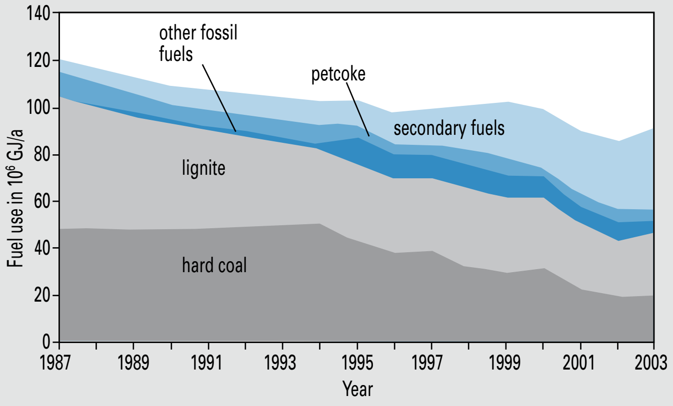


Fig. I-2: Fuel use in the German cement industry

Tab. I-3: Use of secondary fuels in the German cement industry

Secondary fuel	2000 1 000 t/a	2003 1 000 t/a
Used tyres	248	247
Waste oil	140	116
Fractions from industrial and commercial waste, thereof:	372	626
Wood pulp, paper and cardboard		156
Plastics		177
Packaging materials		9
Textile industry waste		15
Others		269
Meat and bone meal, animal fat	[1]	452
Reprocessed fractions from municipal waste	[1]	155
Scrap wood	79	48
Solvents	31	48
Fuller‘s earth	23	20
Sewage sludge	-	4
Others such as:	176	17
Oil sludge		
Organic distillation residues		

[1] listed under ”Others“ in 2000

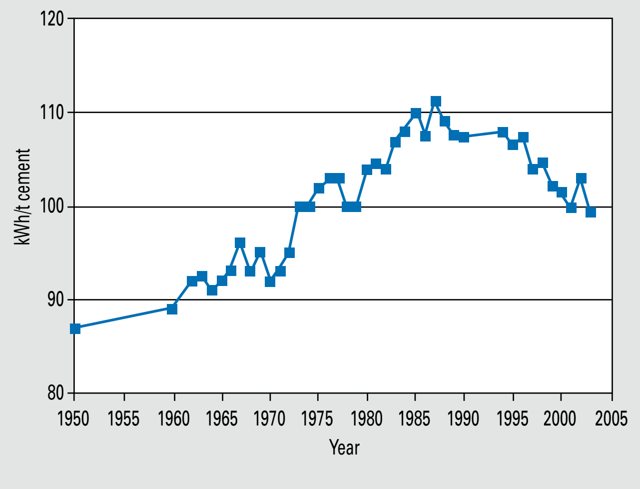


Fig. I-3: Specific electrical energy consumption (up to 1987 old federal states, past 1987 whole Federal Republic)

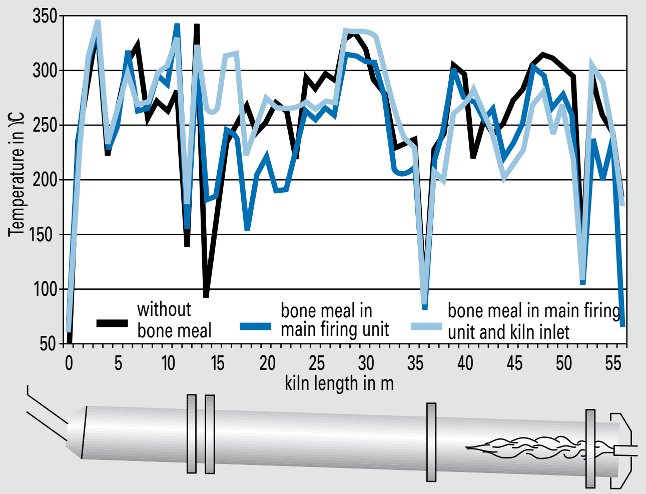


Fig. I-4: Average kiln shell temperature during varied meat and bone meal use

Cements with other main constituents in addition to clinker, such as blastfurnace slag or limestone, consume more grinding energy since they need to be ground finer 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) will be saved. The use of energy-efficient mill types, such as high-pressure grinding rolls, has gained acceptance in the cement industry. Since the working properties of the cement produced in these mills do not correspond to those of cement ground in customary ball mills, however, subsequent grinding in a ball mill is usually still necessary. Therefore, it is still impossible to realise the full potential of energy saving. Even separating the grinding process of the different main constituents and mixing them subsequently in mixing systems apparently does not allow for significant reductions under regular operating conditions.

Plant operation ■

Effects of meat and bone meal use on rotary kiln operation

Whenever the fuel type is changed, the effects on kiln operation, emissions and cement properties have to be taken into consideration. The impact of meat and bone meal utilisation on the operation of rotary kilns and cement properties (see Chapter III) was investigated as part of a research project sponsored by the AiF. Besides phosphates, meat and bone meal also have higher chlorine and sulphur contents as well as elevated nitrogen contents, which may influence recirculating material systems in the kiln plant and NO_x emissions. Furthermore, meat and bone meal particles are markedly coarser than pulverised coal. As a consequence, it may take longer to completely burn up a meat and bone meal particle than a more finely ground coal particle.

Extensive industrial investigations both with and without meat and bone meal use were carried out at three kilns. Furthermore, the feeding point of the meat and bone meal was varied. Two of the kiln plants investigated are classic cyclone preheater kilns, while the third is a pre-calcining system. The kiln trials consisted of investigating the impact of meat and bone meal utilisation on fuel energy consumption, combustion conditions, NO_x emissions and recirculating chlorine and sulphur systems. The influence of meat and bone meal use on fuel energy requirement was only slight in all three kilns. When meat and bone meal was utilised, the measured raw gas temperatures after heat exchanger were slightly higher at all three kilns than without its use. This resulted in slightly higher exhaust losses, which were, however, eclipsed by other effects in some cases (e.g. lower loss of heat through kiln walls due to coating formation in the kiln, and higher oxygen contents in the raw gas at individual operational settings). Insofar, the utilisation of meat and bone meal does not always lead to higher fuel energy requirements.

Meat and bone meal use in the main firing unit apparently caused a longer flame in the rotary kiln in all three plants. On the one hand, this is indicated by elevated temperatures in the kiln inlet area and in the entire preheater, respectively. On the other hand, a change in temperature distribution on the kiln shell was observed at one kiln system. The average kiln shell temperature of that kiln measured along the entire kiln length at different fuel settings is shown in **Fig. 1-4**. The black curve represents the average kiln shell temperature during the use of pulverised pit coal, shredded light fractions of commercial waste (fluff) and waste oil. The dark blue curve maps the temperature profile obtained when 2.5 t/h meat and bone meal were input in the main firing unit. The quantity of fluff added was kept at the same level as during the first measurement, while the mass flows of pulverised coal and waste oil were reduced. When meat and bone meal was utilised, temperatures in the kiln outlet area tended to be lower, while those in the kiln inlet area tended to be slightly higher. The light blue curve represents the temperature distribution on the kiln shell with 1.8 t/h meat and bone meal being utilised in the main firing system, and 0.7 t/h in the kiln inlet. The other fuels remained unchanged. As a consequence, kiln shell temperatures in the kiln outlet area dropped further, while higher shell temperatures were measured in the kiln inlet area. The microscope pictures of polished clinker sections also corroborate that the meat and bone meal use led to the formation of a longer pre-cooling zone.

The utilisation of meat and bone meal in the main firing unit caused a rise in NO_x emissions of up to 20% in two of the three rotary kilns. Meat and bone meals have a comparatively high content of fuel-induced nitrogen, which, depending on the oxygen

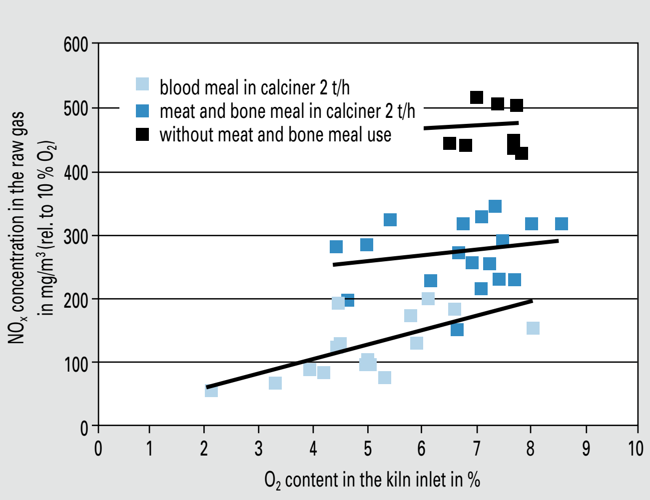


Fig. I-5: Influence of meat and bone meal utilisation on the NO_x concentration in the raw gas of a rotary kiln plant

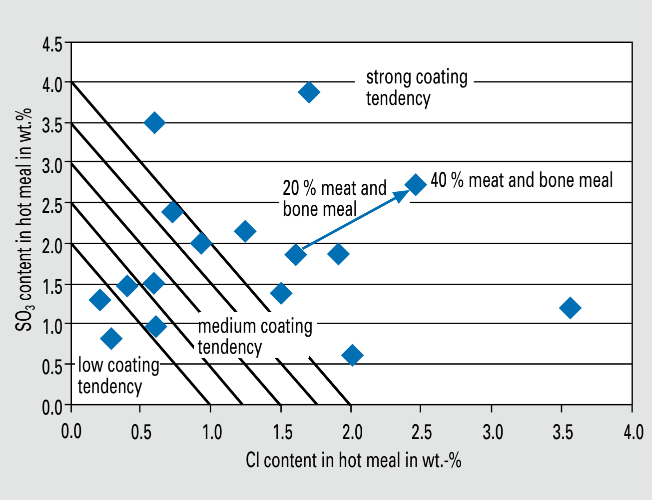


Fig. I-6: Influence of meat and bone meal utilisation on the coating tendency of a rotary kiln plant

supply in the sintering zone, can contribute to NO formation during combustion. Experiences gained at other cement works demonstrate that such a rise in NO_x emissions can, however, be prevented by adapting the settings of the firing unit accordingly. By contrast, the use of meat and bone meal in the kiln inlet or in the calciner led to a reduction in NO_x emissions in comparison to the use of other fuels. The NO_x emissions measured were particularly low when blood meal instead of meat and bone meal was input in the kiln inlet or the calciner. Analogous to the experience regarding the utilisation of used tyres in the kiln inlet, the combustion of meat and bone meal in this part of the kiln system generates near-stoichiometric or under-stoichiometric conditions locally, which may result in the suppression of NO formation from the meat and bone meal, or even in a reduction of NO from the main firing unit.

Meat and bone meal input into the calciner was investigated at a precalcining system. **Fig. I-5** illustrates the NO_x concentrations in the raw gas (relative to 10% O_2) of the plant as a function of the oxygen supply in the kiln inlet. It becomes obvious from the Figure that the fuel type used has decisive influence on the NO formation taking place in the calciner and on NO decomposition, respectively. As far as the fuel type is concerned, the volatile content, the content of fuel-induced nitrogen, the type of bond of the fuel-induced nitrogen, and the fineness of the fuel play a crucial role. When the volatile content is high, fairly large quantities of hydrocarbon radicals and NH_i compounds are released during fuel pyrolysis, which can contribute to NO decomposition. If the nitrogen content of the fuel is fairly high in addition, significantly larger quantities of NH_i compounds are released during pyrolysis, which also promote NO decomposition. At approx. 18 wt.%, the nitrogen content of blood meal is markedly higher than that of meat and bone meal (approx. 9 wt.%). With the use of blood meal, the quantity of NH_i compounds and hydrocarbons formed as intermediate products during pyrolysis, which lead to NO reduction via an SNCR reaction, can therefore be assumed to be significantly higher. The combustion of fuels with a low volatile content (e.g. pulverised coal) takes place much more slowly. Thus, the oxygen available is not consumed as quickly, which results in lower NO decomposition. Furthermore, pulverised coal has a low nitrogen content of merely about 0.6 wt.%. As a consequence, the formation of NH_i compounds and thus NO decomposition is markedly lower than with meat and bone meal or blood meal being utilised.

In all the cases investigated, the input of chlorine in particular and, to a lesser extent, also the input of sulphur into the kiln system increased due to meat and bone meal utilisation. As the bypass systems were operated at a constant bypass rate during the trials, the higher chlorine input resulted in a rise in the chlorine content of the hot meal. A particularly pronounced intensification in recirculating systems was observed at the kiln at which meat and bone meal use was increased from an original 20% to 40% of the firing heat capacity. As can be seen from **Fig. I-6**, the increase from 20% to 40% in meat and bone meal utilisation caused the chlorine content of the hot meal to grow from 1.6 wt.% to 2.5 wt.% within one day. Furthermore, the longer flame accompanying higher meat and bone meal use also resulted in a change in sulphur combination in the clinker. In spite of the increase in the chlorine and sulphur contents of the hot meal, however, coating formation in the preheater was manageable during the trial period. In continuous operation, the rise in the chlorine content of the hot meal would be countered by an adaptation of the bypass rate in order to bring the recirculating chlorine system down to the usual level.

Modelling of the clinker burning process

A process technology simulation model developed at the Research Institute of the Cement Industry can be applied to choose suitable secondary fuels and to evaluate the quantities that can be input into rotary kilns. Furthermore, the programme allows to calculate and optimise the operation of a gas bypass installed at the kiln inlet to limit recirculating chlorine systems between the kiln and the preheater. The model describes the entire clinker burning process from the input of raw materials and fuels up to the discharge of the clinker from the cooler and of the kiln exhaust gas from the stack. It consists of separate models for the cyclones of the preheater, the calciner, the bypass, the rotary kiln and the grate or satellite cooler, respectively, to which the plant components of the external cycle, i.e. the evaporative cooler, the raw mill, the preseparator and the dust collector (**Fig. I-7**) have been added recently. These modules are connected to each other mathematically and allow to determine the steady state of the entire clinker production plant. The

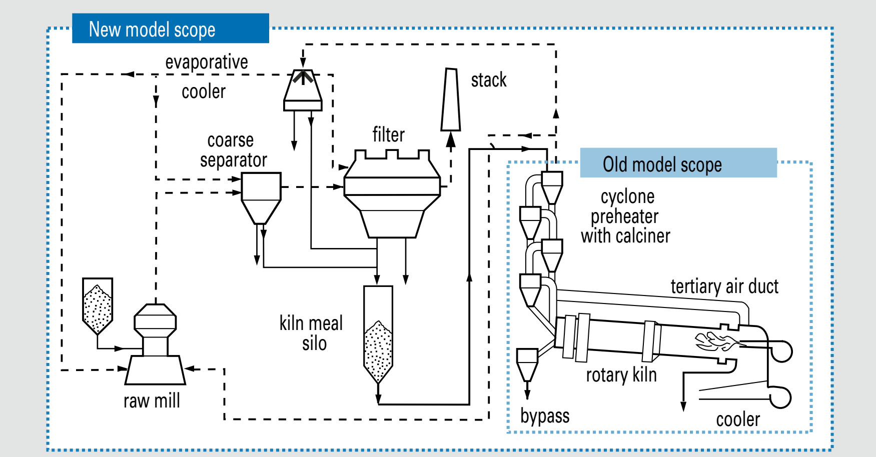


Fig. I-7: Extension of the process engineering model to include calculation modules for the plant sections of the external cycle

modular structure thus permits the individual and flexible simulation of different plants with regard to the parameters of the individual plant components, the plant arrangement, the modes of operation, and the raw materials and fuels. Application of the model focuses on questions relating to energy and materials, with interactions within the process being of particular interest.

In addition to the above-mentioned studies about the use of secondary fuels and the relieving of chlorine recirculating systems via a gas vent, cost-effective and riskless variations of parameters can be performed with fairly little effort. This allows to make statements on the effects of plant rebuilding measures, such as additional or more effective cyclones in the preheater, and of changes in plant operation, such as a reduction of the sintering zone temperature.

The basis from which all these calculation studies proceed is the reference state of a plant, which is developed in cooperation with plant operators on the basis of measurement results and operating experiences and is to reflect the respective current normal operation of the plant as precisely as possible. The calculations based on parameter variations supply extensive data on the relevant process variables for all plant sections. Evaluation in terms of quality and quantity is effected through a comparison with the reference scenario. The mathematical model is based on generally acknowledged basic principles of process engineering, heat transfer and material science, as well as the process know-how gained from numerous kiln and laboratory trials carried out by Research Institute. The verifiability of the calculated results was repeatedly checked and improved by making calculations for different kiln plants and comparing the results with the measurement values. Limestone calcination, clinker phase formation and the firing of fuels constitute the most important chemical reactions, which are calculated in detail for each section of the kiln plant. Since the fuel ashes are taken into consideration as well, the effects of a change in fuel type can thus be calculated both with regard to the quantity and composition of the exhaust gas (O_2, CO_2, H_2O, N_2) and with regard to the clinker phases.

The aspect that is often particularly interesting about a shift in fuel type is the associated change in chlorine input into the plant. Together with sulphur and alkalis, chlorine forms recirculating systems between the rotary kiln and the bottom stages of the preheater or the calciner, respectively. These substances and their compounds evaporate in the kiln and are carried into the preheater together with the gas flow. At low temperatures, they condense there on the meal and the dust as well as the plant walls, on which coatings are formed. Apart from the higher risk of operational malfunctions due to coating formation, the evaporation and condensation lead to heat being transmitted from the kiln into the preheater. This results in higher energy input via the main firing unit and restricts the quantity of fuel that can be fed to the kiln inlet or calciner firing units. For that reason, the model was extended to include the elements sulphur (in the form of not easily volatilised sulphate and volatile sulphide), chlorine and alkalis in the form of the chemical compounds K_2O, Na_2O, KCl, NaCl, K_2SO_4, Na_2SO_4, $CaSO_4$ and $CaCl_2$, which generate recirculating systems. These compounds either enter the process in this form via the raw materials and fuel ashes, or they may be generated in the process. Both their input and their formation were incorporated into the model, with the formation processes only being calculated when the boundary conditions, such as suitable temperatures, sufficient availability of reaction partners and a partial pressure in the gas phase below saturation, correspond to those prevailing in practical use. It has been taken into consideration that compounds may both form or be dissociated into their individual constituents, when the temperatures prevailing are high enough. As a consequence, these constituents will again be available for the formation of new alkali chloride or alkali sulphate compounds in the gas phase. Furthermore, the chemical compounds may evaporate and condense. The evaporation process is restricted by the saturated partial pressure in the gas being reached. For that reason, temperature ranges within which these reactions can take place have been defined for all chemical compounds. In this way, the different degrees of volatility of the compounds is taken into account. Depending on whether the reaction is exothermic or endothermic, the calculated reaction conversion will cause the local gas or material temperature to increase or decrease.

Applied under practical conditions, the simulation programme made it possible for the first time to successfully estimate the effects of a change in the input of chlorine, sulphur and alkalis on process temperatures, and on the build-up of Cl^-, SO_3, K_2O and Na_2O in the hot meal (**Fig. I-8**). In addition to that, the reduction effect which a bypass gas vent has on recirculating systems was determined in terms of quantity. A maximum chloride content in the kiln inlet meal was defined as criterion for the necessary bypass rate (**Fig. I-9**), i.e. the quantity of gas relative to the kiln inlet volume flow that is discharged via the bypass. Accordingly, the thermally relevant recirculating chlorine, sulphur and alkali systems can be represented reliably.

The model is currently being extended to include the behaviour of trace elements in order to allow more exact emission forecasts for trace elements to be made in the future, for example as part of environmental

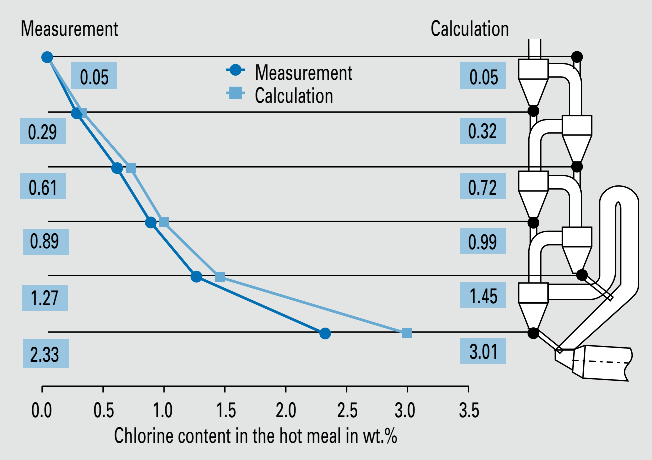


Fig. I-8: Comparison between calculation results and measurement values for gas and meal temperatures and hot meal contents

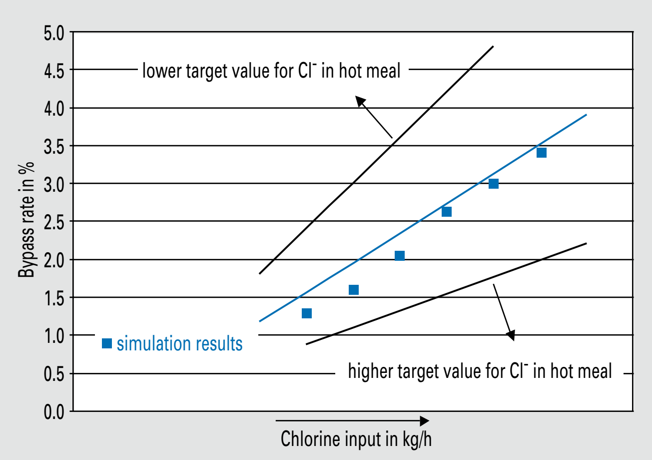


Fig. I-9: Bypass rates needed to relieve recirculating systems as chlorine input increases

impact assessments. The behaviour of trace elements in the clinker burning process is determined by the volatility of the compounds they form, and by the degrees of bonding and precipitation in the various plant sections. Besides gas and material temperatures, relevant process parameters are in particular the dust collection efficiency of the cyclone stages, the supply in the meal and dust of high-surface fine fractions conducive to condensation, and the intensity of the recirculating systems of chlorine, sulphur and alkali already calculated by the programme. To gather the data required for setting up the model, plant trials at three kilns were carried out as part of AiF research project No. 13230N, the final report on which is open to inspection at the Research Institute. Methodically, the simulation will follow a description of the behaviour of chlorine, sulphur and alkalis, and will incorporate the trace elements in its first step in their elemental form.

Recirculating dust systems in the preheater

Investigations aimed at determining the dust content in the cyclone riser ducts of preheaters form the basis for determining the transfer coefficients of various compounds, such as trace elements, for the cyclones and the cyclone preheater as a whole. If the dust content is known, the dust and meal mass flows as well as the dust collection efficiency of the cyclones can be calculated. Furthermore, they will be incorporated in the process technology simulation model developed at the Institute, which describes the entire clinker burning process from the input of raw materials and fuels up to the discharge of the clinker from the cooler and of the kiln exhaust gas from the stack. Both the transfer coefficients and the simulation model allow to scrutinise material flows in the cement clinker burning process, which for example public authorities may refer to for an evaluation of secondary fuel use. The measurement results show the known effect that dust collection efficiency decreases from the top to the bottom stage. Owing to the lower collection efficiency, the recirculating dust systems and, as a consequence, the mass flows passing through the cyclones are bound to increase.

First of all, the cyclone preheater of a rotary kiln system is the place where the moist raw meal is dried; on the other hand, already in this area chemical, physical and mineralogical reactions take place, such as the partial calcination of the meal. The fresh kiln meal is metered into the gas riser duct below the top cyclone and carried into the cyclone by the gas flow. The intense mixing of the hot gas and the solid creates very favourable conditions for the heat transfer. As a consequence, a nearly complete temperature equilibrium of gas and meal is obtained. In this process, the gas cools and the material warms up. The thermal energy withdrawn from the gas is thus utilised efficiently for the reactions taking place in the solid material. These are endothermic reactions on the one hand, i.e. reactions that are dependent on energy being supplied, such as the evaporation of the surface water and the expulsion of the CO_2 from the $CaCO_3$ and the $MgCO_3$. On the other hand, however, the thermal energy is also required to activate the exothermal reactions, i.e. the reactions which imply a release of energy, such as the conversion of organic carbon to CO and CO_2.

In addition to serving the purpose to mix the gas and the meal to achieve efficient heat transmission, the cyclones have the function to separate these materials again as efficiently as possible. The cooled gas is to leave the cyclone separator with a low dust loading to rise to the cyclone stage arranged above. In the case of the top cyclone stage, it is to be discharged as raw gas. Ideally, all the solid material is to issue from the cyclone in the opposite direction in order to re-enter the gas riser and reach the cyclone arranged below, where it is dispersed in the hotter gas. Collection efficiency of 100%, i.e. the complete separation of gas and solids, is, however, achieved in none of the cyclone stages. For one thing, an increase in cyclone separation efficiency always entails a higher pressure drop and thus an elevated energy requirement for gas transport. In line with a rise in temperature, i.e. from the top to the bottom cyclone stage, moreover, the physical properties of the gas change so profoundly as to render the separation of the materials more difficult. Furthermore, the high temperatures in the bottom cyclone separators require designs that are less efficient in terms of separation, but more resistant to temperature and wear. For example, the dip pipes of the lower stages are of shorter construction, which reduces the separation efficiency of the separator.

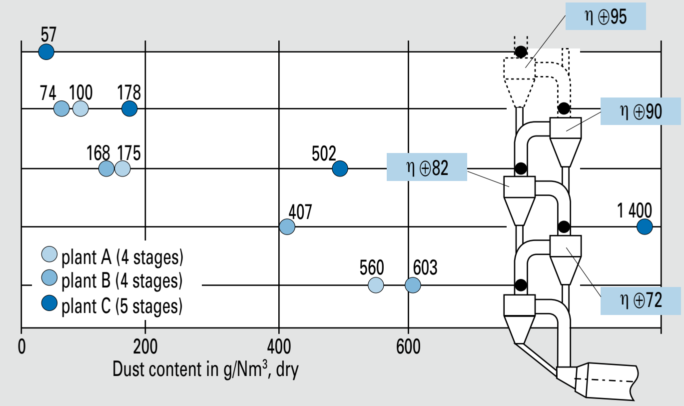


Fig. I-10: Dust contents and cyclone collection efficiency of 3 preheaters

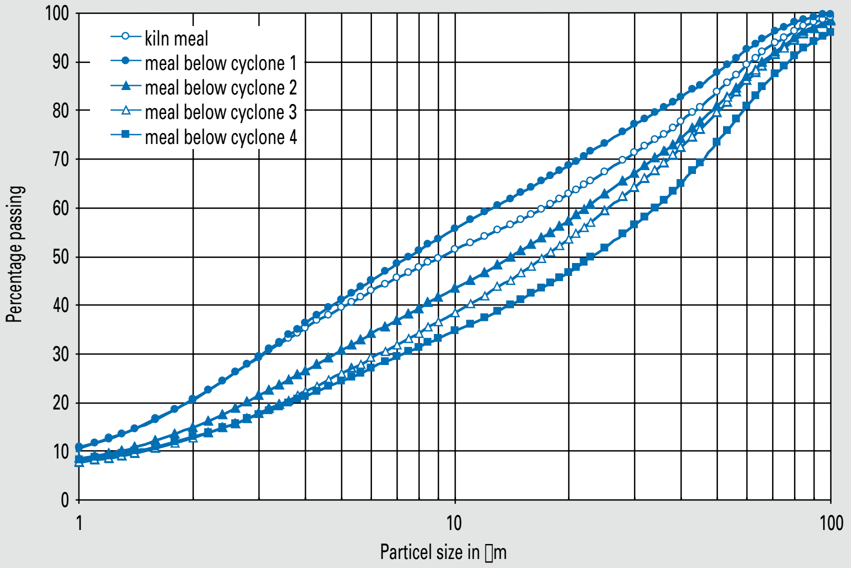


Fig. I-11: Particle size distributions of the hot meals below the cyclone stages of a preheater

The investigations the Research Institute carried out to determine the dust contents were performed immediately above the cyclone covers and below the feeding points for kiln meal or hot meal, respectively, in the cyclone riser ducts. Due to the high dust loading and the coating tendency of the meals at high temperatures, it was not possible to measure the gas velocities and thus the volume flows directly. The volume flows were calculated on the basis of continuous measurements of the gas composition and oxygen balances instead. The suction of the partial gas flows loaded with dust was effected isokinetically using an air-cooled probe and a temperature-resistant filter material made from quartz fibres. As the gas flows in the riser ducts still exhibit a marked swirl generated in the cyclones, the suitable angle for the suction nozzle had to be determined first. The highest dust contents, which can be expected to occur in the main flow direction, were usually obtained at a diversion of about 45° from the vertical. **Fig. I-10** depicts the results of dust content measurements conducted in the cyclone riser ducts of three different preheaters. Furthermore, the dust collection efficiency determined for the individual cyclone stages is indicated. The results clearly show that marked recirculating dust systems primarily form in the lower cyclone stages. As a result, the meal mass flow into the bottom cyclone stage may exceed the mass flow of kiln meal fed by a factor of up to three.

In addition to the dust content, the particle size distribution of the meal and dust samples was determined using the Cilas method. The meals turned out to get substantially coarser as they passed the cyclone preheater on their way from kiln meal to hot meal (**Fig. I-11**). On the one hand, this is attributable to the separation characteristics of the cyclones, which cause the finer grain fractions to be carried upwards with the gas flow in dust form, whereas the fairly coarse solid fractions are moved downwards upon separation. The question whether other effects, such as the formation of durable agglomerates from the hot meal particles which get more sticky as temperatures rise, play a role, too, has not yet been clarified.

Modelling of combustion in the calciner

Industrial investigations carried out by the Research Institute of the Cement Industry have revealed that the optimised input of fuel, meal and air in calciners allows to achieve effective NO_x abatement accompanied by complete burn-out. However, optimising the mode of operation of the calciner frequently implies costly rebuilding measures, e.g. for the rearrangement of fuel or meal ducts. To avoid unnecessary rebuilding costs, the simulation of processes during the burning process and the subsequent implementation of the most promising scheme has proven to be a suitable approach in the field of power plant engineering. VDZ's working group "Operational performance of precalcining systems" therefore proposed to mathematically represent also the processes in the calciner in order to provide the cement industry with a tool allowing it to weigh up various costly rebuilding measures in advance in the future.

Bearing this in mind, the Research Institute of the Cement Industry (FIZ) is now carrying out a simulation project sponsored by the AiF in cooperation with the chair of energy plant and energy process technology (LEAT) of the Ruhr-university in Bochum and the chair of environmental process engineering and plant technology (LUAT) of the Essen/Duisburg university. The project, which proceeds from the results of a feasibility study, aims to support the operational optimisation of precalciner plants regarding the formation of harmful substances, NO_x abatement measures and coating formation by means of numerical simulation. The option of a largely secured simulation of processes taking place in the precalciner renders purposeful operational

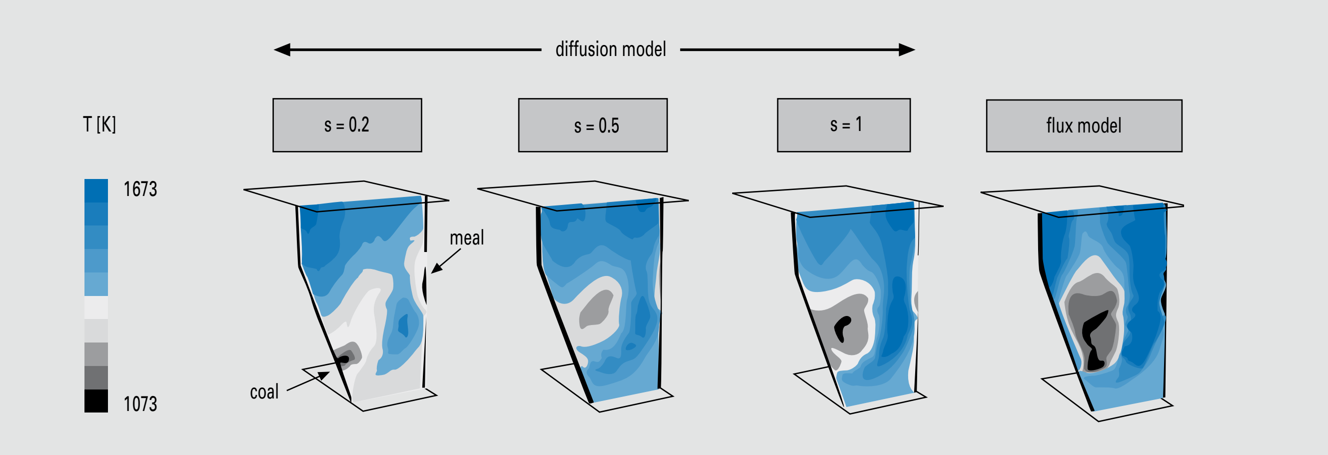
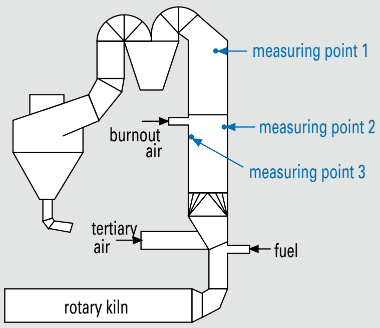


Fig. I-12: Parameter study of the dispersion coefficient s in a diffusion model



	Measured O_2 concentration	Calculated O_2 concentration [given in vol.%]	
		Precursor project	Current results
Measuring point 1	4.9	7.1	5.3
Measuring point 2	4.8	2.0	3.8
Measuring point 3	0.6	7.0	6.1

Fig. I-13: Comparison between calculated and measured O_2 concentration in the calciner in vol.%

optimisation easier and can thus reduce the efforts and expenditure for time-consuming and costly trials conducted at kiln plants during operation. Moreover, it gets easier to make sound statements on the technical feasibility of installing precalciners in existing plants to reduce harmful substances by staged combustion. Further areas of application for numerical simulation in this context include the investigation of damage and concept studies on the design, the thermal optimisation, and the versatile utilisation of secondary fuels.

The simulation is meant to mathematically describe processes such as the local interaction between turbulence and chemical reaction, between ignition and extinction influences, between the two phases at high loading, and the turbulent interaction during the particle phase. Approaches to be applied in power station engineering were developed to solve similar questions. Their application under the conditions prevailing in precalciners was examined in a feasibility study sponsored by FIZ. As part of this study, suitable parameters for a modified turbulence model and a radiation diffusion model were determined. With the aid of this simplified model, initial promising results regarding the flow conditions in the calciner were achieved. However, this simplified model allowed to describe the actual conditions in the calciner as an approximation only. Advanced investigations and adjustments are now being carried out as part of the above-mentioned research project to fine-tune the model in terms of flow conditions and the formation of harmful substances. In this process, the model is continually validated by measurement data from the Research Institute of the Cement Industry.

LUAT is pursuing the target to investigate the influence that the high particle loading has on turbulence and radiation characteristics in more detail than before. Initial results show that the radiation processes in a calciner at high solids loading are reflected most precisely by a modified diffusion model. **Fig. I-12** represents the temperature distribution in the bottom section of the calciner, where the fuel and meal are fed. The dispersion of radiation on the particles, which is indicated by the dispersion coefficients, has decisive influence on the temperature profile. Accordingly, the best results are achieved, when the dispersion coefficient ranges between 0.2 and 0.5.

The work performed at LEAT focuses on a universally applicable and adequately precise calcination and sulphatisation model as well as the influence of the calcination reaction on the distribution of concentration and temperature and thus on the formation/reduction of pollutants. This work is supplemented by experimental fundamental investigations on pollutant formation in the calciner, and by numerical simulation of the mixing, fuel conversion and heat transmission in the rotary cement kiln and the calciner.

The tremendous influence that the high particle loading has on the formation of pollutants and the calcination reaction with regard to turbulence and radiation became apparent from the work performed previously. As a consequence, the use of special model assumptions was necessary. Many details of the existing model approaches had already been refined and adapted to describe the reaction processes in a calciner more accurately. Further adaptations of the model simulating the pollutant formation mechanism and the model simulating the calcination process turned out to be possible. **Fig. I-13** depicts the comparison

Fig. I-14: Cyclone ceiling segment that has fallen out

between the calculated and the measured oxygen concentration. Both the results obtained from the calculations of the preliminary study and the current simulation results are listed opposite the measurement results. It becomes obvious from the figures that the model for calculating the gas composition has been improved in comparison to the previous model. The simulation model allows to determine with adequate precision the high-oxygen and low-oxygen zones identified during the measurement. It also becomes apparent, however, that it is not yet possible to simulate the measurement results with the accuracy desired; this applies to the area where the burn-out air is input (metering point 3) in particular.

The partial models of LEAT and LUAT mentioned above are therefore presently being developed further and adapted more precisely to the actual framework conditions. To that purpose, the partial models are continually adjusted and reviewed using measuring and operational data made available by FIZ. The two partial models are to be combined to form one aggregate model subsequently. In addition to the variation of different staging concepts (meal, fuel and air staging), the influence of different coal types used as fuel is to be investigated with the aid of this model. This is to involve simulating the processes in different calciners and comparing them with actual figures. These investigations will continue to be carried out upon consultation of the Research Institute of the Cement Industry.

Refractory materials

During the period under review, the "Environment and process engineering" committee set up a "Refractory materials" working group, which was assigned the task of summarising and describing the current state of knowledge on this subject. The working group originated from the "Operational performance of precalcining systems" working group, which did good spadework. The new working group will be concerned with the following topics:

- Techniques for state diagnosis
- Selection of refractory materials and anchors at different points of use within the kiln plant
- Influence of conditions of use on the consumption of refractory materials and corrosion damage (use of secondary fuels, kiln tyre attachment, improved recuperation in the clinker cooler, hot spot operation in the calciner, etc.)
- Design of the refractory structure in various plant sections
- Modern de-lining techniques
- Repairs in hot state
- Modern installation techniques
- Industrial safety during work on refractory material
- Input control of refractory bricks
- Drying and warm-up procedures
- Parameters of refractory consumption
- Disposal of spent refractory material

Work was started by drawing up forms for the various plant sections and kiln zones, respectively, in order to compile data on the refractory structure, the materials used, the conditions of use and the experiences gained. Moreover, working groups in charge of the various issues were set up.

Both non-destructive methods and drilling are applied to determine the thickness of the residual lining. Preliminary damage (e.g. corrosion symptoms) can usually only be detected by core drilling or breaking out windows. The factors to be taken into account when selecting the quality of refractory materials for the different kiln sections include the conditions of use, the coating behaviour of the kiln feed, the intensity of recirculating material systems, and the planned service life. The kiln inlet area is usually lined with spinel or chamotte bricks having an Al_2O_3 content > 40 %. The other bricks used are made of spinel or magnesite in the transition zone, of hercynite, magnesite, spinel or dolomite in the sintering zone, and of high alumina or spinel in the kiln outlet area. In some cases, the inlet cone and the kiln outlet are also lined with cast compounds. The kiln design has effects on the wear of the refractory material. Two-support rotary kilns usually have a lower refractory consumption than three-support rotary kilns since they are subject to less mechanical stress. Another aspect which is important for the mechanical stress of the refractory material and thus for its wear is the attachment of the kiln tyres. Geared kiln tyres are obviously more advantageous than loose kiln tyres.

The solutions adopted in designing the refractory structure outside the rotary kiln differ depending on the plant section and the plant operator. As a rule, the refractory structure is made up of a working lining and an insulating layer consisting of 1 or 2 layers. Cylindrical sections and arched ceilings are usually bricked up, while plain surfaces are lined both by bricks or prefabricated elements and by spraycast or cast compounds of varying panel dimensions. The provision of expansion joints and their maintenance play an important role for the durability of the refractory material in many plant sections.

The structural elements outside the rotary kiln that are exposed to the most severe stresses include the ceilings of the lower cyclones (**Fig. I-14**). The anchoring systems in particular are subject to severe corrosion symptoms. For that reason, anchorage frequently consists of a combination of ceramic and steel anchors. Inspection openings should be provided in the cyclone ceilings to allow the state of the cyclone ceilings and the anchoring system to be scrutinised. Prior to installing the refractory lining in the heat exchanger, the condition of the cyclone ceilings must be inspected from outside. When material is removed from cyclone ceilings, it must always be chiselled off downwards through the control openings. Only upon inspection of the cyclone ceiling through the control openings can the refractory material of the cyclone be scrutinised from inside by means of travelling scaffolds, and the scaffolds and working platforms can be installed when the go-ahead is given. For the sake of hazard prevention in case of simultaneous work at different points, the cyclones should be partitioned by means of needle gates.

Experiences with the gasification of secondary fuels

The selection of a fuel to be used in the clinker burning process depends on its availability, the cost, its fitness for storage, its metering properties, safety requirements, and the interferents it contains. Besides, the physical and chemical parameters of the fuels are relevant, too. Dispersibility, moisture content, particle size, calorific value, homogeneity, the chlorine, sulphur, alkali and phosphate content, the fuel-induced nitrogen content and the content of heavy metals all have an impact on process engineering and on emissions, respectively.

As a rule, secondary fuels are fed directly to the burning process. In principle all the hot spots at which standard fuels are input lend themselves to this process. Depending on the type of fuel to be used, however, fuel metering is costly and time-consuming. It can therefore be reasonable in individual cases to subject secondary fuels to preliminary thermal treatment in a separate plant. As several rotary kiln systems in the cement industry were equipped with such plants over the past years, VDZ's "Operational performance of precalcining system" working group studied this technology.

Basically, a distinction between two types of plants must be made. With gasifiers, the fuel is pyrolysed in substoichiometric conditions, and the lean gas thus generated is subsequently fed to the calciner as fuel. The energy required is either supplied from outside or released by partial combustion. In precombustion chambers, by contrast, the fuel is converted to a significantly higher extent in over-stoichiometric or slightly substoichiometric conditions, respectively. The energy thus generated is utilised to calcinate the kiln feed. The proportion of fuel not yet incinerated (residual coke) can subsequently be input into the calciner.

Numerous different technologies for the preliminary gasification/precombustion of waste exist at present. The technologies installed at rotary kilns in the cement industry up to now comprise circulating fluidised beds, precombustion chambers and so-called hot discs. To date there is one circulating fluidised bed and one precombustion chamber in operation in Germany. The latter was designed chiefly for the utilisation of entire tyres. Existing operating experience shows that both methods work reliably, but the process engineering efforts implied must not be underestimated. The circulating fluidised bed exclusively lends itself to the utilisation of fairly fine-grained fuels, while the precombustion chamber is designed for rather coarse fuels. Both plants can be disconnected from the kiln system by means of slides, i.e. the kiln can still be run using primary fuels exclusively. The choice of an adequate plant is primarily determined by capital and operating costs, costs accruing for preparatory fuel processing, availability, discharge of interferents and materials forming recirculating systems, safety concepts that may be required, and caps on the possible use of lean gas / residual coke in the calciner and the main firing unit.

The more suited a plant scheme is for a very wide range of secondary fuels, the more flexibility in terms of secondary fuel choice it offers to the operator. The option of shifting fuels frequently is advantageous in this respect as well. The requirements regarding fineness, homogeneity and calorific value of the secondary fuels and their content of substances forming recirculating systems constitute additional criteria in choosing a suitable method.

The plant scheme and the type of waste largely determine the calorific value of the lean gas (3 600 to 36 000 kJ/m^3). Gases having a lower calorific value can be utilised in the calciner. Input into the main firing unit currently still causes technical problems and is not applied. The effects of the method on total fuel energy consumption depend on the energy efficiency of the aggregate system on the one hand, and on possible impacts on the raw gas quantity and the recuperation of the clinker cooler on the other hand. Smooth kiln operation presupposes a constant energy supply by the pre-gasification/precombustion system. Moreover, the safety concept of the plant and potential impacts on clinker quality and emissions should be checked diligently. **Tab. I-4** summarises some selection criteria established by VDZ's "Operational performance of precalcining systems" working group.

Tab. I-4: Selection criteria for pre-gasification / precombustion plants

Economic criteria	Incorporation into the process	Properties of secondary fuels	Other criteria
Costs for preparatory processing of secondary fuels	Steadiness of energy input	Fineness of preliminary processing	Thermal degree of efficiency
Capital costs / operating costs	Utilisation of preheated tertiary air	Homogeneity	Safety concept
Separation of valuable substances	Impact on emissions	Minimum calorific value	Repair during regular operation
Availability	Removal of substances forming recirculating systems	Flexibility in terms of fuel type shifts	
Possible use of lean gas in the main burner	Separation of undesired fractions	Share suitable for material recovery / correction in case of stoppage	
Use of lean gas at several kiln plants (interconnected solution)	Share suitable for material recovery / correction in case of stoppage	Sensitivity of the plant to substances forming recirculating systems	
Upper limit for the substitution of standard fuels	Effects on plant operation / option to disconnect		
	Control of the plant		
	Effects on product quality		

Dosing of Fe(II)SO_4 to bagged cement

The industry-wide regulation on "Low-chromate cements and products" adopted by the building trade employers' liability insurance association, industrial health and safety authorities, cement users, the specialist building materials trade and the cement industry in 1999 comprises a bundle of measures aimed at improving industrial safety in the manual handling of cementitious products. The exclusive production of low-chromate bagged cements, which have been on offer throughout Germany since 1997, constitutes one element of this agreement. Under the terms of the industry-wide regulation, the German cement industry undertook to guarantee the limit value of 2 ppm water-soluble chromate content pursuant to the Technical Rules on Hazardous Substances (TRGS 613) in all German bagged cements by adding suitable reducing agents. In the meantime, the German cement industry has come out in favour of manufacturing loose cement in chromate-reduced quality as well.

Reducing agents used are either Fe(II)SO_4 or $SnSO_4$, which is, however, much more expensive. In comparison to Fe(II)SO_4, $SnSO_4$ excels by higher storage stability, better solubility and thus higher reduction effectiveness. As a consequence, even significantly smaller quantities (about factor 10 in comparison to Fe(II)SO_4) can guarantee adequate reduction. However, the metering and homogenising technology that needs to be provided must be even more precise than with Fe(II)SO_4.

The precise and reproducible addition of a comparatively small quantity of reducing agent to a large, oscillating mass flow – the cement – involves substantial effort and expenditure regarding plant technology. A plurality of aspects, such as storage, transport, metering, dust removal, pressure relief, interlocking devices etc., including also unforeseen operational states, must be taken into consideration when the individual plants are planned, taken into operation and operationally optimised. The findings derived from this learning process were summarised in a VDZ working group in which representatives from the member works participate. It turned out that there are different process technology solutions for Fe(II)SO_4 addition which yield satisfactory results. Experiences with $SnSO_4$ addition had not yet been gained at the time of reporting.

Temperatures exceeding 60 °C should be prevented both during the transport and the fluidising by pulsated air as well as the storage of the Fe(II)SO_4 if possible. In addition to fusing, the gradual separation of hydration water occurs at higher temperatures. This reduces the solubility and thus the effectiveness of the reducing agent. Moreover, the water released can lead to the formation of massive conglomerations that block discharge facilities and conveyance paths. It is therefore important to protect the reducing agent from additional external moisture as well. A measure that has proven its worth in this context is the use of a refrigeration air drier for the compressed air in transport, and shielding the silo from direct sunlight. Moreover, ensuring a high circulation in the storage silo (storage time < 3 weeks if possible) and not exceeding a certain silo filling height (reduction of autogeneous pressure) turned out to be useful in preventing agglomerations as early as in the storage of Fe(II)SO_4.

Since most dosing systems are integrated in existing plants and the concepts pursued thus differ greatly in some cases, individual special features must be taken into account. However, the gravimetric determination of both the cement and the Fe(II)SO_4 and the mixing of the two material flows, for example on a shaking screen above the hopper upstream of the bagging unit, turned out to be convenient in principle. The mix should subsequently be metered into the bagging machine via a cellular wheel sluice with pressure compensation. The design of the plant concept should ensure that no cement bag leaves the bagging unit in case of system malfunctions (e.g. failure of one material flow). Bags already filled must be rejected. To prevent mistakes in the control of the plant, there should further be an operating manual describing not only standard operation, but also the course of action to be adopted in case of malfunctions and during the fill-up and emptying of the bagging unit and the feed bin.

In the actual dosing of Fe(II)SO_4 to the cement (carried out via a cellular wheel sluice in the present example), particular attention must be paid to the following items to avoid metering mistakes:

- Determination of both material flows (cement and Fe(II)SO_4) prior to mixing in order to allow exact dosage
- Advance feeding of the Fe(II)SO_4 to the cellular wheel sluice before adding the cement (better mixing – "coffee-on-milk effect")
- Pressure compensation in the cellular wheel sluice to prevent uncontrolled mass flows, as well as adjustment of dust removal
- Regular maintenance of metering devices and the cellular wheel sluice
- Suitable safety precautions in case of deviations from standard operation (malfunctions, start-up, shut-down) – studies of hazardous incidents.

With regard to the stability of the Fe(II)SO_4, not only mere handling aspects, but also the temperature of the cement during metering must be paid attention to in order to preserve the effectiveness of the reducing agent. It may therefore be advisable in individual cases to cool the cement.

Apart from the reducing effect of the Fe(II)SO_4, the addition of sulphate agents strongly influences the characteristics of cements from their workability up to their strength development. This is another reason why diligent metering of the reducing agent is indispensable. For example, the dose of chromate-reducing agents added to the fresh concrete as concrete admixtures in the form of heptahydrate is limited to a maximum of 0.5 wt.% pursuant to the approval since cement is already made with optimised sulphate agents in view of its workability. However, a sufficient allowance is inevitable to make sure that the product is safe for users. One value applied for this allowance is the so-called "overdose factor", which indicates by how much the reducing agent was overdosed beyond the mere stoichiometric requirement as a function of the original chromate content. At an average overdose factor of more than 30, i.e. addition of a quantity 30 times higher than the quantity that would be necessary to reduce the original chromate content to below 2 ppm, the product can be assumed to be safe even after fairly long storage times if storage is appropriate (see **Tab. I-5**).

Particle size distribution with intergrinding

The strength of cement made from several main constituents is primarily influenced by the reactivity and the mix proportions of the cement constituents, and to a lesser degree by the particle size distributions of the individual constituents. Intergrinding does not allow to influence the particle size distributions of the constituents separately. They are determined by the grindability of the constituents and the mode of operation of the grinding plant. Constituents that are not easily ground build up in fairly coarse fractions, while those that are easily ground build up in fairly fine fractions correspondingly.

A research project sponsored by the AiF was aimed at investigating whether the mode of operation of the grinding plant influences the fineness and particle size distributions of the individual constituents on top of having an impact on the particle size distribution of the cement as a whole. It has been known from publications that the particle sizes of the components blastfurnace slag and clinker do not differ substantially in cements containing blastfurnace slag which were ground in roller mills. As intensive internal material cycles occur in roller mills, the influence of the circulation factor was of paramount interest.

To investigate the influence of the circulation factor on the particle size distribution of the individual components, the processes taking place in a grinding circuit when several components are interground were first simulated by a computer programme. The simulation calculations confirmed the well-known correlation according to which the slope of the particle size distribution of the classifier fines rises with an increase in the circulation factor. At low circulation factors, also the clinker, which is the more easily ground component, was characterised by higher fineness in the interground product than the blastfurnace slag component (**Fig. I-15**). However, the discrepancy in fineness decreases with an increase in the circulation factor; thus, the difference between the particle size distributions of the components clinker and blastfurnace slag is only slight when the circulation factor is high (**Fig. I-16**). The effect observed and described above can thus be attributed to the high circulation factor in these mills.

Tab. I-5: Reduction of Cr(VI) in German bagged cements

	Value range	Average
Cr(VI) content before addition	2 – 18 ppm	9 ppm
Fe(II)SO_4 input[1]	0.1 – 0.6 wt.%	0.32 wt.%
Overdosage[2] (stoichiometric)	average overdosing factor > 30	
Average Cr(VI) content in bag	< 0.5 ppm	

[1] primarily applied as granular Fe(II)$SO_4 \cdot n\,H_2O$, with n = 6-7

[2] factor = 1 in case of stoichiometric dosage for a reduction of Cr(VI) to < 2 ppm

Fig. I-15: Particle size distribution of the classifier fines and the components clinker and blastfurnace slag at a low circulation factor

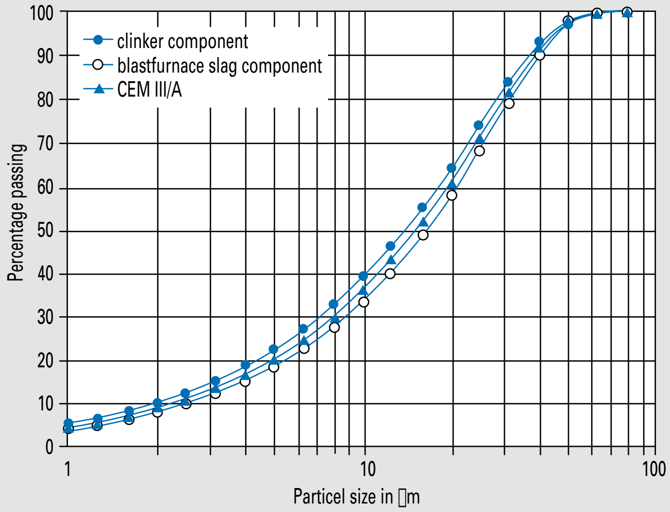
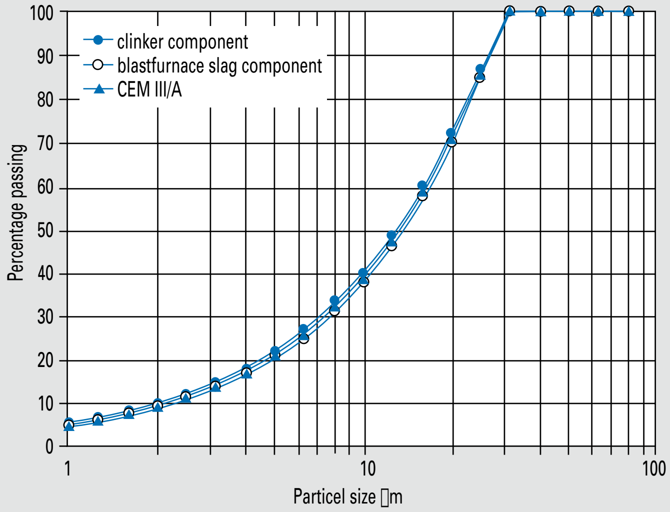


Fig. I-16: Particle size distribution of the classifier fines and the components clinker and blastfurnace slag at a high circulation factor



The results obtained from simulation calculations were verified by grinding tests conducted in the Research Institute's semi-industrial grinding plant. The mill feed used was a mixture consisting of 50% clinker and 50% blastfurnace slag. The grinding plant was first run in open-circuit mode. Subsequently, grinding was effected in a circuit with the classifier, with both a low circulation factor of about 3 and a high circulation factor of about 10 being set. As expected, the particle size distribution of the mill feed was fairly wide at n = 0.88 in open-circuit grinding. In line with a rise in the circulation factor, the particle size distribution of the mill feed became more narrow, reaching a slope of n = 1.06 at a high circulation factor.

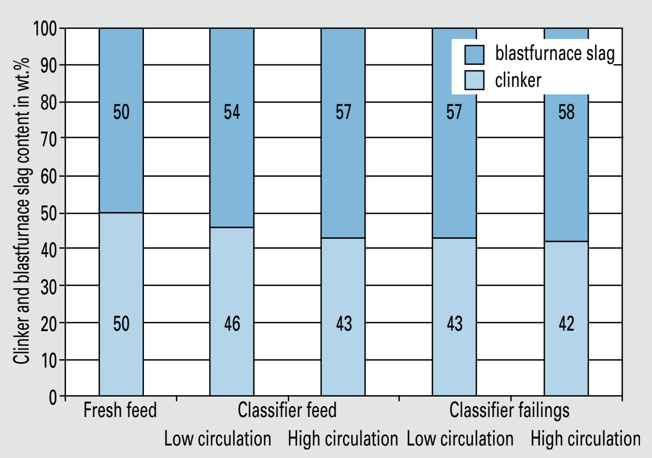


Fig. I-17: Clinker and blastfurnace slag content of the classifier feed and the classifier tailings as a function of the circulation factor

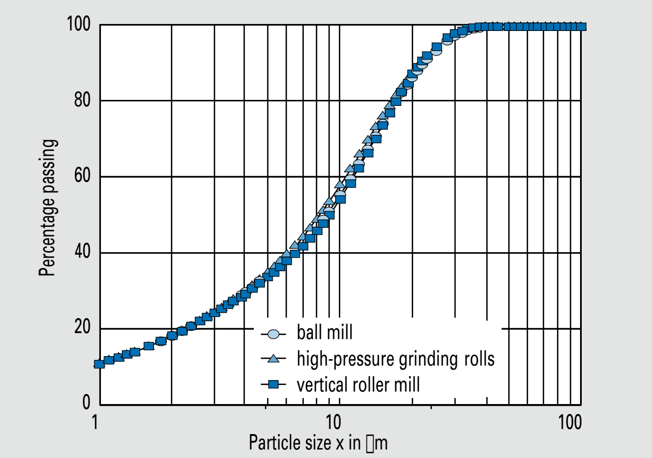


Fig. I-18: Particle size distribution of the clinker meals produced using varied grinding systems

The classifier feed, tailings and fines produced in the grinding tests and the basic materials clinker and blastfurnace slag were chemically analysed, and the clinker and blastfurnace slag contents of the samples were determined by weighted average calculation. The results are shown in **Fig. I-17**. It becomes apparent from the Figure that the not easily ground component blastfurnace slag mainly builds up in the classifier tailings. The blastfurnace slag contents measured there exceeded those in the fresh feed and the finished product by up to 8 wt.%. However, the blastfurnace slag contents determined in the classifier feed were higher than those in the fresh feed and the finished product as well. As a result of the increase in the circulation factor from 3 to 10, the blastfurnace slag proportion grew from 57 to 58 wt.% in the classifier tailings, and from 54 to 57 wt.% in the classifier feed.

To determine the particle size distributions of the individual components, the classifier fines were split up into fractions by screening and analysed chemically. The particle size distributions of the individual components were determined by weighted average calculation. The results of the grinding tests corroborated the results of the simulation calculations. In the case of the cement manufactured at a low circulation factor, the particle size distributions differed markedly. By contrast, the differences in the fineness of the individual components observed in the cement manufactured at a high circulation factor were only slight.

Influence of the grinding system on cement properties

The manufacture of cement in different grinding systems usually leads to different particle size distributions. The influence that the fineness and the particle size distribution of the cement have on its properties was investigated extensively in the past decades (see e.g. Activity Report 1996-1999). In a number of more recent investigations conducted by different authors, however, cements manufactured in different grinding systems were found to also possess different properties even though their particle size distribution was nearly identical. The different cement properties observed can be attributed either to different mill atmospheres or to different comminution mechanisms.

The comminution mechanisms used can chiefly be subdivided into pressure, beater and impact comminution as well as abrasion. While high-pressure grinding rolls primarily crush by pressure, a combination of comminution mechanisms is applied in vertical roller mills and ball mills. The Research Institute is currently investigating the influence of grinding systems on cement properties, when the particle size distribution is identical. These investigations, which are conducted as part of a research project sponsored by the AiF, consist of grinding different clinkers and blastfurnace slags to identical particle size distributions in different semi-industrial grinding plants. Two fineness levels, about 3 000 and about 4 000 cm^2/g, respectively, are being set. Grinding is performed in a semi-industrial vertical roller mill at the physical laboratory of Gebr. Pfeiffer AG in Kaiserslautern, in semi-industrial high-pressure grinding rolls at KHD Humboldt-Wedag AG in Cologne, and in a semi-industrial closed-circuit grinding plant comprising a ball mill and a classifier at the Research Institute of the Cement Industry.

Up to now, the results of corresponding grinding processes with 2 clinkers have been available. It turned out to be possible to produce clinker meals with nearly identical particle size distributions in the different grinding systems by choosing appropriate settings of the operating parameters. **Fig. I-18** exemplifies the particle size distributions generated for a clinker which had been ground in the grinding systems mentioned above. The fineness of the clinker meals totalled 4 130 cm^2/g in the vertical roller mill, 4 160 cm^2/g in the high-pressure grinding rolls, and 4 150 cm^2/g in the ball mill. The clinker meals were subsequently mixed with anhydrite and hemihydrate meal, and the cement properties were determined.

The water demand and setting behaviour of the cements manufactured in this way hardly differed at all. The standard compressive strengths are shown in **Fig. I-19**. The cement made in the high-pressure grinding rolls possessed higher strength after 2 days, and the cement ground in the ball mill lower strength after 28 days, than the respective cements manufactured using the other grinding methods. The standard compressive strengths of the corresponding clinker meals with a fineness level of approx. 3 000 cm^2/g did not confirm these differences. Although the cement made

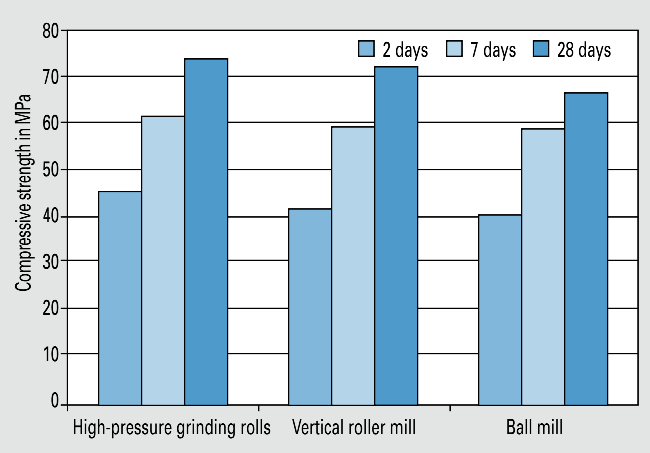


Fig. I-19: Compressive strength of cements produced using varied grinding systems

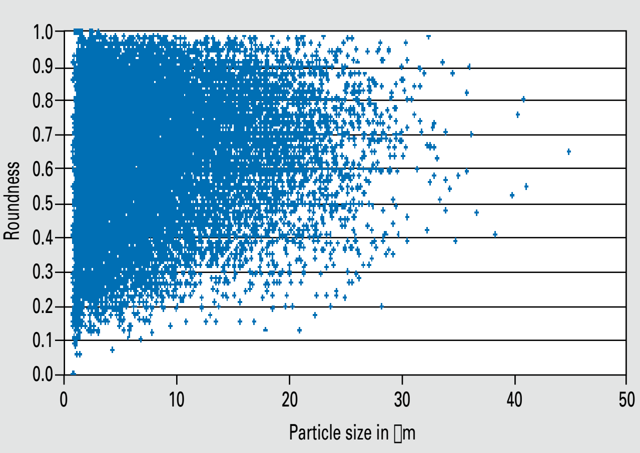


Fig. I-20: Roundness distribution of a clinker meal

in the high-pressure grinding rolls again possessed a slightly higher 2-day strength than the cements manufactured using other grinding methods, its 28-day strength lagged behind that of the cements ground in the ball mill and the vertical roller mill. As the number of samples is currently still too low, these results cannot be generalised yet.

Moreover, the question of whether the clinker meals manufactured in various grinding systems differ in terms of their grain shape is being looked into as part of the research project. To that purpose, an analysis instrument is used in which the clinker meal is dispersed by means of compressed air and is precipitated on a specimen slide. The individual particles are recorded optically by means of a high-resolution camera and measured by image evaluation software. In each measurement, a total of 10 grain shape parameters (e.g. average diameter, circumference, roundness, ratio of maximum length and width) is determined for 25 000 individual particles. By way of example, the roundness of the particles of a clinker meal is plotted against their average diameter in **Fig. I-20**. The value 1 on the ordinate stands for the ideal roundness of a particle. Needle-shaped particles have a value near 0. As only few measurements had been completed by the time the present report went to press, a comparative statement on the differences in grain shape as a function of the grinding system cannot yet be made presently. Additional chemico-mineralogical examinations on the clinker meals obtained by different grinding methods are planned. The main focus will be placed on the question of whether the individual clinker phases build up in different particle size ranges when different comminution mechanisms are applied.

Further grinding processes with blastfurnace slag, which are to be carried out on the 3 different semi-industrial plants, are presently being prepared. The blastfurnace slag meals produced are to be investigated with regard to the vitreous structure of the blastfurnace slag first; in this process, different methods are to be applied. Moreover, the properties of blended cements made from these blastfurnace slag meals will be examined.

II

Environmental protection in cement manufacture

The great importance the cement industry attaches to environmental protection is reflected by the numerous activities pursued by the Research Institute. Numerous new legislation projects and updated technical regulations had to be attended and evaluated from the cement industry's perspective during the period under review. In addition to discussions about the new European legislation on chemicals and substances, especially the increasing requirements for emissions monitoring are to be mentioned in this context.

In the period under review, particular focus was placed on the trading in CO_2 emissions allowances, especially with regard to the proper implementation of national laws and the pertinent sets of rules annexed to them. The monitoring guidelines adopted at European level had to be interpreted technically and defined correspondingly from the cement industry's perspective as well.

The utilisation of suitable secondary fuels is of particular importance for the cement industry. Secondary fuel use directly implies tight stipulations for the monitoring of emissions, e.g. of mercury. Numerous rotary kilns have meanwhile been equipped with analysers for continuous mercury emission measurement, the applicability of which must, however, be verified on a case-by-case basis. There are still plants in which no analyser readily available on the market could be installed successfully. The Research Institute is in close contact with the plant operators and the manufacturers of the analysis instruments to solve these problems.

The Research Institute further conducted measurements of particulate matter emissions in the chimneys of rotary kilns. The exhaust gas cleaning devices installed in rotary kilns today are largely state of the art. This is the only way of reliably complying with the tight national specifications for dust emission limits. As a consequence of the low overall emission level, the dust emissions from rotary kilns have virtually no relevance for ambient pollution any more. In spite of that, knowledge about the particulate matter content in the emissions from rotary clinker kilns is important in view of the overall dust scenario.

Investigations on various measures aimed at reducing nitrogen oxides centred on the abatement potential of staged combustion in cyclone preheater plants equipped with calciners, among other topics. The possibilities of selective non-catalytic nitrogen oxide reduction were investigated further as well. This reduction method was shown to possess a high abatement potential under optimised conditions.

Sophisticated technology for supplying mixed fuels

Legislation

Effects of the amendment of the 17th BImSchV on the cement industry

The amendment of the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV) took effect on August 20, 2003. The German legislature thus transposed the specifications of the European Waste Incineration Directive 2000/76/EC into national law. For existing plants, the requirements laid down in the amended 17th BImSchV will apply as of December 28, 2005. Not least because of numerous licenses for plant modifications in conjunction with the continuous rise in substitute fuel utilisation over the past years, however, the scope of the 17th BImSchV has already extended to existing plants, too. As a consequence, initial experience on the practical implementation of the amended 17th BImSchV has been gained by now.

The amended 17th BImSchV places the same requirements on co-incineration plants (cement works and power stations) as on pure waste incinerators. Pursuant to the amendment, cement works have to comply with the same stringent limit values as waste incinerators for all trace elements, dioxins and furans, HCl and HF, and in principle also for SO_2, total organic carbon and CO. The weighted average calculation for specifying emission limits for co-firing plants that had been enshrined in the old legislation virtually ceased to apply.

The ordinance takes account of the process-specific framework conditions of clinker burning as a material conversion process by allowing for exceptions for certain raw material-related emissions being granted upon request by the operator. In these cases it must be proved that the corresponding emissions are not caused by waste incineration. These raw material-related exceptions are possible for SO_2, total organic carbon, CO and, under certain underlying conditions, also for mercury.

Regarding mercury, rotary cement kilns utilising the thermal content of wastes always have to comply with a daily average of 0.03 mg/m^3 and a half-hour mean of 0.05 mg/m^3. As mercury input via the natural raw materials fluctuates heavily depending on the respective sites, rotary cement kilns cannot always comply with these stringent requirements in spite of strict adherence to the state of the art. To be exempted from these stringent regulations, operators have to furnish proof that the elevated mercury emissions are attributable to raw material composition. By establishing a great number of mass balances, the Research Institute has been able in the meantime to prove that some 80% of the mercury input in the clinker burning process derives from the natural raw materials. Such a mass balance consists of sampling all input materials (raw materials and fuels) and determining their mercury contents over a given period. On the basis of this data, the contribution of the raw materials to mercury input and thus to Hg emissions can be identified. In conformity with European legislation, the 17th BImSchV lays down a value of 0.05 mg/m^3 as the cap for specifying mercury emissions from rotary kilns in the cement industry.

In accordance with the amended ordinance, emission limits for total organic carbon and CO emissions will have to be specified in the future as well. The 17th BImSchV stipulates a limit value of 10 mg/m^3 (daily average) for TOC emissions, while CO emissions are subject to a limit of 50 mg/m^3 (daily average as well). These limits ensure the complete burnout of the fuels in incineration plants. By contrast, the rotary kilns of the cement industry are material conversion plants. Organic constituents of raw materials lead to higher emission concentrations although the combustion conditions ensure the complete burnout of the fuels. Legislators therefore provided the option for cements works to file requests for corresponding raw material-related exceptions for CO and total organic carbon as well.

This course of action conforms to the conception that the Federal Committee for Air Pollution Control (LAI) had adopted with regard to the "old" 17th BImSchV. With the questions expressing its doubts on the interpretation and application of the 17th BImSchV, the LAI proposed in 1994 to entirely refrain from specifying emission limits for TOC and CO if proof can be furnished that the corresponding emissions were induced by raw materials. In this respect, the new regulation constitutes a tightening of previous specifications although it includes the option to file requests for exceptions.

The Research Institute conducted corresponding raw material investigations which served to substantiate such exceptions. A laboratory set-up installed there allows the simulation of the processes taking place when the raw materials are heated in the preheater. Based on these results, a so-called emission forecast is established, which can be referred to when requests for exceptions are filed.

The regulations that the amendment of the 17th BImSchV lays down for SO_2 are similar to those governing TOC and CO. The contributions that raw materials make to SO_2 emissions can also be estimated using simulations in the laboratory set-up and chemical analyses in combination with calculations, respectively.

In deviation from the European directive on waste incineration, the German implementation of the 17th BImSchV provides for more stringent requirements regarding dust and NO_x. Accordingly, a weighted average calculation both for dust and for NO_x is still stipulated in the case of rotary kilns that substitute waste for more than 60% of firing heat capacity. In this way, tighter NO_x and dust limit values are to be imposed on rotary kilns in the cement industry that utilise high waste proportions. The amendment of the 17th BImSchV provides for a transition period for nitrogen oxides ending on October 30, 2007, by which date the specifications must be implemented. This fact is particularly important for the cement industry since it is not yet sure at present whether the current state of the art will allow an emission limit of 200 mg/m^3 for nitrogen oxides to be complied with at all in the cement industry. Corresponding tests will have to be performed.

In comparison to its precursor ordinance, the amended 17th BImSchV constitutes a further tightening of environmental stipulations for rotary kiln plants co-incinerating wastes. All emissions from German cement works are summarised in the "Environmental data", which are compiled and published by the German Cement Works Association once a year. This publication each time also comprises an overview of the waste utilised in the German cement industry.

REACH

In October 2003, the EU Commission adopted a draft regulation on the Registration, Evaluation and Authorisation of Chemicals, the so-called REACH regulation, which is to introduce new European policies on chemicals. It is foreseeable that the profound implications of the planned regulations will not be restricted to the chemical industry, but affect the entire economy. More in particular, the regulations will immediately affect branches of industry other than the chemical industry as well, since the REACH regulation, at least in its current draft, also covers numerous materials like cement and lime. In its core, REACH thus rather constitutes an attempt to reform European material policies. The planned regulation is scheduled to replace more than 40 existing directives and regulations. Its centrepiece is the so-called REACH system, which is an integrated way of proceeding in the registration, evaluation and authorisation of chemical substances. Companies that produce or import chemicals and certain other materials are to be obliged to evaluate the risks involved in their use and to take measures aimed at controlling the risks they have identified. In this way, the obligation to ensure safety during the handling of the materials regulated by REACH would be shifted from the state to the economic sector entirely.

In its current version, REACH would affect the cement industry in two ways: as manufacturer of a product subject to mandatory registration (clinker) on the one hand, and as "downstream user" of materials already registered, such as grinding aids or blast-furnace slag, on the other hand. The exact scope of effects on the cement industry cannot yet be estimated at present, as many parties (industry, politicians, environmental associations) have called for modifications of the draft regulation. The regulation is therefore not expected to be adopted by the European Parliament and the European Council until 2006. In order to confer the necessary significance to its own position, the cement industry, represented by its European association CEMBUREAU, has joined forces with 11 other industrial associations to form the so-called "REACH alliance", which comprises the lime, gypsum, precast concrete, ready-mixed concrete, minerals, ore, paper, ceramics, glass and non-ferrous metal industries as well as the iron and steel industry. Between them, these branches of industry form an industrial sector having 2 million employees, sales of € 360 billion and an annual output of 1 500 million t. By contrast, the world-wide annual output of chemicals totals only about 400 million t. A joint statement was issued to draw politicians' attention to the significant impact REACH will have on the above-mentioned "non-chemical" industries. Although the basic idea behind REACH and the important role safety datasheets play in conveying information are embraced, there is fundamental criticism of part of the contents of the draft regulation.

Although REACH was originally conceived for man-made "organic" chemicals, it now is to cover natural products and raw materials, too. Thus, the basic materials used by the "REACH alliance" industries, i.e. minerals, ores and other naturally-occurring materials as well as reprocessable materials and wastes, are currently included in REACH, while the starting materials used by the chemical industry – gas, crude oil and coal – are not. This is unequal treatment. Moreover, the fact that the potential risks inherent in the largely inorganic raw materials and products have already been regulated by other laws. Cement and other building materials are subject to the Construction Products Directive (89/106/EC).

Additional reservations relate to the materials being evaluated by quantity instead of risk. Cement and most other inorganic products involve low risks, but large bulk. According to the current plans, they would be assigned to the category with the most stringent specifications due to their great mass flows. The alliance has called for a modified yardstick for evaluation that puts the main emphasis on risk. Moreover, it is not clear whether REACH will also affect waste, recycled materials and secondary materials. The utilisation of these materials is an important element of the sustainability concept pursued by the cement industry. Their inclusion in REACH would entail double regulations in this sector as well and would inevitably have an adverse influence on the current utilisation practice. A crucial goal the cement industry pursues together with the REACH alliance is therefore to achieve the revocation of the mandatory registration of cements and other inorganic and mineral materials manufactured by mineralogical or physico-chemical processes. In addition to that, materials utilised in conformity with the Waste Incineration Directive (2000/76/EC) should be exempted from the scope of application of REACH entirely.

DIN EN 14181 – new standard for continuous emission monitoring

The new European standard DIN EN 14181 "Stationary source emissions – Quality assurance of automated measuring systems" was published in September 2004. The standard describes the scope and course of the annual performance test and the calibration to be carried out every 3 years. In addition to that, however, also plant operators will have to perform regular quality controls on the continuous emission measuring equipment. Their scope is laid down in the new standard as well. The new specifications are aimed at instituting harmonised Europe-wide procedures in the testing and monitoring of emission measuring equipment which operates continuously. A transition period for implementing DIN EN 14181 that expires in December 2005 is applicable for plants subject to the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV). Plants governed by the German Clean Air Specifications (TA Luft) will officially not be included in the scope of the new standard until VDI 3950, Sheet 1 has been revised.

The new standard comprises a number of additional requirements that relate to the course and evaluation of calibrations in particular. Moreover, the requirements for continuous quality assurance to be met by operators have been stepped up significantly. DIN EN 14181 stipulates 3 so-called quality assurance levels (QAL 1 to QAL 3) and an annual performance test for automatic emission measuring equipment. QAL 1 stipulates the use of measuring equipment that has undergone suitability tests, which has long since been common practice in Germany. QAL 2 comprises the proper installation and the calibration of the automatic measuring equipment using standard reference test methods, as well as the determination of the measuring uncertainty pursuant to a precisely specified method. QAL 3 refers to drift controls that operators have to perform regularly. The standard does not include specific stipulations regarding the frequency of these checks.

In contrast to present practice, calibration will require measurements to be spread over 3 days and a period of at least 8 hours each in the future. A minimum of 15 samples will have to be taken in this process. If unmistakable and distinguishable operating states exist, additional measurements have to be taken and corresponding calibration functions have to be established. The performance test to be carried out annually has been extended to represent a "small" calibration, since it has to comprise 5 measurements using the standard reference test method. In this way, the time and cost associated with calibrations and performance tests is increased markedly.

The calibration function is valid for a limited range only. The validity range extends from 0 to 1.1 times the maximum value obtained from the reference measurements. Plant operators have to verify compliance with the valid calibration range once a week. Complete recalibration has to be performed, when the valid calibration range is exceeded by more than 5% of the values measured per week (period from Monday to Sunday) over a period of more than 5 weeks, or by more than 40% of the values measured within 1 week.

The determination of the confidence and tolerance range pursuant to VDI 3950, Sheet 1 applied previously has been dispensed with. Measuring uncertainties/variabilities have to be determined and compared with the values given in Annex III to the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV) instead. Each half-hour mean is converted to standard conditions and, if necessary, to the oxygen reference value. The measuring uncertainty is deducted from this standardised value. The values are classified only afterwards. The validity range of the calibrating function is taken into account when the half-hour and daily means are classified. Values outside of the valid calibration range are recorded in separate classes. In order to fully implement all the requirements of the standard, emission calculators need to be equipped with new evaluation software.

As the transition periods have not ended yet, no comprehensive experience regarding the new DIN EN 14181 has been gathered so far. It is foreseeable, however, that the time and cost involved in connection with monitoring and testing continuously operating emission measuring instruments will rise considerably. This applies both to the activities of the notified measuring bodies and to the internal maintenance work done by the operator. It further remains to be seen whether the European standard will actually be implemented on the same scale in all member states of the European Community. If this should not be the case, the effort expended and, as a consequence, the costs incurred for the monitoring of instruments would be significantly higher in countries demanding stricter implementation than in countries where implementation is less stringent.

DIN EN 13284

European standard EN 13284-1 “Stationary source emissions: Determination of low range mass concentration of dust, Part 1: Manual gravimetric method” appeared in November 2001. In September 2004, the standard was supplemented by Part 2 entitled “Automatic measuring equipment”. EN 13284-1 specifies a standard reference method for measuring low dust concentrations within a concentration range of less than 50 mg/m^3 in controlled gas flows. It was validated for the range around 5 mg/m^3 on the basis of a sampling duration of half an hour in particular. Part 2 of the standard describes the quality assurance of automatic measuring equipment for the determination of dust in exhaust gases.

Since EN 13284 is a European standard, it has to be granted precedence over the national VDI guidelines in the determination of emissions. The VDI guidelines of the 2066 series, which were previously authoritative for dust measurements in most cases, are therefore currently being revised in conformity with EN 13284. In comparison to the measurements previously carried out on the basis of the VDI guidelines, the European standards will entail various new aspects, which will be outlined briefly below.

Pursuant to the new European specifications, the exhaust gas inlet section now has to correspond to the 5-fold hydraulic diameter. Based on the old regulations, a section corresponding to only 3 times the hydraulic diameter was sufficient in the past. By contrast, the outlet section needs to total only twice the hydraulic diameter now. If, however, the exhaust gas duct ends behind the measuring plane, the 5-fold hydraulic diameter will have to be provided in the outlet section, too, in the future. These new stipulations will have substantial consequences for numerous measuring sites.

Interference in the exhaust gas cleaning devices during the calibration of a dust measuring instrument presupposes prior consultation of the authorities according to the new standards. Analogous to DIN EN 14181, moreover, performance tests of dust emission measuring equipment will have to be accompanied by reference measurements pursuant to the standard reference method (individual measurements) in the future. The number of individual measurements can be reduced from 5 to 3 if the calibration range ends below 30% of the emission limit value.

The bottom line is that European standards 13284 Sheets 1 and 2 will also imply greater effort and, as a consequence, higher costs in connection with the monitoring of equipment for dust emission measurements than the previous regulations.

Climate protection ■

Form the voluntary agreement to emissions trading

In November 2000 the German federal government and leading associations of the German business community decided to further develop the agreement on climate protection, in which the German cement industry participates as well. One of the benefits which the federal government had pledged in return under the terms of this climate protection agreement was to give the industrial sector a say in the decision on the introduction of further instruments, such as emissions trading. In the year 2001 the EU Commission published the green book on emissions trading, which represented the starting point for drawing up the directive on emissions trading at European level. The German cement industry voiced its profound scepticism about this instrument from the outset. This was not due to its rejection of emissions trading as such. Much rather, there were worries that the composition of this instrument would result in further competitive disadvantages for European industry, and more particularly for energy-intensive industries.

A major difference between the voluntary agreement on the one hand and emissions trading on the other hand is the level at which the two instruments are organised. The voluntary agreement to climate protection is conceived at industrial sector level, thus allowing measures to be taken where they are most cost-effective. By contrast, emissions trading is conceived at plant level, thus severely curtailing the industry’s flexibility in choosing its measures. Moreover, the cement industry is particularly severely affected since the value added of its products is lower than that of other industrial sectors.

Furthermore, the voluntary agreement and emissions trading refer to different system boundaries. The CO_2 emissions of the cement industry consist of direct emissions caused by the combustion of fossil and secondary fuels as well as the calcination of limestone on the one hand, and of indirect emissions attributable to power consumption on the other hand. The objective pursued by the voluntary agreement is to reduce the energy-related CO_2 emissions of the cement industry, which include the direct emissions from fossil fuels and the indirect emissions from electrical power consumption. Emissions trading, by contrast, covers the CO_2 emissions caused by the combustion of fossil and waste-derived (secondary) fuels as well as process-induced emissions (see **Fig. II-1**).

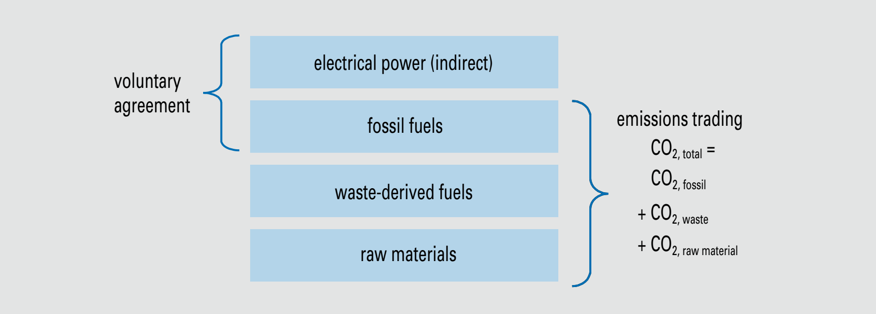


Fig. II-1: Scope of application of voluntary agreement and emissions trading

The fact that the monitoring pursuant to the voluntary agreement comprises all cement works, including the grinding plants without clinker production, while emissions trading merely relates to works with clinker production, constitutes another difference. Finally, different emission factors for the fuels are applied in some cases. Thus, the data published under different reporting systems cannot be compared, but converted into each other.

Composition of emissions trading

CO_2 emissions trading in the European Union started on January 1, 2005. Like most other energy-intensive branches of industry, the cement industry is subject to this new instrument of climate protection policy. As there were delays in the allocation of emission permits and in the release of the register by the European Commission, however, actual trading in Germany only commenced in the course of spring.

The German Federal Cabinet passed the National Allocation Plan (NAP) for the Federal Republic of Germany on March 31, 2004 and forwarded it to Brussels on the same day. The NAP was transposed into German legislation through the Greenhouse Gas Emissions Trading Act (TEGH), the Allocation Act 2007 (ZuG 2007) and the Allocation Ordinance (ZuV) in the course of the year 2004. The allocation plan provides for a reduction in the CO_2 emissions of the industrial and energy management sectors from 505 to 503 million t CO_2/a in the first trading period (2005 to 2007) (see **Fig. II-2**). In the second trading period (2008 to 2012), a reduction to 495 million t per year is to be achieved. This corresponds to a decrease of 0.4% in the first trading period, and of another 1.6% in the second trading period.

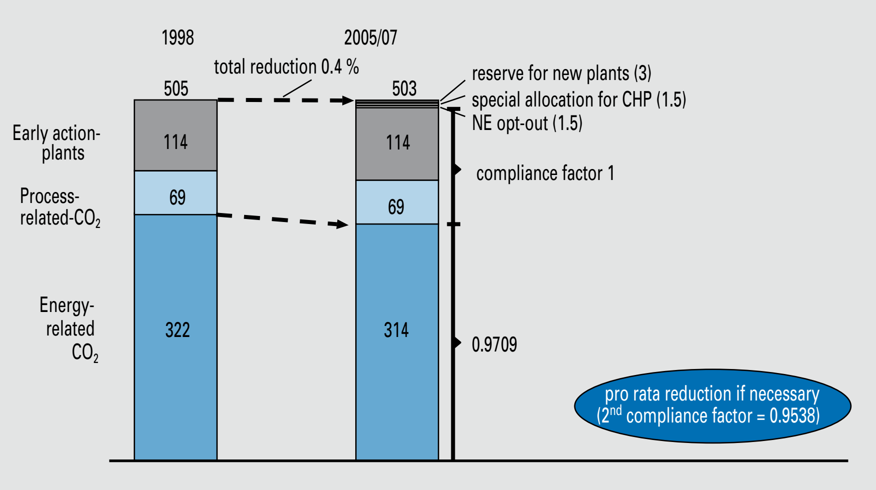


Fig. II-2: Compliance factor in the German Allocation Act 2007

Process-induced emissions and emissions from so-called early action plants need not be reduced over the entire period ending in 2012. This results in an overall reduction requirement of –2.91% (which corresponds to a so-called compliance factor of 0.9709) for the remaining energy-related CO_2 emissions. Furthermore, industrial enterprises applied for permits exceeding the total amount available to the emissions trading sector by 14 million t/a. Thus, the so-called proportional reduction ("2nd compliance factor") will be applied to many plants, which will result in an additional reduction of 4.62% for the plants concerned. All in all, 61 million t CO_2 annually was approved for process-related emissions. This figure is made up of 40 million t/a for the steel industry and 21 million t/a for the cement, lime and glass industries.

Regarding the allocation of emission permits, the Allocation Act (ZuG) provides for two options for the operators of plants subject to emissions trading: they can file applications based either on grandfathering or on benchmarking. In the case of grandfathering, allocations are granted on the basis of emissions generated in the base period from 2000 to 2002. Since the cement industry experienced an economic slump entailing comparatively low output in these years, allocation pursuant to the grandfathering method would have led to a dramatic shortfall in their provision with emission permits for many companies. The so-called benchmarking method can result in a higher allocation for these enterprises than the grandfathering principle. However, operators must accept in turn that allocation is based on "best available techniques (BAT)" and adjusted in accordance with actual output at the end of the allocation period. Only downward adjustment is possible.

A benchmark, which is denominated in CO_2 emissions per t of cement clinker, is made up of a figure for the energy efficiency of a kiln plant and a specific emission factor. The BAT paper for the cement industry specifies an energy efficiency figure of 3 000 kJ/kg clinker as BAT for cement clinker manufacture. This figure was set so low that even state-of-the-art rotary kilns cannot comply with it, averaging higher values per year. However, realistic energy efficiency figures are used for calculating the CO_2 benchmark. They take into ac-

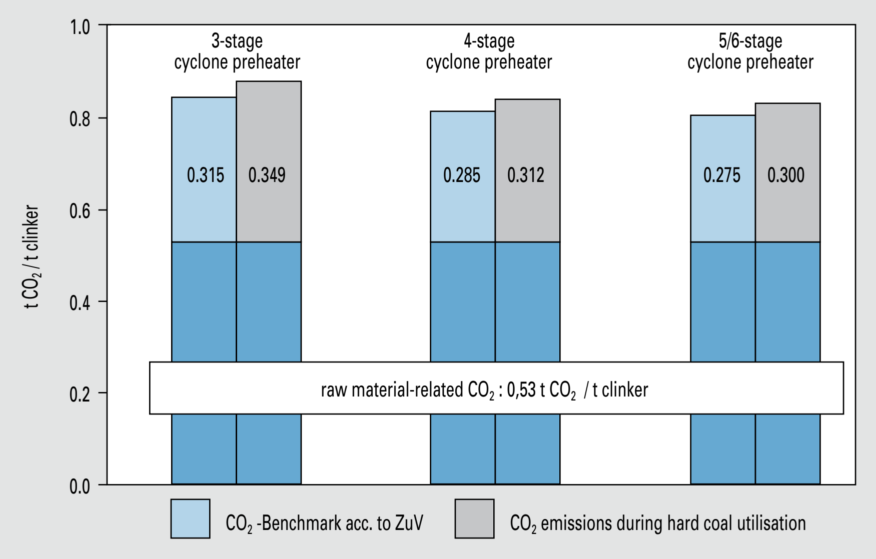


Fig. II-3: Benchmarks for clinker production specified under the terms of emissions trading

count, for example, that the fuel energy consumption of a rotary cement kiln is influenced by various technical parameters, such as, e.g., raw material moisture.

Emission factors are determined on the basis of the actual average fuel mix of the cement industry during the base period from 2000 to 2002. The CO_2 benchmarks thus calculated (275 kg CO_2/t clinker for kiln systems with cyclone preheaters comprising 5 or 6 stages, respectively, 285 kg CO_2/t clinker for kiln systems with a 4-stage cyclone preheater, and 315 kg CO_2/t clinker for kiln systems with a 3-stage cyclone preheater) exceed the value originally proposed by approx. 50%. Since, however, they were specified for new plants, these figures still result in a certain shortfall which existing plants that are granted allocations pursuant to the benchmarking method have to accept. **Fig. II-3** lists the specified benchmarks mentioned above compared to the specific CO_2 emissions generated at corresponding fuel energy consumption when hard coal is fired. It becomes obvious from the Figure that existing kiln plants can only comply with the benchmarks for the cement industry laid down in the allocation ordinance, when a certain proportion of biomass fuels is fed.

The allocation procedure provides that the operators of the plants concerned file corresponding applications for emission permits. To that effect, the production and emission data for the years from 2000 to 2002 had to be prepared and audited by a recognised verification body.

CO_2 reporting

The CO_2 emissions trading started now presupposes reliable, verifiable and eventually also justiciable reporting on the CO_2 emissions by all companies concerned. To ensure uniform reporting, the EU Commission adopted “Guidelines for monitoring and reporting with regard to greenhouse gas emissions”, which, among other things, include detailed specifications for the reporting of CO_2 emissions for the clinker burning process. Under practical conditions, however, it is hardly possible to implement these guidelines on a one-to-one basis, as they comprise technical errors in part and would entail disproportionate analysis efforts on top of that. The established, proven reporting systems applied by the cement industry disregard the EU guidelines for CO_2 reporting.

The German Greenhouse Gas Emissions Trading Act provides for division of labour between the federal and state levels. The federal states are in charge of monitoring CO_2 emissions, i.e. reviewing the annual reports and, if necessary, modifying the permits. For that reason, the Federal Ministry for the Environment dispensed with a nationwide ordinance on the implementation of the EU guidelines. The Federal Committee for Air Pollution Control (LAI) therefore set up a working group in late 2004 that is to compile uniform regulations applicable throughout Germany. However, these will only be available in the course of 2005 or later. Since the EU guidelines have to be applied directly by the supervisory authorities in this case, the companies that intend to deviate from the guidelines in their CO_2 reporting need to submit a corresponding proposal for their reporting to their regulatory authorities before the beginning of the trading period. In order to achieve uniform regulations at least for the cement industry, VDZ set up a working group which elaborated a joint proposal. This proposal has been adopted also by the European cement industry association CEMBUREAU in the meantime.

The EU guidelines specify requirements for the accuracy of the data to be compiled that differ depending on the overall emissions from a plant. They are subdivided into three groups (up to 50 000 t CO_2/a, between 50 000 and 500 000 t CO_2/a, and more than 500 000 t CO_2/a). Given the fairly high specific CO_2 emissions of the clinker burning process, all German cement works with clinker production have been assigned to the two latter groups. The requirements for measuring accuracy and the methods for determining the fuel-induced CO_2 emissions, respectively, which are laid down in the EU guidelines stipulate that all cement works conduct regular analyses to determine the calorific value and carbon contents, respectively, of all solid fuels, for example. While the calorific value is commonly analysed at the works laboratory anyway for operational reasons, elemental analyses have to be performed additionally. By contrast, the cement industry’s solution proposes to use statistically secured standard values in calculations as far as possible and to restrict analyses to these substances for which such a data base is not available (see **Tab. II-1**). In addition to that, the analyses are required to be carried out in accredited laboratories. As analysis at the works laboratory would thus not be permissible, these stipulations would incur considerably higher costs. The same applies to the determination of process-related CO_2 emissions, for which either an extremely precise measurement of clinker production or representative mass balances have been called for. Neither can be effected with reasonable effort and expenditure. VDZ has therefore proposed the method of combining a mass balance of the process input (“forward calculation”) with a reverse calculation on the basis of cement dispatch, which has proven its worth in the cement industry (see **Fig. II-4**). This proposal is based on the precise weighing of input materials, such as purchased fuels or interground additives, on calibrated input scales. Reverse calculation proceeding from cement dispatch is also based on the weighing of the products dispatched on calibrated dispatch scales. Although the process scales used in the clinker burning process and the cement manufacturing process, respectively, cannot match the measuring accuracy stipulated in the EU guidelines, the experience gathered by FIZ-Zert as part of the verification of CO_2 emissions from German cement works reveals that this method allows to comply with the overall accuracy of the EU guidelines.

Development of CO_2 emissions

The greenhouse gas potential of emissions from the cement industry is almost exclusively attributable to carbon dioxide. The quantity of other greenhouse gases, such as the ones listed 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. Moreover, fuel energy is consumed for the processes involved in drying the other main cement constituents, such as blastfurnace slag. The specific fuel-related CO_2 emissions decreased from 0.195 to 0.156 t CO_2/t cement in the period from 2000 to 2003. In absolute terms, this corresponds to a reduction of 6.83 million t CO_2/a to 5.20 million t CO_2/a. In accordance with the systematics of the voluntary agreement, this figure does not include the CO_2 emissions caused by secondary fuel utilisation, as they are a full substitute for fossil fuels. Since the waste would otherwise release its carbon content to form CO_2 or other greenhouse gases somewhere else, the utilisation of secondary fuels leads to an overall reduction in CO_2 emissions.

This classification of secondary materials 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 biogenous 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 costs. 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 by waste-derived fuels. It remains to be seen whether

Tab. II-1: Determination of fuel-induced CO_2 emissions (proposal by the cement industry)

Fuels	Fuel quantity	Calorific value	Emission factor
coal	method: purchase	analyses (works laboratory1) or supplier)	standard factor (BMU / RISA)3)
lignite	method: purchase	analyses (works laboratory1) or supplier)	standard factor (BMU / RISA)3)
petcoke	method: purchase	analyses (works laboratory1) or supplier)	standard factor (BMU / RISA)3)
heavy fuel oil	method: purchase	standard factor (e.g. norm)	standard factor (BMU / RISA)3)
light distillate oil	method: purchase	standard factor (e.g. norm)	standard factor (BMU / RISA)3)
natural gas	method: purchase	information by supplier	standard factor (BMU / RISA)3)
used tyres	combination: method purchase and weighing before kiln	standard factor	standard factor (BMU / RISA)3)
waste oil/solvents	method: purchase	analyses (works laboratory1) or supplier)	analyses2)
reproduced fractions of - industrial wastes - municipal wastes	method: purchase	analyses (works laboratory1) or supplier)	analyses2)
other solid fossil secondary fuels	method: purchase	analyses (works laboratory1) or supplier)	analyses2)

1) external reference analysis, e.g. 4 times a year by an accredited laboratory

2) usually external, e.g. 4 times a year by an accredited laboratory; in the medium run, the specification of statistically secured standard factors (constants) is to be aimed at

3) BMU = German Federal Ministry for the Environment; RISA = Software for filing applications

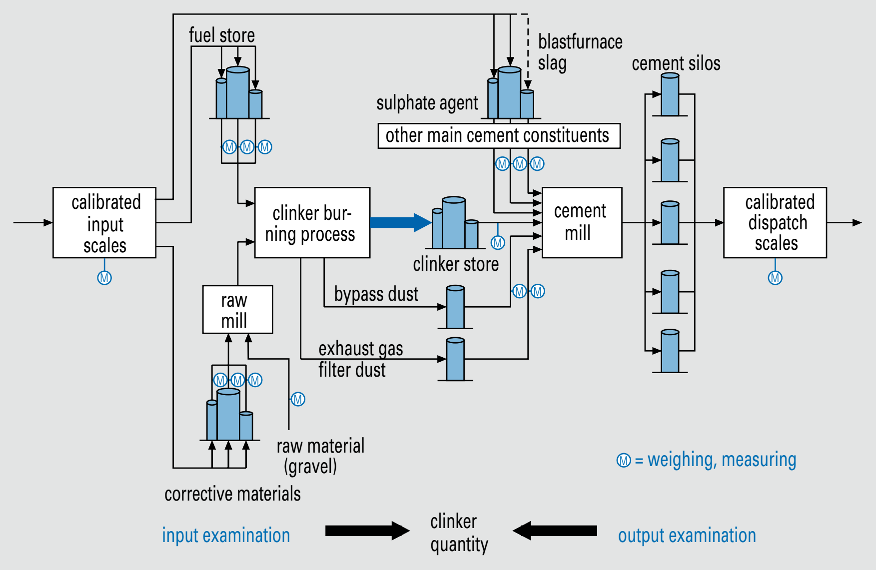


Fig. II-4: Determination of clinker production as part of CO_2 reporting

Tab. II-2: CO_2 emissions of the cement industry from 2000 to 2003

	Absolute CO_2 emissions in million t/a				Specific CO_2 emissions in t CO_2/t cement			
	2000	2001	2002	2003	2000	2001	2002	2003
Thermally induced[1]	6.83	5.78	5.16	5.20	0.195	0.179	0.168	0.156
Electrically induced	2.38	2.15	2.12	2.22	0.068	0.067	0.069	0.067
Raw material induced	15.10	13.37	12.70	13.37	0.431	0.415	0.413	0.401
Energy related	9.21	7.93	7.28	7.42	0.263	0.246	0.237	0.223
Total	24.31	21.30	19.98	20.81	0.694	0.661	0.650	0.624

[1] excluding secondary fuels

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

Year	Emissions from thermal energy consumption[1]	Emissions from electrical power consumption	Emissions from limestone calcination	Total
1987	0.317	0.075	0.456	0.848
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

[1] excluding secondary fuels
[2] basis year of the voluntary agreement of 2000

the utilisation of biomass fuels will play a particular role in the future.

The emission factors agreed upon and applied under the terms of the voluntary agreement differ from the values specified by emissions trading as well. 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 utilisation – is higher. In the years from 2000 to 2003, the CO_2 emissions induced by power consumption ranged between 0.067 and 0.069 t CO_2/t cement. In absolute terms, they edged down from 2.38 (in 2000) to 2.22 (in 2003). The scale on which the German cement industry generates its own electricity is very low.

CO_2 emissions derived from raw material

CO_2 is released during the calcination of limestone (CaO_3 in chemical terms), which is the most important raw material. The raw material-derived CO_2 emission per tonne of clinker produced depends on the raw material mix formulation, but varies only slightly. It totals approx. 0.53 t CO_2/t clinker, or between 0.401 and 0.431 t CO_2/t cement in the period from 2000 to 2003, respectively, in Germany. The overall raw material-derived CO_2 emissions by the German cement industry decreased from 15.1 million t CO_2 in the year 2000 to 13.4 million t CO_2 in 2003, which was primarily attributable to the decline in output. As a consequence, the specific and absolute CO_2 emissions listed in **Tab. II-2** were generated in the period under review. A reduction in raw material-derived CO_2 emissions relative to one tonne of cement can be achieved on a limited scale only by increasingly manufacturing cements with several main constituents. Reduction relative to one tonne of clinker is virtually impossible.

In conclusion, the specific CO_2 emissions of the German cement industry in the period from 1987 to 2003 are summarised in **Tab. II-3**. The base year for the cement industry's voluntary agreement in the version converted to specific energy-related CO_2 emissions is 1990. The data recorded in 1987 is listed for information.

Reducing gas and dust emissions ■

Environmental data

Since the year 1998, VDZ has published the "Environmental Data of the German Cement Industry" every year. The current issue for the year 2003 can be downloaded as pdf file from the publications / environmental data section under www.vdz-online.de. The brochure documents the utilisation of raw materials and fuels for clinker and cement manufacture. The quantities of secondary materials utilised in particular are shown in detail. Accordingly, the average proportion of total fuel energy consumption that secondary fuels accounted for topped 38% in the year 2003.

In terms of content, the main focus of the environmental data was placed on the emissions of rotary kiln systems shown as being representative of the German cement industry. In addition to the dust component, the exhaust gas components NO_x and SO_2, trace elements and organic exhaust gas constituents are considered. Their concentrations in the clean gas and the associated releases, i.e. the quantities emitted in kg/year, have been traced in graphs. When the respective substance was detectable by measurement, definite statements both on concentration and annual releases can be made. In case of measurement values not secured or measurements below the detection limit, however, this is not possible. In these cases no emission concentrations are indicated. As regards the releases, only a theoretical upper limit can be given. It is calculated on the basis of the assumption that the concentration of the substance in the clean gas reaches the detection limit.

This kind of estimates using upper limits is often inevitable in the determination of trace element emissions from the rotary kilns of the cement industry. Given their behaviour in the clinker burning process and the high separation efficiency of the dust collectors, the concentration of trace elements is often below the detection limit of the measuring method. By way of example, **Fig. II-5** illustrates the emission concentrations of the trace element thallium in mg/m³. In 2003, a total of 96 values for thallium concentration in the clean gas was determined by measurements conducted at 41 kilns. However, merely the nine values plotted (dots) exceed or match the detection limit, which ranges between 0.004 and 0.006 mg/m³ depending on the method of measurement or analysis. For that reason, definite thallium releases obtained via concentration values and clean gas volume flows (m³/year) can be given for 4 plants only (triangles) in **Fig. II-6**. For 37 plants, the emissions have to be estimated on the basis of an assumed concentration value of 0.004 mg/m³ (lines). The releases actually emitted correspond to the upper limits shown in a worst-case scenario only, which has to be taken into account especially when the figures are evaluated under environmental policy aspects.

Fig. II-5: Thallium concentration values measured (year 2003) in the clean gas of 41 rotary kiln plants

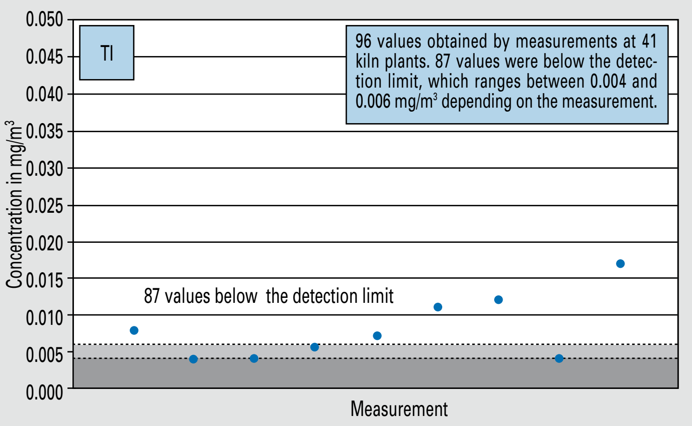
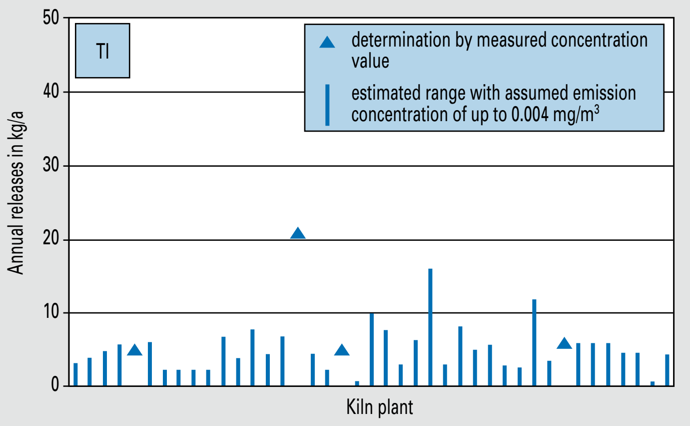


Fig. II-6: Thallium emissions (annual releases in 2003) of 41 rotary kiln plants



Tab. II-4: Limit values for trace element emissions pursuant to TA Luft and 17th BImSchV

Limit values for trace elements	TA Luft 2002 mg/m³	17th BImSchV 2003 mg/m³
Hg	0.05	0.03
Tl	0.05	0.05
Cd	0.05	
As		0.5
Ni, Co, Se, Te, Pb	0.5	
Sb, Cr, Cu, Mn, V, Sn	1	

Trace element behaviour during the clinker burning process

The trace element emissions of the clinker burning process are limited by law and enacted by corresponding caps in the licences. Accordingly, the emissions have to be determined regularly by measurements and reported to the supervisory authorities. The German Technial Instructions on Air Quality Control (TA Luft) and, if secondary fuels are utilised, the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV) constitute the pertinent legal basis (**Tab. II-4**). Furthermore, cementitious products applied in domains relevant to health undergo critical scrutiny to verify whether the trace elements contained are safely bound in the cement matrix over long periods of time. For example, concrete elements used in the drinking water domain are subjected to leaching tests.

Trace elements are input into the cement clinker burning process both via the raw materials and the fuels. The trace elements are present in these feed materials in concentrations which are natural and induced by geogenous factors. Raw materials usually account for the highest input, since their mass flow is about 10 times higher than that of the fuels. The behaviour of trace elements in the clinker burning process is chiefly determined by the volatility of their compounds. In this context, not only the forms of bond present in the feed materials are decisive, but also the compounds newly formed in the kiln. Measurements, some of which were very complex and laborious, were performed at various points of the process (raw and clean gas, meals, dusts) in the past to evaluate the characteristic behaviour of trace elements. These investigations showed that it is reasonable to subdivide trace elements and their compounds into four classes (non-volatile, not easily volatilised, easily volatilised and highly volatile elements).

The non-volatile and not easily volatilised elements are virtually irrelevant to emissions and are almost fully bound in the clinker. Arsenic, vanadium, nickel, chromium and copper are examples for non-volatile heavy metals.

Not easily volatilised elements, such as cadmium and lead, can evaporate in the rotating kiln and – like chlorine, sulphur and alkalis – form internal recirculating systems. In the gas phase between the rotating kiln and the preheater, the trace elements react with the chlorides and sulphates available to form not easily volatilised compounds. At temperatures between 700 and 900 °C in the preheater these compounds condense on the kiln feed particles due to the large surface area available. The retention capacity of the preheat-

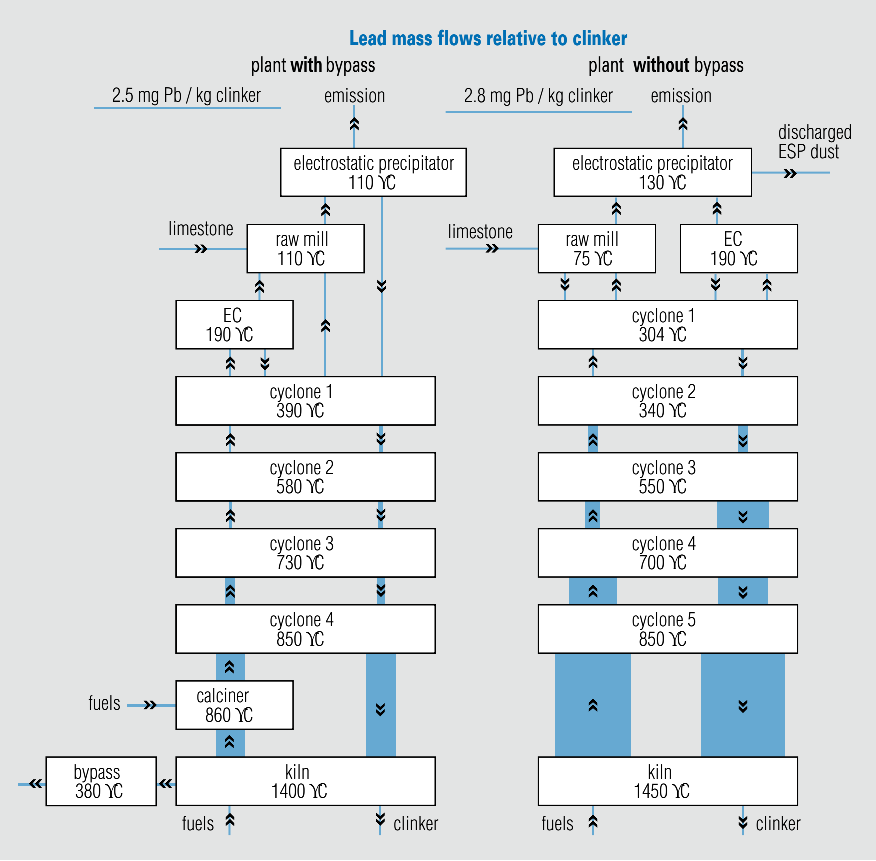


Fig. II-7: Markedly elevated lead mass flows in a plant without bypass and with an elevated recirculating chlorine system in comparison to a bypass-equipped plant with a moderate recirculating chlorine system

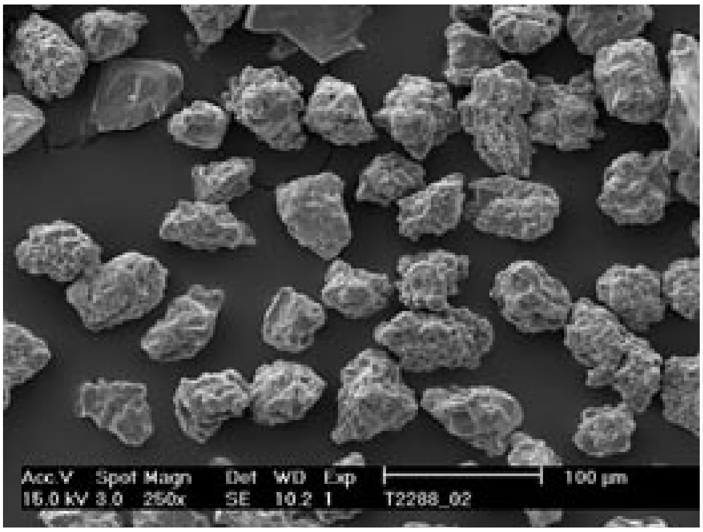


Fig. II-8: ESEM photograph of the screened fraction with particle sizes between 32 and 40 µm

er obtained in conjunction with the high collection efficiency of the cyclone stages allows only a very small proportion of not easily volatilised trace elements and their compounds to leave the kiln system with the raw gas. Much rather, these compounds re-enter the kiln in condensed state to be discharged with the clinker for the most part. The proportion that evaporates again in the kiln contributes to the recirculating system between kiln and preheater again. The formation of this internal recirculating system, in which the not easily volatilised elements build up locally, depends on the sulphate and chloride supply available for reaction.

Build-up of easily volatilised thallium was found to occur in the hot meal of the two upper cyclone stages. In the bottom part of the preheater or even in the clinker, thallium is seldom detectable. Much rather, the trace element and its compounds evaporate in the upper cyclone stage section and are conveyed to the plant sections of the external cycle, i.e. the evaporative cooler (EC), the raw mill and the dust collector, together with the raw gas. Due to the decrease in temperature and the intense contact between gas and solid, the thallium almost fully condenses on the meal particles, thus rarely ever having any relevance for emissions. It builds up in the dust of the evaporative cooler and the dust collector instead and is again fed to the heat exchanger together with the kiln meal. To relieve this recirculating system, a part of the separated meals is discharged and conveyed past the kiln to the finish mill.

The highly volatile element mercury reacts to form compounds that are not precipitated or retained in the kiln and preheater area. As a consequence, mercury cannot be expected to occur in the clinker. This assumption was confirmed by numerous analyses. In spite of that, mercury at low concentrations is occasionally detected in the clinker. The corresponding form of bond, or the mechanism of combination in the clinker has, however, not been identified yet. Similar to thallium, mercury, too, forms an external recirculating system between the preheater, the raw mill and the dust precipitator. The measure most effective in reducing mercury emissions is the lowering of the gas temperature upstream of the filter, accompanied by the discharge of part of the separated raw meal.

A process technology simulation model developed at the Research Institute of the Cement Industry can be used to choose suitable secondary fuels and assess their possible maximum input quantities. This programme further allows to calculate and optimise the operation of a gas bypass at the kiln inlet to restrict recirculating chlorine systems between the kiln and the preheater. The practical application of the simulation programme made it possible for the first time to successfully estimate the effects that the elevated input of chlorine, sulphur and alkalis via different secondary fuels have on process temperatures and build-up in the hot meal. Moreover, the reducing effect a bypass gas vent has on recirculating systems was determined in terms of quantity. Accordingly, the relevant recirculating chlorine, sulphur and alkali systems can be represented reliably.

The model is currently being extended to include trace element behaviour in order to allow material flow calculations markedly more accurate and geared to practice to be performed for these substances, too, in the future. The behaviour of trace elements in the clinker burning process is simulated in accordance with their volatility and their degree of bonding and precipitation in the various plant sections. In addition to gas and material temperatures, the relevant process parameters particularly include the dust collection efficiency of the cyclone stages, the supply in the meal and dust of high-surface fine fractions conducive to condensation, and the intensity of recirculating chlorine, sulphur and alkali systems. To gather the pertinent data required to set up the model, investigations at the physical laboratory and the laboratories of the Research Institute as well as industrial trials at three kiln systems were carried out.

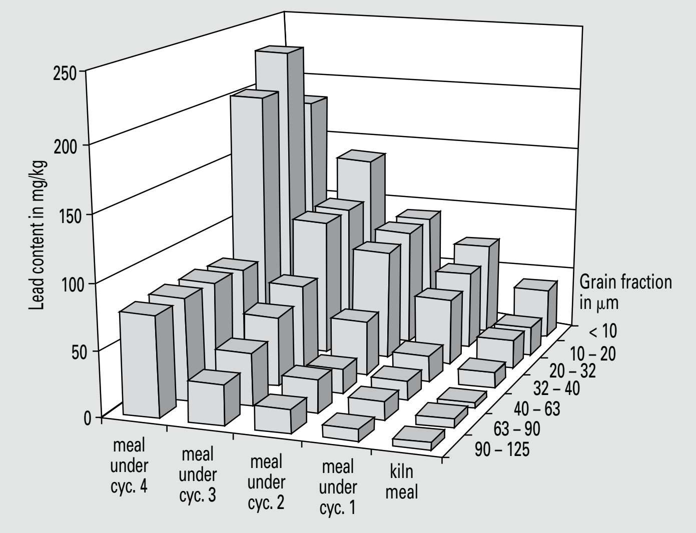


Fig. II-9: Build-up of the element lead in the fine fractions of the hot meals in the preheater

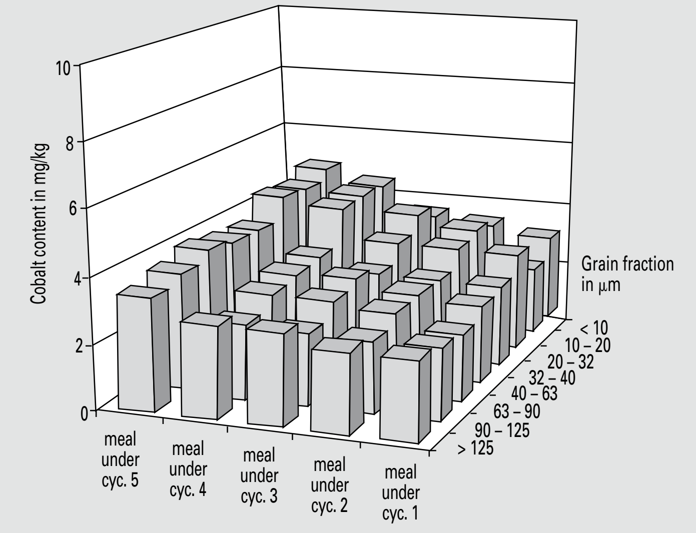


Fig. II-10: Cobalt does not build up in the hot meals of the preheater

At first, the measurements necessary for the evaluation of plant operation and the establishment of precise mass balances of the external and internal recirculating material systems were conducted. This involved taking samples of the materials input and output, determining volume and mass flows, and carrying out gas analyses and temperature measurements. Moreover, a separate mass balance with regard to trace elements was drawn up for the plant sections belonging to the external cycle, i.e. the evaporative cooler, the raw mill and the dust collector. Extensive sampling of process meals and dust as well as gas analyses were performed in the preheater, too. For one thing, the dusts in the cyclone riser ducts were sampled by extraction. In contrast to the fabric or basket filters frequently applied, no filter cake was formed as separation took place in a sampling cyclone. This measuring method prevented gas constituents which normally pass the filter from condensing on the filter cake, thus allowing to obtain dust samples with unadulterated trace element contents. For the other, the dust contents in the cyclone riser ducts were measured in order to be able to calculate the dust and meal mass flows in the preheater. To that purpose, it was necessary to modify the measuring instrument used for determining the dust contents in the raw gas by a ventilated probe and high-temperature resistant filter materials.

The mass-balance measurements carried out to examine the contents in the meals and dusts confirmed the well-known behaviour of trace elements in the clinker burning process. A comparison between a plant equipped with a bypass, which displayed a correspondingly weak recirculating chlorine system, and a second plant without gas bypass, which had an intensive recirculating chlorine system, demonstrated that the presence of chlorine boosted the volatility of trace elements, and thus their tendency to form recirculating systems. The not easily volatilised elements lead and cadmium were found to build up in the hot meals of the bottom cyclone stages and get combined in the clinker to a lower extent when the chloride supply was elevated (**Fig. II-7**). These elements were detected in their gaseous phase in the hot zone of the preheater as well.

The particle size distributions of the meal and dust samples were determined to investigate the influence of meal and dust fineness on the condensation and build-up of trace elements. The meals turned out to get considerably coarser as they passed the cyclone preheater on their way from kiln meal to hot meal. Some of the samples were dissected into fractions by means of dry and wet screening and examined for trace elements. The quality of fractionation by screening was reviewed and corroborated by scanning electron microscopy photographs (ESEM, **Fig. II-8**). The elements thallium, cadmium and lead were found to have built up in the fine fractions of the hot meals in the preheater (**Fig. II-9**). As expected, no build-up of non-volatile elements, such as arsenic, nickel, chromium, cobalt, manganese and vanadium, was detected in the fine grain fractions (**Fig. II-10**).

To have a closer look at the range of particles having a diameter of less than 15 µm, a cascade impactor was used to further subdivide and fractionate the process meals withdrawn from the preheater in a semi-industrial plant of the Research Institute. In spite of the considerable experimental effort expended, however, the results obtained by the trace analysis of the fractions produced were not definite. It was mainly due to the low loading of the impac-

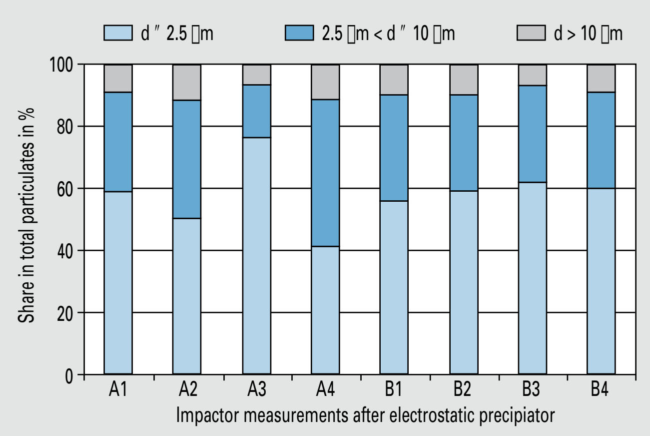


Fig. II-11: Measurements in the clean gas of plants A and B downstream of electrostatic precipitators using the Johnas II impactor. The limiting particle diameter d describes the aerodynamic diameter d_{ae} of an equivalent ball of identical physical properties.

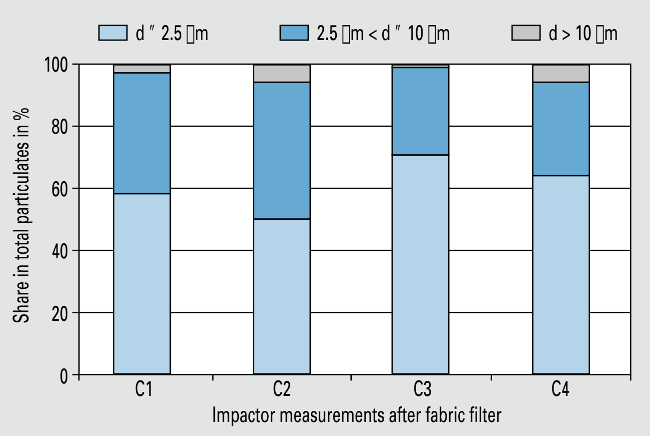


Fig. II-12: Measurements in the clean gas of plant C downstream of the fabric filter using the Johnas II impactor. The limiting particle diameter d describes the aerodynamic diameter d_{ae} of an equivalent ball of identical physical properties.

tor stages that not all trace elements were detectable on the impactor stages in some measurements. As a consequence, statements on the build-up effects within the fines range were rendered more difficult.

Furthermore, direct fractionating dust measurements in the clean gas of the kiln plants and subsequent trace analyses were conducted. The clean gas dust did not exhibit any remarkable features regarding either non-volatile or volatile elements.

PM 10

The World Health Organisation WHO believes that particulate matter having a particle diameter of less than 10 micrometers (PM10) is responsible for damage to people's health. For that reason, the European Union laid down an ambient pollution limit (annual average) of 40 µg/m^3 for particulate matter. Moreover, the daily average must not exceed 50 µg/m^3 more than 35 times a year. Both limit values were transposed into German law by the amendment of the German Clean Air Specifications (TA Luft), which took effect on October 1, 2002.

Road traffic is a major source of ambient pollution by particulate matter in agglomerations. This became apparent in the wake of the current discussions on air pollution abatement plans in several big European cities. By contrast, the dust emissions from the kiln and grinding plants of the cement industry are so low that they have hardly any relevance in the vicinity of the cement works. In spite of that, they became a talking point again in the past years due to their particulate matter proportion. The question about the PM 10 emissions from production plants of the cement industry thus arises regardless of whether further emission reductions in industrial plants are of any use in reducing the overall ambient pollution impact at all. The Research Institute therefore recently measured the particulate matter concentration in the clean gas of several rotary kiln plants. The measurements were conducted downstream of electrostatic precipitators and, for the first time, also downstream of a fabric filter. Impactors are used to determine the particulate matter concentration and the particle size distribution, respectively, of the dust emitted. The 3-stage impactor Johnas II was utilised for the measurements. The fractionating measurements were simultaneously accompanied by the determination of the total dust concentration.

Fig. II-11 illustrates the particle size proportions of the dust < 2.5 µm, 2.5 to 10 µm, and > 10 µm emitted from rotary kiln plants A and B. Both plants use electrostatic precipitators to separate the dust from the raw gas. While the results obtained for plant B show a very uniform picture for all 4 measurements, major fluctuations were observed at plant A. These relate to the subdivision of the fractions < 2.5 µm and 2.5 to 10 µm. The proportion < 10 µm accounts for 90 wt.% on average, with the fraction < 2.5 µm totalling some 60 wt.%. These results range within the bandwidth of particulate matter measurements carried out previously, in which PM 10 proportions of 80 to 95% and PM 2.5 proportions of 30 to 70% were determined.

A further impactor measurement in the clean gas of plant C downstream of the fabric filter was carried out to investigate whether the distribution of the particles downstream of a fabric filter used for collecting the dust from the raw gas displays any fundamental differences (**Fig. II-12**). The measurement was very time-consuming as the total dust loading of the clean gas was only a few mg/m^3. Thus, long extraction times were necessary to obtain sufficient dust deposits on all 3 filters of the impactor. The results are relatively constant and show a PM 2.5 proportion of about 60%, which corresponds to the concentration downstream of electrostatic precipitators. The PM 10 share of approx. 95% tallies with the range of measurement results after electrostatic precipitators, too. Since this, however, was the only investigation conducted downstream of a single fabric filter to date, the results cannot be generalised yet.

Relevance of quartz in emissions from rotary kiln plants

Crystalline silicon dioxide is made up of different mineral modifications, the most frequent of which is quartz. The cancerogeneous effect of particulate matter containing quartz has been the subject of discussions for some time. The dust fraction having a particle size of less than PM 4, which can pass the alveola, is considered as particulate matter. These are particles with an aeordynamic diameter of 4 µm, of which a share of 50% can be collected in a suitable precipitation system.

On May 7, 2002, the Hazardous Substances Committee (AGS) passed a resolution pursuant to which crystalline silicon dioxide in the form of quartz and cristobalite is to be regarded as cancerogeneous in humans. As a consequence of this classification by

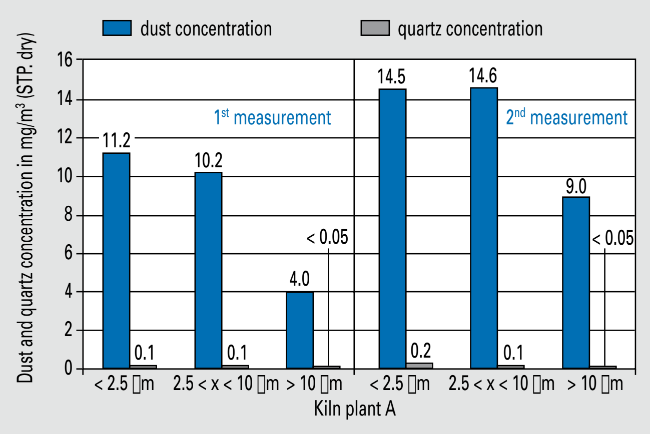


Fig. II-13: Dust and quartz concentration as a function of the particle size in the exhaust gas of rotary kiln A (2 measurements)

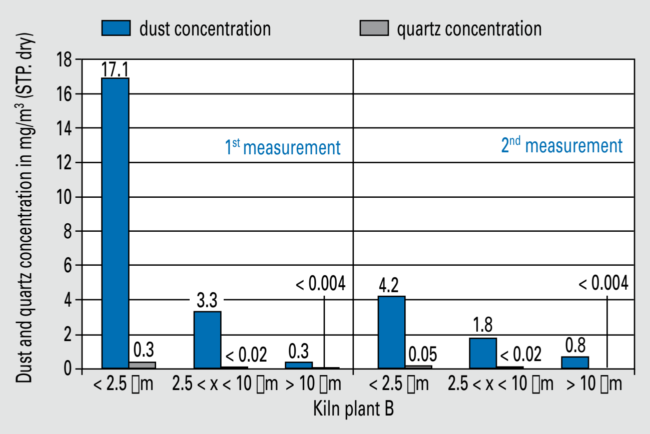


Fig. II-14: Dust and quartz concentration as a function of the particle size in the exhaust gas of rotary kiln B (2 measurements)

the AGS, an emission limit for particulate quartz has become a talking point. As particulate quartz is not included in the German Clean Air Specifications (TA Luft) list of substances No. 5.2.7.1.1 summarising cancerogeneous substances, classification is to be based on the cancer risk. According to the current status of discussion, particulate quartz is to be assigned to class III of cancerogeneous substances according to TA Luft. This would result in an emission value of 1 mg/m³ for crystalline particulate quartz (PM 4). As this is a cumulative value, it must not be exceeded even if several substances from one class occur.

While the determination of particulate quartz has been common practice in the field of industrial health and safety for years, the measurement of particulate quartz concentrations in the emissions from plants is new territory. Problems occur both in connection with the selective collection of the PM 4 fraction and the chemical analysis of the crystalline SiO_2 proportion. VDI 2066 Sheet 10 specifies a standardised method for measuring the emission concentration of PM 2.5 and PM 10 (Johnas impactor). The development of a modified Johnas impactor is currently underway to allow the sampling of PM 4 for emission measurement.

The filter materials used for sampling must meet particular requirements. The quartz filters commonly used in other applications are inadequate in this case since the amorphous filter material cannot be distinguished from the crystalline quartz dust during analysis. Filters made from nitrocellulose or acetyl cellulose as well as metal fibre could be used alternatively. Depending on the kind of application, the temperature resistance of nitrocellulose filters (up to 100 °C) and acetyl cellulose filters (up to 180 °C), respectively, is insufficient. Metal fibres can be utilised in high-temperature applications, but the entire dust sample then has to be transferred to another support medium prior to analysis. The analysis methods applied are infrared spectroscopy (FTIR) and X-ray diffractometry, which have already proven their worth in workplace investigations.

The Research Institute of the Cement Industry has carried out measurements at 2 kiln plants so far to gain an initial insight into the relevance of particulate quartz emissions for the rotary kiln systems of the cement industry. The Johnas impactor, which had been equipped with acetyl cellulose as filter material, was utilised to that effect. As already outlined above, only the PM 10 and PM 2.5 fractions could be measured as the measuring technology for PM 4 does not exist yet.

The variation of the sampling process described here and its subsequent combination with an analysis of the quartz proportion constitutes an in-house development of the Research Institute of the Cement Industry. The objective pursued at first was to gain initial information on the quartz emission from rotary kiln plants of the cement industry. Concluding investigations to determine the measuring uncertainty are yet to be carried out.

The dust and quartz concentrations measured at the two rotary kilns are shown in **Figs. II-13** and **II-14**. Two measurements were conducted at each plant. The overall dust emission and the overall quartz emission are derived from the cumulative value of the three individual values. The dust concentrations of kiln plant A were comparatively high. The associated overall quartz emission totalled 0.25 and 0.35 mg/m³, respectively. The dust emissions at kiln plant B were lower. Quartz was only detected in the fraction < 2.5 µm. The values amounted to 0.3 and 0.05 mg/m³ quartz, respectively.

The values measured at these two plants lay below the emission limit of 1 mg/m³ currently discussed. Depending on the deposit or the raw meal composition, certain fluctuation bandwidths are probable. The Research Institute of the Cement Industry will therefore carry out measurements at other rotary kiln systems and push ahead with the advance of measuring technology with regard to particulate quartz emissions.

SNCR process is state of the art

The SNCR process (selective non-catalytic reduction) has been applied for NO_x abatement at industrial combustion plants for more than 25 years. It consists of reducing nitrogen oxides (NO_x) to N_2 and H_2O by injecting a reducing agent, which is usually ammonia. The German cement industry has gained extensive operating experience with the application of the SNCR process by now. This secondary NO_x reduction method is applied at more than 30 German kiln plants, which include rotary kilns with cyclone preheater and rotary kilns with grate preheater as well as plants with a staged secondary combustion unit in the calciner. The SNCR process is increasingly being applied for NO_x abatement at cement plants in other European countries as well.

Prior to applying the SNCR process, it is advisable to lower the NO_x starting level as far as possible by means of various primary measures or by fuel selection. When the SNCR process is additionally applied as a secondary measure, a substoichiometric injection of the reducing agent yields good reduction results.

The efficiency of the SNCR method can be evaluated on the basis of the NO_x reduction rate and the NH_3 escape that occurs. To achieve high reduction rates, it is usually necessary to inject the reducing agent at an over-stoichiometric ratio, i.e. at a molar NH_3 / NO ratio > 1. This can entail emissions of unreacted NH_3, which are called NH_3 escape. NH_3 emissions can increase during direct operation (i.e. without combined drying and grinding) in particular. The NH_3 emission concentrations occurring in interconnected operation are markedly lower for the most part since a considerable portion of the ammonia contained in the raw gas is deposited on the raw meal in this case. As the share of direct operation phases is mostly small, the long-term average of NH_3 emissions is low as well.

When the unreacted ammonia builds up in the raw meal and the ESP dust, an external recirculating system can build up. This recirculating system is relieved in direct operation, which can result in a rise in the NH_3 emission concentration as well. If the filter dust is discharged and input to cement grinding, the ammonia content of the dust must be taken into consideration for reasons of product quality. The experience gathered at numerous kiln plants over many years has shown, however, that the SNCR method is not detrimental to product quality.

The objective pursued by optimisation trials is to enhance the NH_3 yield. The factors that are of decisive importance for achieving the highest possible conversion with nitrogen oxides include the temperature, the residence time of reactants in the temperature range and the intermixing of the reducing agent (droplet size, throw, covering of the injection cross-section(s), measuring and control engineering). The type of reducing agent used influences the decomposition reactions, too.

25% ammonia solution (aqueous ammonia) is still considered the standard reducing agent. In many cases, however, waste water from photo development (i.e. processed developers and fixers generated in the photographic process) is utilised as a reducing agent as well. The total N content (NH_4^+ and possibly urea) usually ranges between 1.5 and 5%, but in spite of this low concentration the reduction results achieved are good to excellent at times. The reducing agent urea (in the form of a solution or prills) plays a subordinate role in the cement industry.

To designate particularly high NO_x abatement rates accompanied by low NH_3 escape, the term “High efficiency SNCR” is used in the literature. The target value aimed at in the optimisation of SNCR plants is often a very low NO_x concentration, which may be as low as 200 mg/m^3. In some cases, such a low level was even reached in industrial trials for a short time. However, it was frequently found to be accompanied by elevated NH_3 emissions.

From an environmental perspective, attention must not only be directed to NO decomposition, but also to NH_3 emissions. International environmental policies therefore pursue the goal to limit the input of ammonia and ammonium into the environment. These requirements were documented in the so-called Gothenburg Protocol and in the European Directive 2001/81/EC (National emission ceilings for certain atmospheric pollutants). To put things in perspective, however, it has to be pointed out that the share of total ammonia emissions the industrial sector accounts for is very low at approx. 1 to 2%. As the cement industry in turn contributes only a small portion to industrial NH_3 emissions, these releases can be considered irrelevant on the whole.

For the purposes of an integrated assessment of the process, which takes into consideration all environmental aspects as well as economic efficiency, it can be reasonable not to apply the SNCR process with the target of maximum NO_x abatement, but to aim at a possibly somewhat lower reduction rate accompanied by lower NH_3 escape. Also representatives of public authorities have meanwhile approved of this course of action. Given this scenario, the SNCR process can be regarded as the most effective NO_x abatement method for the cement industry. Due to the vast operating experience gathered in the cement industry over many years, the SNCR process is considered “state of the art” or “best available technique” (BAT). The specific costs incurred by the SNCR process (capital and operating costs) range between 0.50 and 0.70 € / t clinker according to a fairly recent estimate.

Staged combustion in the calciner

New rotary kiln plants in the cement industry are equipped with precalcining technology without exception today. Operating experience shows that the application of this technology allows NO_x to be reduced effectively. Although this method has been employed for many years, knowledge about the correlation between NO formation and NO decomposition in the calciner is still fragmentary, which makes it more difficult to optimise the mode of operation in terms of NO_x, secondary fuel utilisation and kiln operation.

The crucial influencing variables for NO_x abatement by staged combustion are:

- the stoichiometric air ratio in the reducing and burnout zones,
- the fuel properties,
- the temperature in the reducing and burnout zones,
- the NO_x loading from the first stage (sintering zone) prior to entry into the reducing zone,
- the gas residence time in the reducing and burnout zones and
- the mixing of the gas and solids flows, respectively.

The very number of these essential influencing variables indicates that the chemical and physical processes causing NO_x to be formed or decomposed, respectively, in the calciner are very complex. Substantially, the technical measures taken consist of fuel or air staging to influence the local stoichiometric air ratio, meal staging to influence temperature distribution, and selection and preliminary processing of the fuels to influence reaction kinetics.

Optimisation of the stoichiometric air ratio in the reducing zone

The stoichiometric air ratio, which is defined as the ratio of the oxygen quantity actually available and the quantity required for complete fuel utilisation, can be influenced both by the type and quantity of fuel and by the ratio of air and fuel. An optimum value for the stoichiometric air ratio in the reducing zone, which allows to achieve maximum NO_x abatement, is known to exist from publications. Where this optimum lies in turn depends on the fuel, the residence time and the temperature. The optimum stoichiometric air ratio for gaseous fuels is often said to range between 0.7 and 0.85. Under oxidising conditions (stoichiometric air ratio > 1) NO formation increases. At stoichiometric air ratios markedly smaller than 1, by contrast, the intermediate products containing nitrogen (HCN and NH_2^-) are converted incompletely at first. Some of them subsequently oxidise to form NO again in the downstream plant sections.

Meal staging

High temperatures have long since been known to bring forward NO decomposition in the reducing zone of staged combustion. The reason for this is that the rate of NO decomposition reactions increases as temperatures grow. A technical measure to influence the temperature in the reducing zone of a calciner is meal staging. **Fig. II-15** illustrates the effects of meal staging on the NO formation in a calciner made by Krupp Polysius. In the trial without meal staging, all the meal from the second cyclone stage from the bottom was fed to the lower section of the calciner. As a result, a temperature of 870 °C was obtained in the reducing zone. The calciner fuel input was lignite. At the final count, the quantity of NO_x decomposed in the calciner exceeded the quantity formed. In the trial including meal staging, about half of the meal was fed into the upper section of the calciner. As a result, the temperature in the reducing zone rose to up to 1 170 °C. It becomes evident from the Figure that this resulted in significantly more effective NO_x decomposition. What is interesting is the fact that CO degradation was also accelerated due to the elevated temperatures in the burnout zone. In this way, both markedly lower NO_x emissions and somewhat lower CO emissions were achieved.

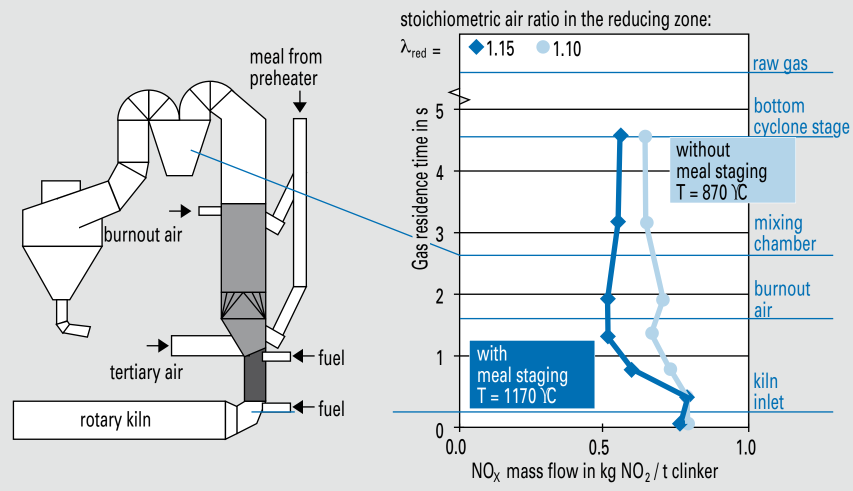


Fig. II-15: Effect of meal staging on NO formation in the calciner

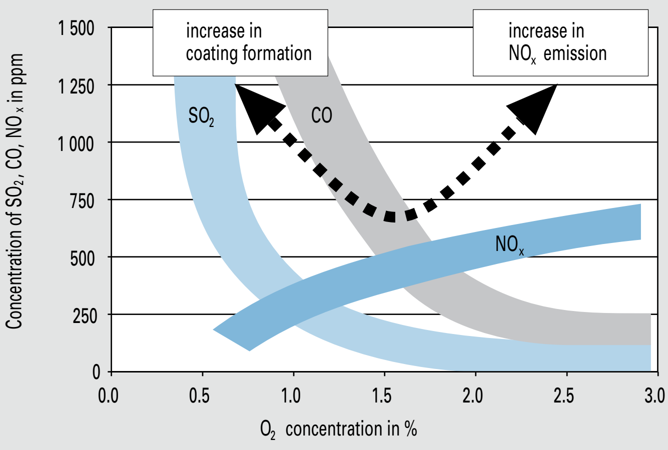


Fig. II-16: Emissions of NO_x, CO and SO_2 as a function of the oxygen supply in the sintering zone

Limitations of NO_x abatement by staged combustion

The industrial trials performed further revealed that the mode of operation of the precalciner kiln can be optimised in terms of minimum NO_x emission. In some cases very low NO_x emissions were achieved. On the other hand, it was often not possible to maintain operation at these extreme settings over a long period as operational problems emerged. Shifts in operational settings, such as extreme air staging, have an immediate impact on the air distribution in the kiln system and thus on the combustion conditions both in the rotary kiln firing unit and in the calciner.

Process technology also imposes limitations on the possibility of using meal staging to influence the position of the temperature zones and thus the efficiency of nitrogen oxide reduction. Variations in the quantity of meal fed in the calciner cause changes in the pressure conditions prevailing in the system. These pressure drops subsequently influence the gas currents within the kiln plant. Moreover, a change in the air distribution in the kiln system has an immediate effect on the combustion conditions and thus on NO formation in the rotating kiln. The more fuel is fed to the kiln line, the lower the oxygen content in the kiln inlet gets. This in turn has a reducing effect on NO formation in the rotary kiln firing system.

On the other hand, a reduced oxygen supply in the sintering zone harbours the risk of combustion conditions that are not optimised. **Fig. II-16** illustrates the well-known relationship between the oxygen supply in the sintering zone and NO_x formation on

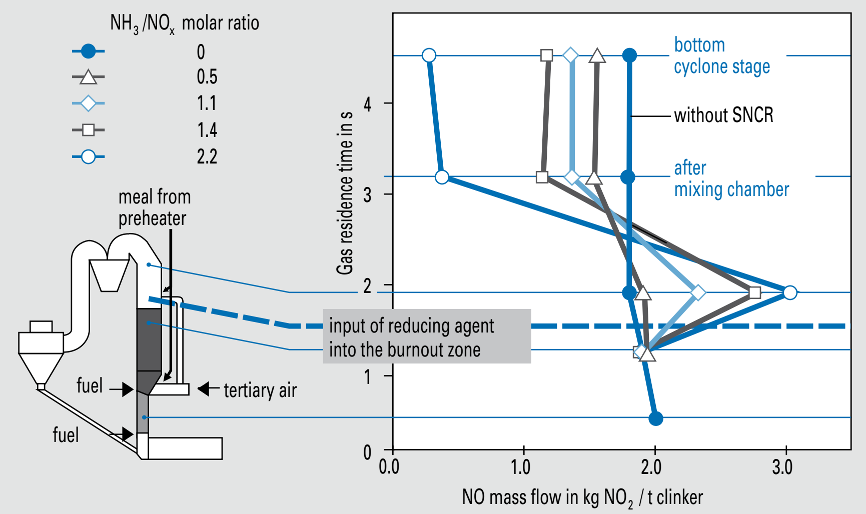


Fig. II-17: Profile of the NO mass flow upon injection of the reducing agent into the burnout zone

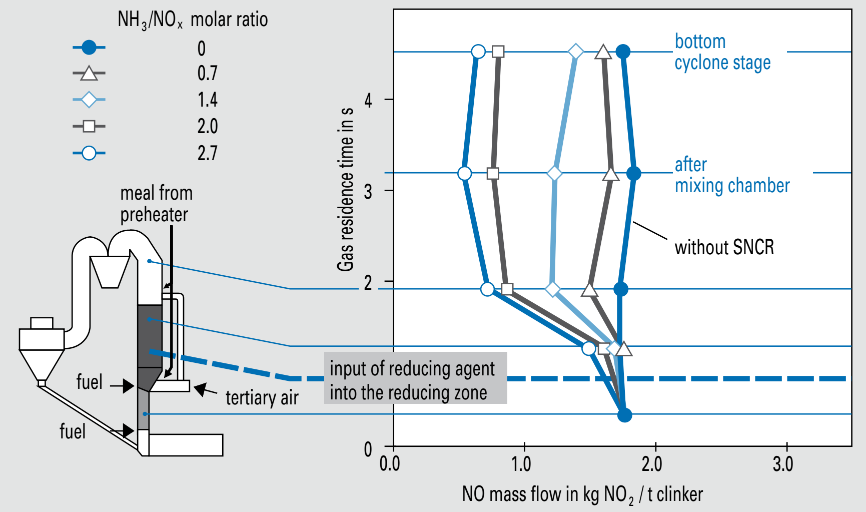


Fig. II-18: Profile of the NO mass flow upon injection of the reducing agent into the reducing zone

the one hand and formation of CO and SO_2 on the other hand. During the industrial trials it was not possible to run some of the kilns at operational settings implying extreme air and fuel staging, respectively, for several consecutive days since coating formation in the kiln inlet area and the gas riser duct increased as a consequence of the kiln being operated at lower oxygen supply.

When secondary fuels are utilised in the calciner, it has to be ensured in particular that they are as dispersible as possible. If coarse fuel particles are not carried along by the gas flow, they fall into the kiln inlet, where they can create locally reducing conditions. This also results in diminished sulphur combination and thus in more intensive recirculating sulphur systems and coating formation. It is not of any help in this case, to utilise for example highly volatile, processed plastics wastes in the calciner, if these are not converted in the reducing zone.

Combination of staged combustion and the SNCR method

A combination of modern precalcining systems with the SNCR technology may be necessary to safely comply with a low daily average for NO_x emissions (500 mg/m^3). The European BAT reference document dating from the year 2000 already referred to the combination of the two processes as a so-called "emerging technique", i.e. a "technique that might be applied in the future". At that time, however, knowledge about the potential interaction of the two processes was fragmentary. Both processes take place in the same temperature range (850 to 950 °C). While, however, staged combustion requires a reducing zone in this range, the SNCR process is known to be more effective if there is excessive air. The FIZ investigations described below therefore pursued the target of determining the influence which the feeding point of the reducing agent and the quantity of reducing agent fed in particular have on the NO_x reduction rate and on the CO burnout.

The results will be illustrated hereinafter based on the example of a kiln plant of Polysius design. The reducing agent used was treated waste water from photo development with an equivalent NH_3 concentration of approx. 5%. **Fig. II-17** represents the profiles of the NO mass flow obtained upon input of the reducing agent into the burnout zone of staged combustion when different molar ratios had been set. Analogously, **Fig. II-18** depicts the ratios obtained upon addition of the reducing agent in the reducing zone. The curves clearly show that the SNCR reaction plus mixing takes more than 0.5 seconds to complete its course, if it is applied in the calciner. This is particularly true for fairly high quantities of reducing agent. If input is effected in the burnout zone, significant NO formation occurs shortly before the reducing agent is introduced. This suggests that the reducing agent is converted to NO by combustion. This increase in NO was, however, subsequently compensated by very intense NO decomposition induced by the reducing agent. When the reducing agent is input into the reducing zone, however, no increase in NO can be observed. In turn, NO decomposition is markedly lower in comparison to the preceding trial. The major differences between the turbulence conditions prevailing at the two feeding points presumably constitute one of the reasons for these vastly different reaction courses. Addition in the upper section of the calciner was effected in combination with the input of burnout air, which arguably allows relatively thorough intermixing with the gas flow. On the other hand, the oxygen concentration prevailing there is fairly high at first, thus contributing to the combustion of part of the reducing agent.

Moreover, the trial results made apparent that a rising NH_3/NO molar ratio impedes the burnout of CO underway in the calciner as well. Deceleration occurred particularly when the reducing agent had been input in the reducing zone. CO burnout is obviously impeded more severely, when the SNCR reaction takes place in the reducing zone instead of the burnout zone. This deceleration was observed until up to about 0.5 seconds after addition of the reducing agent. This shows how closely the decomposition of CO and NO are coupled. CO oxidation cannot take place unimpeded until the SNCR reaction is fully completed. At the kiln plant investigated, however, the residence time of 1.8 to 2.5 seconds between input of the reducing agent and discharge from the bottom cyclone stage, i.e. the end of the combustion zone, did not suffice to fully compensate for the deceleration of CO burnout under the operating conditions that had been set. As a result, the CO concentration downstream of the heat exchanger increased.

The bottom line is that these interactions are attributable to the fact that, just like the CO oxidation reaction, the SNCR process requires OH radicals to convert NH_3 to NH_2 (the actual reducing agent for NO) by oxidation. If the excess of OH radicals is not sufficient, which is the case at the temperature level prevailing, the two processes impede each other. It is therefore an important consideration in designing new calciners to provide for adequate residence time to allow both processes to be applied as independently of each other as possible. To this end, a minimum residence time of one second for the SNCR process has to be allowed for. This is the only way of preventing higher CO emissions or ammonia escape.

Evaluation of the SCR process

The selective catalytic reduction (SCR) of nitrogen oxides is an abatement process that, like the SNCR process, consists of adding ammonia to convert nitrogen oxides to N_2 and H_2O by reduction. As a catalyst is present, however, the temperature range for the decomposition reaction is shifted to the range between 300 and 400 °C. In rotary kilns of the cement industry, this temperature range prevails in the raw gas downstream of the preheater. Basically, there are two options: the dust-loaded raw gas can either be channelled through the catalyst (high-dust method), or the exhaust gas can be subjected to dust collection and subsequently be channelled through the catalyst after being re-heated (tail-end method).

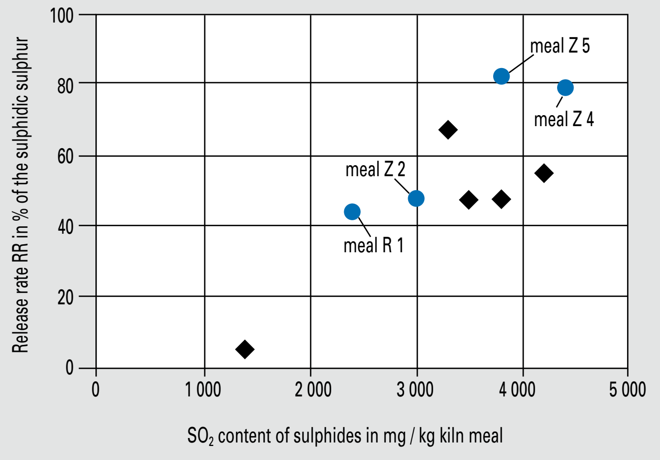


Fig. II-19: Release rates of kiln meals from different plants

While the SCR process has proved itself in power stations and waste incineration plants for many years, its industrial-scale application in the cement industry has been tested worldwide only on a single rotary kiln system in Germany to date (high-dust method). The Federal Environmental Office supported the execution of the project. Up to now, the plant has substantially been run in such a way as to allow an NO_x emission concentration of 500 mg/m^3 to be complied with. The Federal Environmental Office is yet to summarise the results and evaluate the project. More precisely speaking, it is not clear whether the catalyst will prove its worth in continuous operation over many years. The underlying economic conditions constitute an essential criterion for evaluating a process in accordance with the IPPC Directive (96/61/EC, Integrated Pollution Prevention and Control). For that reason, VDZ's "NO_x abatement" working group drew up a current estimate of the cost accruing both for the SCR and the SNCR process.

The calculations were done for 4 kiln plants of different capacity (1 500 / 2 500 / 3 500 / 5 000 t/d). Accordingly, the specific costs (capital costs and operating costs) range between 1.0 and 1.9 € / t clinker depending on the NO_x starting level, the reduction rate and the kiln capacity. By contrast, the specific costs calculated for the SNCR process ranged between 0.5 and 0.7 € / t clinker (or less, e.g. if inexpensive reducing agents are used).

The EU Commission initiated the process of amending the BAT Reference Documents (BREF Documents) in early 2005. The corresponding BREF Document for the cement and lime industries will be one of the first codes to be revised. In the current document (as of December 2001), the panel of experts did not reach a consensus on the classification of the SCR process. For that reason, SCR cannot be regarded as a best available technique pursuant to the European IPPC directive yet. It remains to be seen which result the discussions on the SCR process scheduled to be held in conjunction with the amendment of the BREF Document now will yield. It is a fact, however, that the costs incurred by an SCR plant will be significantly higher than those for non-catalytic nitrogen oxide reduction according to present knowledge. Moreover, verifiable long-term experience has yet to be gathered.

Raw material-related SO_2 emissions

The SO_2 emissions from rotary kilns in the cement industry have been known for many years to be chiefly attributable to inorganic, highly volatile sulphur compounds, which decompose to form SO_2 at temperatures of approx. 400 °C when the kiln meal is fed to the plant. These pyrites and marcasites can be assumed to decompose completely at first. Mass balance investigations have shown, however, that varying proportions of the SO_2 thus released are fixed again in the preheater or in downstream parts of the kiln system.

Operational parameters can be excluded under laboratory conditions. **Fig. II-19** summarises the results of laboratory investigations on the degasification from different technical kiln meals (gas atmosphere: 30 % CO_2, 2.5 % O_2, remainder N_2) carried out by the Research Institute. The

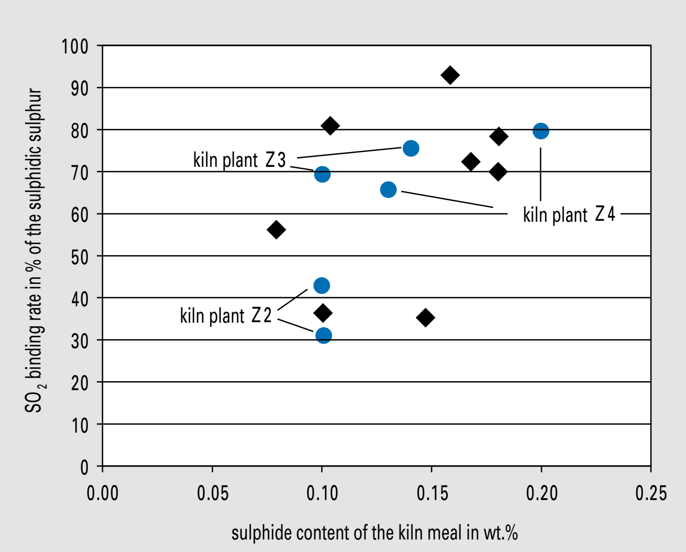
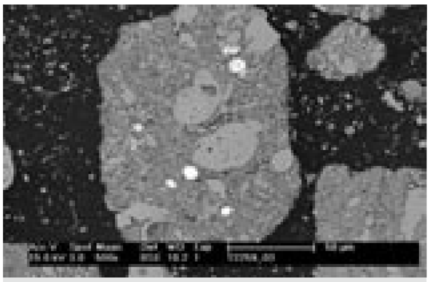


Fig. II-20: Influence of the sulphide content in the kiln meal on SO_2 binding

Tab. II-5: Sulphur contents of the kiln meals investigated

Sulphur species	Unit	Kiln meal			
		Z2	Z4	Z5	R1
Sulphate	wt.% SO_3	0.15	0.23	0.31	0.10
Sulphide		0.38	0.55	0.48	0.30
Sulphite		0.03	0.03	0.04	0.01
Total sulphur		0.56	0.81	0.83	0.41



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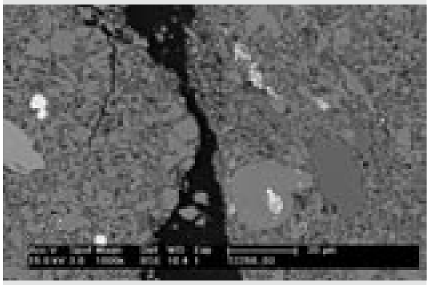

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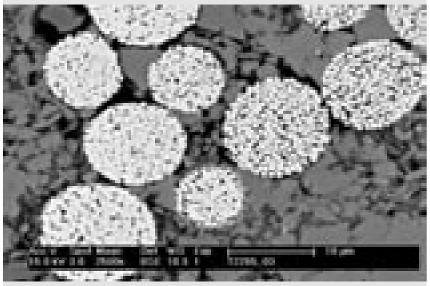

2500-fold magnification

Fig. II-21: Sulphide distribution in kiln meal Z2

Figure depicts the proportion of sulphidic sulphur measured as SO_2 after a laboratory kiln, when the kiln meal has been heated to 1 000 °C by the ambient temperature. In the following, this proportion will be referred to as the "release rate", while the proportion not liberated or emitted, respectively, will be called "binding rate". It becomes evident from Fig. II-19 that a relationship between the SO_2 release rate and the sulphide content of the kiln meal (given as SO_2 here) does exist under laboratory conditions. What is striking is the fact that none of the meals investigated released 100% of the oxidisable sulphidic sulphur under the reaction conditions prevailing. With most meals, the quantity of SO_2 released fluctuated between 45 and 80%. Emitting a proportion of a mere 5%, a kiln meal having a comparatively low sulphidic sulphur content stands out significantly from the other meals. The low SO_2 release from this meal might indicate that a certain minimum portion of SO_2 is fixed again directly by the other kiln meal constituents, i.e. already in the particle.

The results of mass balance investigations carried out by the Research Institute show, however, that such a relationship cannot be identified under practical operating conditions. **Fig. II-20** summarises the results of such mass balance investigations. The Figure depicts results obtained at different kiln plants in which kiln meals with different sulphide contents are processed, showing the binding rate for the various kiln meals from different plants. Between 30 and 90% of the sulphidic sulphur available was found to be fixed again directly under practical operating conditions. This corresponds to a release rate of between 10 and 70%.

The extent to which the kiln meals differ in terms of the presence and the distribution of sulphides was the subject of subsequent investigations. The sulphur contents of the kiln meals investigated, which were classified by the bond type of the sulphur, are shown in **Tab. II-5**. As the supply of reaction surface differs depending on the place where the sulphides are oxidised, it is conceivable that varying portions of SO_2 are fixed again directly.

Figs. II-21 to **II-24** show scanning electron microscope (SEM) pictures of polished sections of the meals investigated. As their mean atomic number is higher than that of the kiln meal matrix, the iron sulphides appear as nearly white areas in this mode. The details shown in the pictures were selected so as to capture the manifestations of the iron sulphides typical of the respective meals. The sulphides contained in kiln meal Z2 (Fig. II-21) almost exclusively occur inside porous kiln meal particles. For the most part, globular iron sulphide agglomerations having a diameter of up to 10 µm are discernible. It becomes apparent at higher magnification that these agglomerations are made up of a plurality of idiomorphously crystallised little pyrite crystals. The particle size of these crystals falls short of 1 µm. This kind of pyrite represents so-called "mineralised bacteria".

Fig. II-22 shows the SEM pictures of kiln meal Z4. The manifestation of the sulphides present in kiln meal Z4 is comparable to those found in kiln meal Z2. The globular agglomerations made up of small pyrite crystals predominate here as well. In contrast to kiln meal Z2, however, they chiefly occur near the edges of the kiln meal particles. Moreover, individual particles that exclusively contain sulphides and occur separately in the meal are discernible. On the whole, the kiln meal particles are less porous than those of kiln meal Z2.

Like in the kiln meals described above, globular agglomerations of small pyrite crystals are present in kiln meal Z5 (Fig. II-23). These are primarily contained round the edges of the kiln meal particles, but occasionally also inside them. Apart from that, bigger and more compact iron sulphide particles can be made out in this kiln meal. These are not intergrown with other kiln meal constituents and reach a particle size of up to 15 µm. In this meal, too, the kiln meal particles of silicate and carbonate nature display only low porosity. Like in kiln meal Z5, the iron sulphides of kiln meal R1 are present both as agglomerations of small pyrite crystals and as fairly large compact crystals. In this meal, the individual small pyrite crystals forming the agglomerations are arranged at a greater distance than in the other meals and are thus spread over a wider range of the kiln meal particles (Fig. II-24 on the right).

In addition to the iron sulphides described above, strontium sulphate was detected as well in kiln meals Z5 and R1 (cf. **Fig. II-25**). These crystals occur as coarse particles having a size of up to about 100 µm. It can be assumed, however, that the strontium sulphate will not decompose and thus not cause SO_2 to be released at the temperature range investigated as it does not decompose until temperatures exceed 1 200 °C.

The investigations outlined demonstrate that there are discrepancies in the manifestation of the iron sulphides in the kiln meal. These can be identified by the different particle size distributions of the sulphide particles on the one hand, and by the extent to which they are intergrown with other kiln meal constituents on the other hand. It is not possible to simply establish a direct relation between the results of these investigations and the relationship between the rate of SO_2 release and the sulphide content in raw meals depicted in Fig. II-19. In spite of that, the investigations show that both the particle structure itself (e.g. porous or dense particles) and the presence of sulphide in the kiln meal particles can differ vastly and thus have an impact on the local concentration of SO_2 during pyrite decomposition and on the diffusion by the kiln meal particles of the SO_2 thus generated.

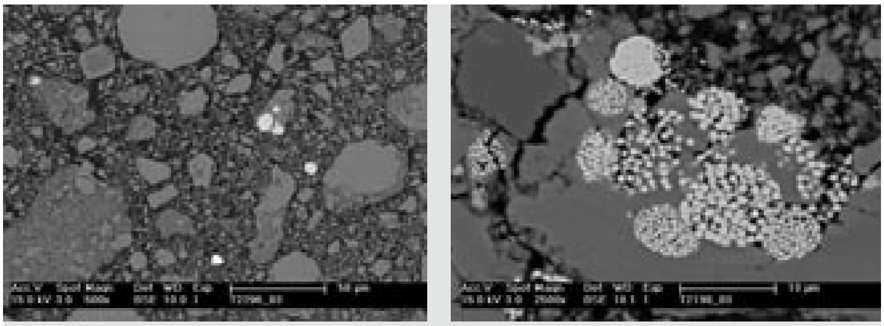
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Fig. II-22: Sulphide distribution in kiln meal Z4

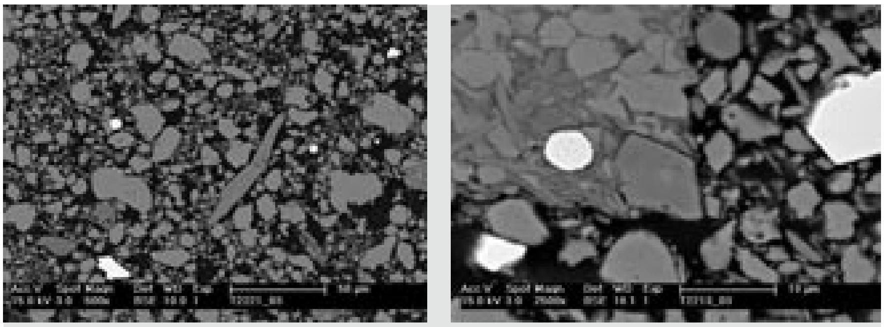
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Fig. II-23: Sulphide distribution in kiln meal Z5

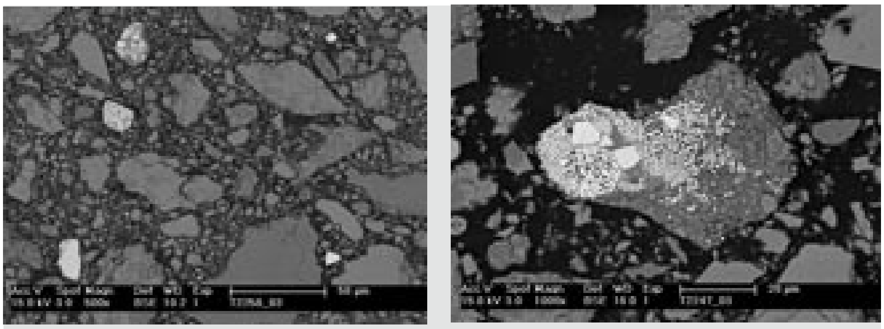
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Fig. II-24: Sulphide distribution in kiln meal R1

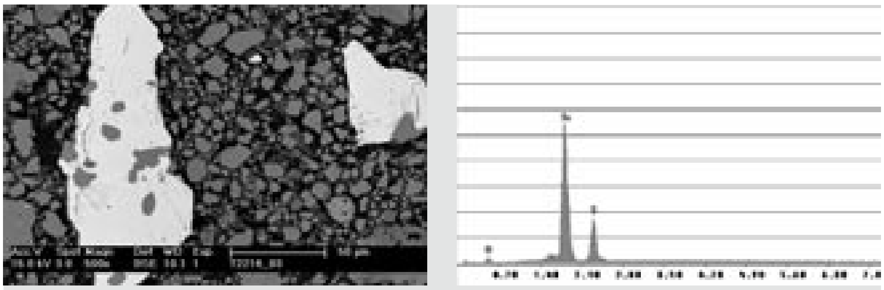
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Fig. II-25: Strontium-sulphur compounds in kiln meal Z5

Utilisation of sewage sludge in the cement industry

Until the beginning of 2001, the municipal sewage sludge in Germany was largely used in landscaping and in agriculture, respectively. This disposal solution will be severely restricted in the future for various reasons (substantially health, hygiene and environmental compatibility). This inevitably results in the search for other adequate utilisation measures. The clinker burning process presents a particularly interesting option in this context, as it allows both the energy content of the sludge and its material content to be made use of. Because of these advantageous features, municipal sewage sludge has been utilised in cement works for quite some time in Switzerland, for example.

In addition to cement works, also (lignite) power stations, single-material combustion plants dedicated to sewage sludge, and occasionally also waste incinerators are basically eligible for utilising the thermal content of municipal sewage sludge in Germany. The national quantity of municipal sewage sludge ranges between approximately 2.3 and 2.5 million t of dry substance annually. A current compilation of data from the power plant industry revealed that the energy suppliers operating in Germany have capacities for co-incinerating municipal sewage sludge to an order of magnitude of some 1.3 to 1.5 million t annually. If the other incineration capacities enumerated above (single-material combustion plants, waste incinerators) are taken into account, this leaves about 300 000 t of dry substance for which national disposal solutions will have to be found.

From an environmental point of view, the trace elements, and most particularly mercury, play a significant role in the utilisation of sewage sludge in the rotary kilns of the cement industry. According to recent analyses, the mercury contents of sewage sludge average between 0.8 and 1.2 mg/kg. Higher values may, however, occur in individual charges. Several independent trials showed that rotary cement kilns allow the environmentally compatible and harmless utilisation of municipal sewage sludge. The industrial trials demonstrated that the limit values laid down in the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV) can be safely complied with.

Up to now, virtually all municipal sewage sludge utilised in the rotary kiln systems of the German cement industry had been thermally dried (more than 95% dry substance [DS]). In general, the granules produced during this drying process can be fed into the system via ordinary metering units without any problems. However, the thermal drying of municipal sewage sludge involves enormous technical effort. In addition to that, many smaller sewage treatment works, and especially those located in rural areas, are not equipped with their own drying plants. For that reason, the alternative of utilising sludges that have been dewatered mechanically in the rotary kilns of the cement industry is being given first consideration presently. This would, however, call for further changes, e.g. in the metering devices used. Furthermore, these mechanically dewatered sludges will entail further challenges, for example in connection with health protection and hygiene.

Status of continuous mercury emission measurement

Pursuant to an amendment of the 17th Federal Ambient Pollution Protection Regulation (17th BImSchV) dating from 1999, the continuous measurement of mercury emissions from waste incinerators and co-combustion plants is mandatory. Since then, an increasing number of continuously operating instruments for mercury emission measurement have been installed in the rotary kiln plants of the cement industry. It turned out that such a measuring instrument cannot necessarily be employed at any rotary kiln plant for reliable emission monitoring even though it underwent suitability testing. Although most of the factors possibly causing problems with the equipment are well-known by now, it is still not possible to principally predict whether a certain instrument can be applied in a rotary kiln. Much rather, this still requires an individual test. In spite of that, a large number of rotary kilns in the German cement industry have been provided with calibrated, continuously operating mercury emission measuring equipment in the meantime.

Mercury emission measuring equipment has a modular structure. Its gas-wetted units include the chimney probe, the dust filter, the heated gas sampling duct, the reducing stage and the analyser. Two types of measuring instruments are applied in principle. With the so-called thermo-catalytic instruments, the mercury compounds in the sampled gas are reduced with the aid of a heated fixed bed catalyst. By contrast, the so-called wet chemical instruments comprise a reaction stage with a liquid reducing agent (usually tin (II) chloride). Photometers are used in all instrument types to detect elemental, i.e. fully reduced mercury. For that reason, the complete reduction of the mercury compounds present in the sampled gas constitutes an indispensable prerequisite for the continuous measurement of mercury emissions. At present, the cement industry preferably employs instruments with a thermocatalytic reducing stage. This has mainly practical reasons, as the handling of chemicals can be dispensed with. Depending on the exhaust gas composition it may, however, be necessary to use wet chemical equipment that is less sensitive to certain interferents in the exhaust gas matrix.

The measuring sensitivity of mercury emission measuring equipment is significantly higher than that of ordinary measuring instruments e.g. used for NO_x, SO_2 or TOC measurement. Accordingly, the performance of Hg measuring and testing technology is subject to high quality requirements. To meet the requirements for the linearity of the characteristic curve as well as the zero drift and the span drift, the quality of the equipment components and the kind of reactants or catalysts used must be such as to enable them to withstand the continuous stress during measuring operation. In practical application it became necessary in individual cases to modify the measuring instrument at the chimney after a trial phase of several weeks in order to fine-tune it with the particular exhaust gas composition of the emission source.

Such modifications for example included the installation of a high-flux bypass to minimise the wall effects in excessively long gas sampling ducts between the chimney and the measuring instrument. In other cases, rinsing options were installed to clean the path of the sampled gas from salt-type deposits. Tin oxide precipitations occurring occasionally were to be prevented by modifying the reducing solution.

In order to allow the reliable continuous measurement of mercury emissions from a rotary kiln system, the corresponding instrument must be calibrated first. Most of the instruments – some of them after undergoing a site-specific modification in advance – have turned out by now to meet the minimum requirements placed on the calibratability of automatic measuring equipment. However, there is also a number of cases in which the reliable continuous monitoring of mercury emissions is still not possible. The Research Institute of the Cement Industry is cooperating with instrument manufacturers and plant operators to solve the problems that still exist in this context.

In addition to the influence that variations in exhaust gas composition can have, also deposits in gas sampling ducts (presumably sublimated ammonium salts) caused the measuring instruments to display indication errors at several sites. These difficulties were, however, remedied in most cases by adequately modifying the instruments. Moreover, the performance of the thermocatalytic equipment in particular was enhanced in individual cases by increasing the catalyst temperature.

The diligent execution of equipment maintenance, regular performance tests and calibration represent an essential precondition for ensuring the long-term use of continuous mercury emission measuring technology. In performance testing in particular, attention should be paid that the entire measuring instrument is swept both by elemental and ionic mercury test gas if possible. In this way a quick statement on the principal operability of the measuring equipment can be made without costly comparison measurements.

Initial results of the speciation of Hg emissions

The mercury present in the exhaust gas of incineration plants, i.e. also in the exhaust gas of the rotary kilns of the cement industry, exhibits different types of bond. Investigations carried out at incineration plants revealed that mercury is primarily emitted from there as elemental gaseous mercury (Hg^0) and combined gaseous mercury chloride ($HgCl_2$).

Fig. II-26: Basic working principle of a continuous mercury measuring instrument

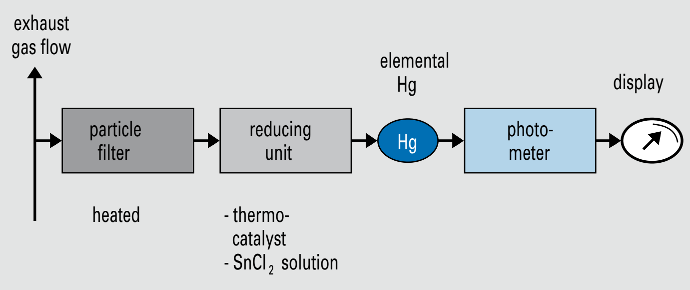
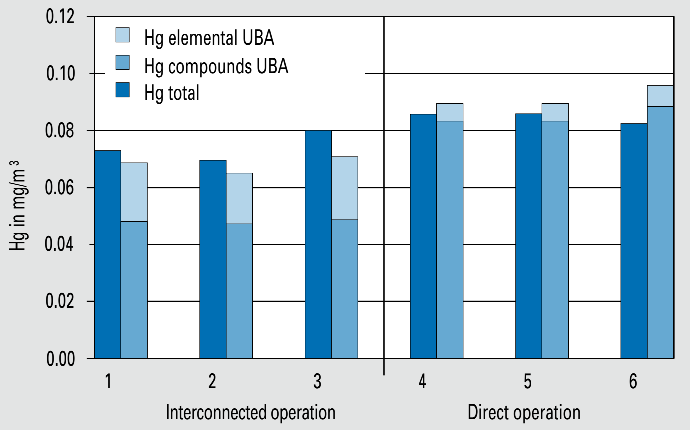


Fig. II-27: Results of speciation investigations at a rotary kiln plant



The occurrence of mercury in different types of bond is a major cause for the difficulties associated with continuous mercury measurement (see paragraph on the left). The photometer employed for detection can only record elemental mercury. The mercury compounds therefore have to be converted to elemental mercury in an upstream stage referred to as reducing unit. The instruments currently available on the market utilise a thermocatalyst or tin(II) chloride solution for reduction (**Fig. II-26**). The composition of the exhaust gas matrix can considerably lessen the effectiveness of the reducing unit. In that case, continuous mercury measurement can only be conducted after the measuring equipment has undergone a modification tailored to that very case.

In addition to measuring the total mercury concentration, discontinuous measuring methods are therefore applied as well. These allow elemental mercury (Hg^0) and combined mercury ($HgCl_2$) to be determined separately. The break-down of the total mercury concentration is obtained on the basis of a process developed by the Federal Environmental Office (UBA) pursuant to which a wash bottle with diluted hydrochloric acid arranged upstream collects combined mercury ($HgCl_2$) exclusively. The wash bottle arranged downstream contains potassium permanganate as an adsorbent and primarily collects the elemental mercury from the sampled gas flow.

The results of investigations carried out at a rotary kiln plant are shown in **Fig. II-27**. Three measurements each were conducted during interconnected and direct operation. These included both the determination of the total mercury concentration according to VDI 3868, Sheet 2, and the speciation pursuant to the UBA method. The results yielded good conformity of the total mercury determination and the sum of elemental and combined mercury pursuant to the UBA method. At this kiln plant, the share of combined mercury predominates in interconnected and direct operation. The proportion of elemental mercury is substantially smaller in direct operation than in interconnected operation. One possible cause of this is the fact that elemental mercury bound by "fresh" raw material is immediately released at the temperatures in the raw mill without entering the subsequent process. Since the precipitation of elemental mercury on dust particles is inferior to that of combined $HgCl_2$, further investigations will place their main focus on finding out to what extent the type of bond of the mercury influences the precipitation conditions in the electrostatic precipitator. Moreover, it must be examined whether the present result can be transferred to other kiln plants.

III

Performance of cement

The influence phosphate can have on clinker performance formed one of the key research topics in the period under review. Since the ban on feeding meat and bone meal was passed in the year 2000, the thermal content of meat and bone meal has been utilised in German cement works on a major scale. This entails input of phosphate into the clinker. The Research Institute conducted extensive investigations on the effects of elevated phosphate contents on product quality. The investigations primarily concentrated on clinker mineralogy, setting behaviour and strength development.

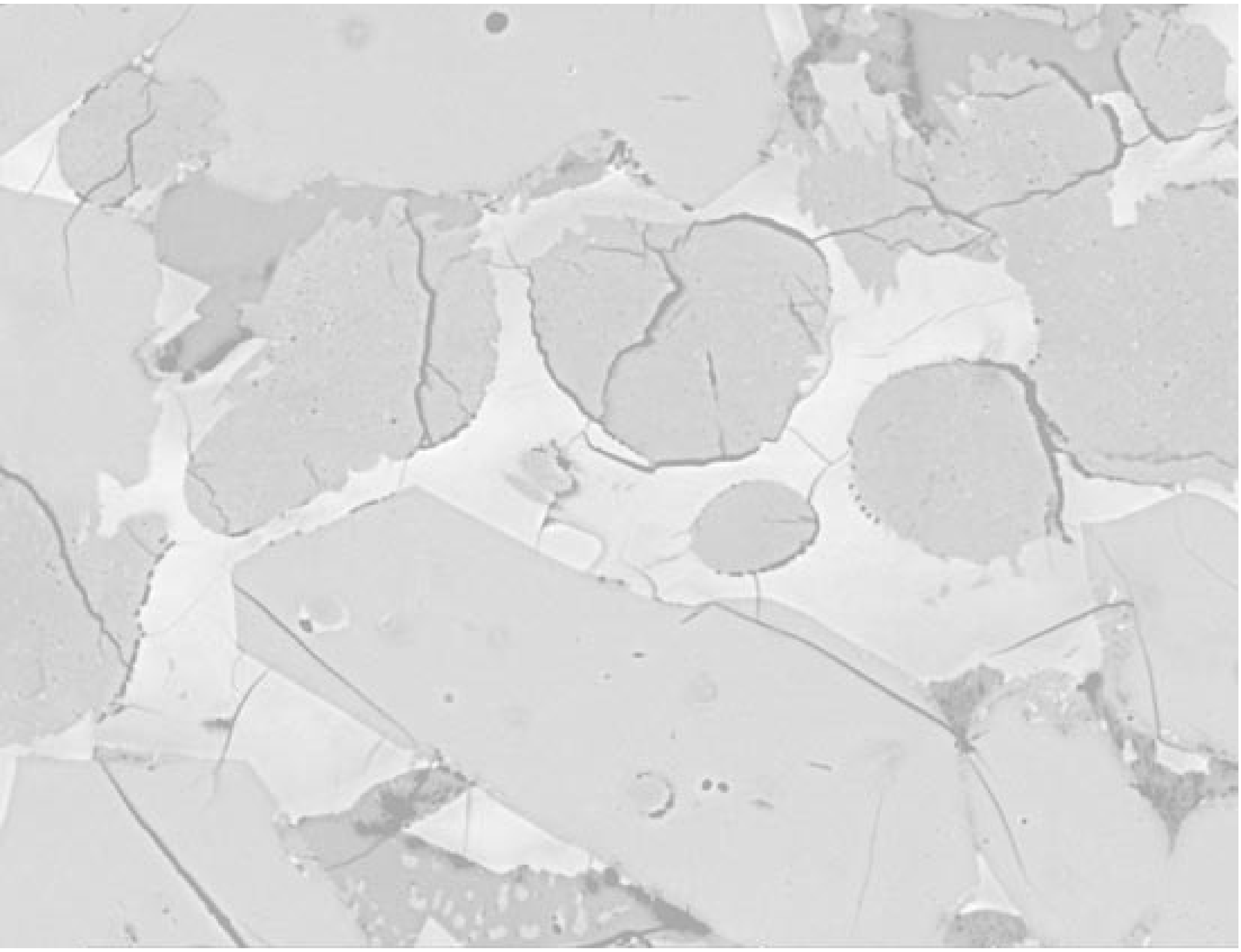
The performance of cements with several main constituents formed the subject of various research activities. The work on the relationship between the chemical reactivity of blastfurnace slags and their influence on the compressive strength development of cement was intensified. Contrary to previous assumptions, the results obtained by the Research Institute show that the use of blastfurnace slags of low chemical reactivity in particular allows to achieve high compressive strengths. The performance of cements with several main constituents is known to depend not only on reactivity, but also on the grinding fineness of the different constituents. Investigations on separately ground cements containing blastfurnace slag were carried out in this context.

The investigations on the influence of various main cement constituents on the effective alkali content of the cement were continued in the period under review. The objective of these investigations was to identify the chemico-mineralogical processes causing alkali binding and to evaluate the stability of the bond.

The development of new methods of measuring and testing as well as standardisation constituted another area of work. The Research Institute was decisively involved in the development of a new European testing method for the determination of water-soluble chromate in cements and cementitious preparations (prEN 196-10). The analytical details of the final test standard are currently still being discussed. The Research Institute is also involved in the development of the cement test standard (EN 196-2.2), which is expected to be finalised in 2005.

Since Mid-2003, the Research Institute has a TAM-Air model isothermal heat flow calorimeter at its disposal. Current investigations aim to find out whether heat flow calorimetry is a suitable alternative to the heat of solution method. Another topic the Research Institute was concerned with was the development of quick tests for determining the sulphate resistance of cements. The evaluation of numerous test results shows that the existing quick tests yield verifiable results only for the differentiation of the chemical sulphate resistance of Portland cements, but not for cement/fly ash mixes.

Backscattered electron image of a polished clinker section



Chemico-mineralogical composition

In the wake of the introduction of EN 197-1, a plurality of cements of different composition have been standardised Europe-wide. Since then, the number of cements applied for or approved by the building inspectorate, respectively, has risen in Germany as well. These particularly include cements having more than two main constituents. Primarily the cements CEM II/M(S-LL), CEM II/M(V-LL), as well as CEM IV and CEM V containing blastfurnace slag, natural pozzolana or siliceous fly ashes have gained a foothold in the German market.

Against this backdrop, the methods for the quantitative determination of cement constituents have been advanced. The method of selective dissolution has been laid down as the reference method for cements with several main constituents in test standard DIN V ENV 196-4. If the cement constituents are available separately, an alternative method of calculating the cement composition can be applied. It is based on the determination of a set of chemical compounds, each of which should be characteristic of one of the constituents. The analysis of the cement and its constituents is carried out by means of X-ray fluorescence. The contents of clinker and other constituents in the cement can then be calculated on the basis of the chemical compositions of the individual materials by solving a linear equation system. Adequate homogeneity of the materials analysed is a prerequisite for the reliability of this method.

Up to now, a combined microscopic and chemical method was applied to determine the blastfurnace slag content of Portland-slag cements (CEM II/S) and blastfurnace cements (CEM III) as part of quality surveillance. Since, however, the separate grinding and subsequent mixing of clinker and blastfurnace slag is increasingly becoming common practice, the Research Institute has had to apply the more laborious reference method of selective dissolution more frequently again. With cements the constituents of which were ground separately, blastfurnace slag counting in the 30-40 µm fraction by microscope does not always reflect the correct composition. Clinker and blastfurnace slag can build up in different grain fractions. The grinding fineness of the individual constituents often differs so substantially that it cannot even be captured by subsequent mathematical correction. With selective dissolution, by contrast, uncertainties will presumably not occur unless the cement constituents exhibit a dissolution behaviour that deviates from theory. This applies to blastfurnace slag containing several wt.% of crystalline phases, for example.

Tab. III-1: Chemical composition of the blastfurnace slags (given in wt.%, including loss on ignition)

	HS A	HS B	HS C	HS D	HS E
SiO_2	32.96	31.96	35.09	35.90	38.01
Al_2O_3	14.78	17.43	11.33	10.83	9.21
TiO_2	0.58	0.99	1.39	0.87	0.33
P_2O_5	0.18	< 0.01	< 0.01	< 0.01	< 0.01
Fe_2O_3	0.37	0.41	1.33	0.44	0.29
Mn_2O_3	0.57	0.47	0.36	0.57	1.18
CaO	44.58	36.06	40.31	37.75	38.02
MgO	4.19	10.84	7.88	11.05	10.58
SO_3	0.28	< 0.01	< 0.01	< 0.01	< 0.01
K_2O	0.62	0.45	0.63	0.78	1.03
Na_2O	0.39	0.42	0.42	0.47	0.39
CO_2	0.13	0.17	0.24	0.22	0.20
H_2O	0.08	0.11	0.24	0.33	0.11
S^{2-}	0.58	1.29	1.40	1.47	1.22

Reactivity of blastfurnace slags

The use of blastfurnace cements has proved its worth in the building industry for many decades. As they generate low heat of hydration during the hydration process, their utilisation in the manufacture of bulky concrete elements is advantageous. As their proportion of cement clinker and thus also of C_3A is lower than that of Portland cements, blastfurnace cements are further often assigned to the group of sulphate-resisting cements. Their strength development is, however, slower than that of Portland cement, especially in the early hydration phases.

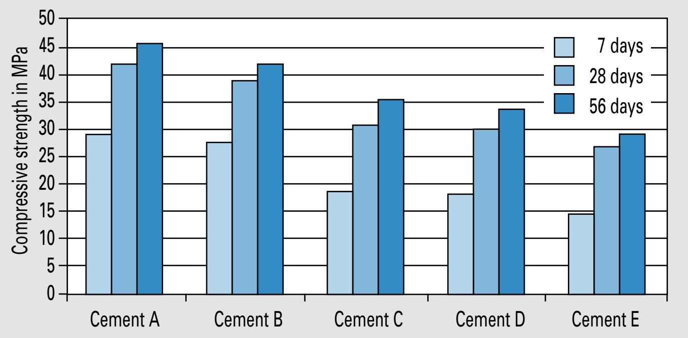
Understanding of the chemical reactivity of blastfurnace slags and of its impact on the physical properties of corresponding cement-bound building materials is indispensable for the purposeful and efficient utilisation of cements containing blastfurnace slags. Previous research activities almost exclusively proceeded from the assumption that the strength development of blastfurnace cement-bound building materials and the chemical reactivity of the blastfurnace slags contained were proportional to each other. Current research activities by the Research Institute of the Cement Industry, however, suggest the very opposite. Accordingly, high-performance blastfurnace slags exhibit rather restrained chemical reactions in terms of compressive strength development. By contrast, low-performance blastfurnace slags react more rapidly in an aqueous medium and combine more water. In this process, the latter form clearly differentiated strata in their outer zones penetrated by water. The aluminium portion still available after dominant early reactions – especially with magnesium – plays a key role in the hydration of blastfurnace slags. This aluminium portion may form compounds that reduce the velocity of further water absorption and thus that of the progress of hydration. It becomes apparent from the pertinent scientific work of the Research Institute of the Cement Industry that the extent of glass corrosion is also closely related to the sulphate resources of the cement undergoing hydration. Ettringite formation may be playing a key role in this process.

What does "reactivity" of blastfurnace slag mean?

Up to now, the reactivity of blastfurnace slag has almost exclusively been defined via the strength development of blastfurnace cement-bound building materials. A blastfurnace slag that results in high standard compressive strengths of cement when used as a cement constituent is called a "reactive" blastfurnace slag. Rapid strength development is equated with rapid chemical reaction of the blastfurnace slag. During the compressive strength test it is, however, not the chemical reactivity, i.e. the degree of hydration of blastfurnace slag as a cement constituent, that is determined, but the compressive capacity of the entire standard mortar microstructure. The compressive load is borne by the aggregates (sand, gravel) present in the mortar and concrete, respectively, as components of largely negligible chemical reactivity. This gives rise to the question of whether the chemical reactivity of blastfurnace slags in aqueous media is actually proportional to the strength development of the corresponding blastfurnace cements. The Research Institute of the Cement Industry investigated 5 vastly different blastfurnace slags (**Tab. III-1**) under this aspect. These blastfurnace slags HS A to E were ground to a fineness of approx. 3 700 cm²/g according to Blaine. Corresponding blastfurnace cements (cements A to E) were manufactured by mixing the blastfurnace slags (65.00%) with Portland cement (PZ; 29.76%), gypsum (G; 2.67%) and anhydrite (A; 2.67%) (**Fig. III-1**). The new research results obtained actually reveal that blastfurnace slags of high technical performance are rather inert chemically.

For that reason, the measures taken to enhance the performance of blastfurnace slags, such as finer grinding and “chemical stimulation” may be technically effective, but misunderstood from a mechanistic perspective. Under these preconditions, the “trial and error” method is the only way of optimising the product and maintaining the technical performance characteristics of blastfurnace cements even though the chemical properties of blastfurnace slag may vary. Understanding of the correlation between the chemical reactions of the blastfurnace slag in concert with the other constituents of blastfurnace cement is therefore of outstanding importance for purposeful and goal-oriented manufacture of blastfurnace cement.

Fig. III-1: Standard compressive strength of the 5 blastfurnace cements according to EN 196-1 after 7, 28 and 56 days



Tab. III-2: Water absorption of the blastfurnace slags after 7-day shaking in de-ionised water and pH value of the aqueous extract

	HS A	HS B	HS C	HS D	HS E
Blasfurnace slag in suspension (g)	400	400	400	400	400
Water supply (g)	800	800	800	800	800
Water reclaimed (g)	673	507	536	407	213
Water adsorbed (g)*)	125	282	262	383	565
Water absorbed (g)	2	11	2	10	22
pH value of the suspension after 7 days	11.67	12.64	11.99	12.60	12.69

*) Water vaporable at 40 °C (gel water and physically adsorbed water)

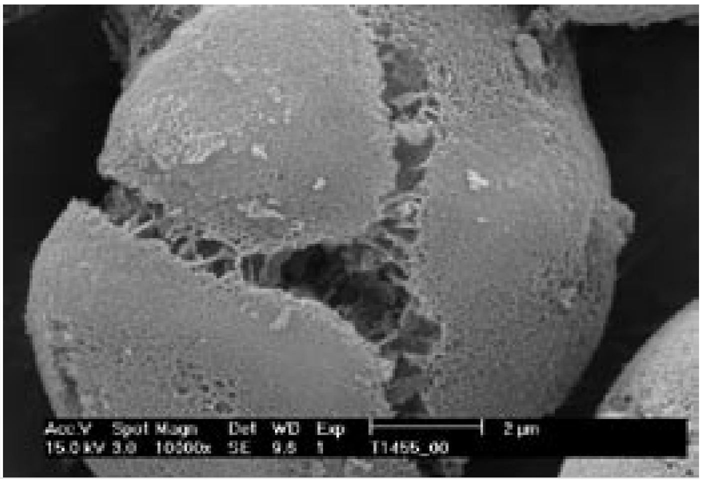


Fig. III-2: SEM photograph of ground blastfurnace slag HS D after 7-day suspension in water (at 10 000-fold magnification).

“Low-performance” blastfurnace slag is of higher chemical reactivity

Even in pure water, blastfurnace cements that display inferior performance with regard to the compressive strength development of corresponding blastfurnace cements show a significantly more pronounced chemical reaction than high-performance blastfurnace slags. This becomes very clear from the different water absorption that the blastfurnace slags exhibit when they are suspended in demineralised water (**Tab. III-2**). In the case of blastfurnace slag HS E, the water retained in the filter cake after vacuum filtration of the suspensions totals about 150% of the slag’s own mass, while this figure amounts to a mere 30% in the case of HS A. The suspensions of blastfurnace slags D and E emit a strong odour of hydrogen sulfide and are coloured green-blue. Neither of these attributes applies to the other blastfurnace slags.

The different water absorption of the blastfurnace slags is reflected by the surface modifications of the suspended blastfurnace slag particles, which are clearly discernible under the scanning electron microscope. The shaking of the suspensions caused the blastfurnace slag grains to rub against each other. As a consequence, the grain surfaces of blastfurnace slags HS D and HS E were rounded considerably (**Fig. III-2**). By contrast, the blastfurnace slags generating high standard compressive strengths in cement displayed either slight changes (HS B) or no changes at all (HS A) (**Fig. III-3**).

After 7-day suspension, the polished sections of the ground blastfurnace slags embedded in resin which were examined under the scanning electron microscope showed that the water in the suspension filter cake had not only been adsorbed physically, but chemically in hydrous gel rims (**Fig. III-4**).

Fig. III-3: SEM photograph of ground blastfurnace slag HS A after 7-day suspension in water (at 10 000-fold magnification)

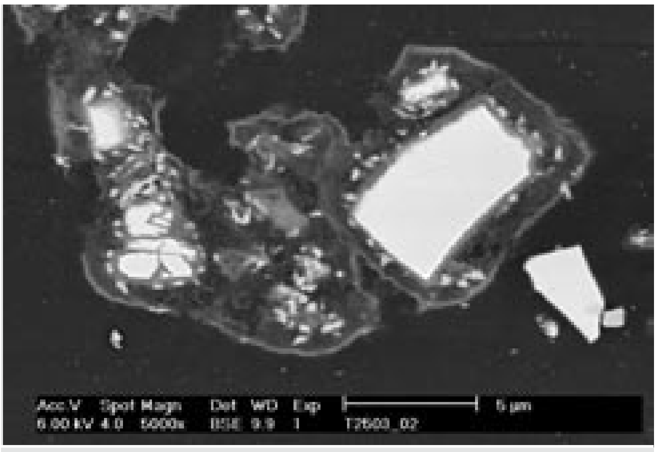


Fig. III-4: SEM photograph of a polished specimen of the ground blastfurnace slag HS D after 7-day suspension in water (at 5 000-fold magnification)

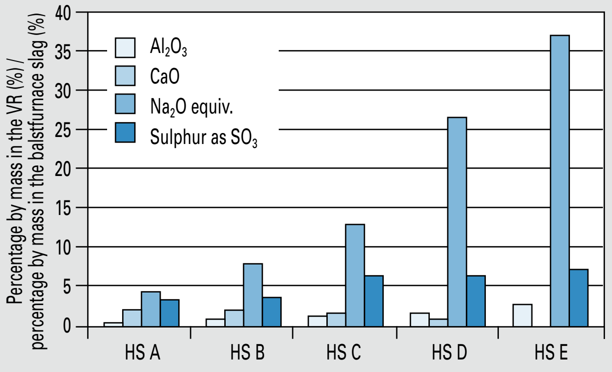


Fig. III-5: Ratio of the percentage of the element-oxide content in the vaporisation residue (VR) of the suspension filtrate and in the blastfurnace slag (loss-on-ignition-free)

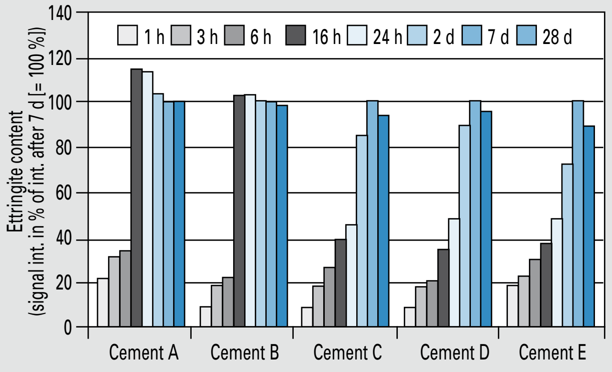


Fig. III-6: Ettringite formation in the cements investigated (X-ray diffractometry; the signal intensity of the selected ettringite reflex after 7 days was standardised to 100%)

The pH values of the suspension filtrates exhibit the same pattern as the quantity of water adsorbed chemically. The same pattern is also found in the MgO content of the blastfurnace slags. Magnesium apparently has a decisive influence on the reaction of the blastfurnace slags with water, i.e. their corrosion.

Different solubility of chemical constituents in water

Part of the aqueous filtrate from the suspensions was vaporised at 40 °C. The vaporisation residue (VR) was annealed at 960 °C and characterised chemically by means of X-ray fluorescence analysis.

As the portions of chemical constituents in the blastfurnace slags differ, it is reasonable to obtain a direct comparison of their dissolution behaviour on the basis of weighted representation. For some dissolved constituents, the ratio of their share in the evaporation residue and their total content in the blastfurnace slag is illustrated in **Fig. III-5**. The extent to which the blastfurnace slag constituents build up in the aqueous portion of the suspensions of blastfurnace slags HS A to E differs. The relative proportion of dissolved sodium and potassium increases continually along the sequence of blastfurnace slags that have been arranged in the order of their decreasing performance as a cement constituent; by contrast, the quantitiy of calcium dissolved declines continually. Magnesium is absent from the aqueous solution. In this respect, its behaviour is different from that of the homologous calcium. The high aluminium content of the blastfurnace slags is not reflected in the evaporation residues of the eluates. Only a small portion of silicon compounds is present in the solution. They can be either undissolved or have been bound once again after dissolution.

Phase development in hydrating blastfurnace cements is revealing

The formation and decomposition of crystalline phases in the hydrating cements A to E was observed by means of X-ray diffractometry. To that end, the hydration of divided samples was stopped after different time spans (1 h, 3 h, 6 h, 16 h, 24 h, 2 d, 7 d and 28 d) by adding acetone. The samples were subsequently dried upon addition of diethyl ether. The signal intensity of the individual phases obtained after the different hydration times was determined from the X-ray diffractograms and plotted against a signal intensity standardised at 100%.

Differences in the phase development chiefly occur during the formation of ettringite and the decomposition of gypsum. In the case of cements A and B, the formation of gypsum skyrocketed between 6 h and 16 h (**Fig. III-6**). With cements C and D, the even pace in ettringite formation observed initially was followed by a slightly accelerated formation between 24 h and 2 d. With cement E, the rise in the ettringite content was largely constant over the 7 d period.

The development of the gypsum content in the hydrating blastfurnace cements is inversely proportional to their ettringite

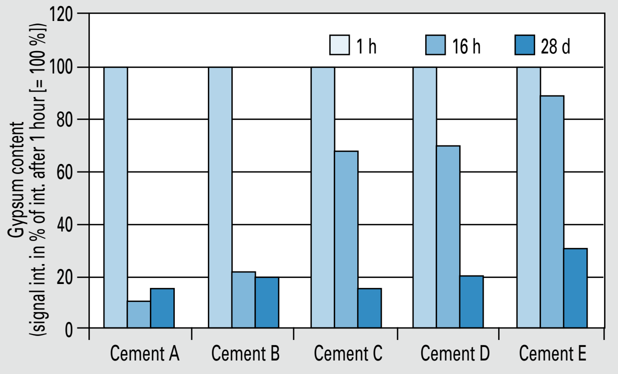


Fig. III-7: Change in the gypsum content of the cements investigated after 1 and 16 hours as well as 28 days (X-ray diffractometry)

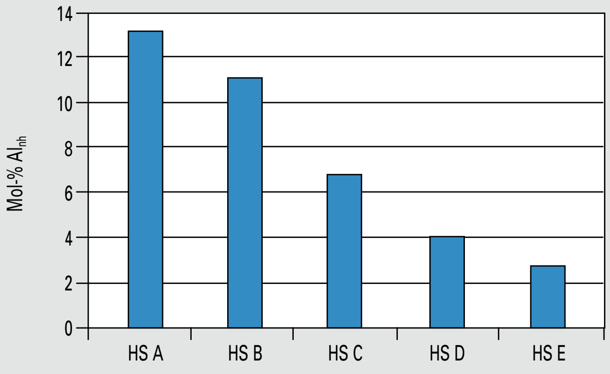


Fig. III-8: Calculated portion (in mol-%) of the aluminium of blastfurnace slags HS A to E which is not required for the formation of hydrotalcite (Al_{nh})

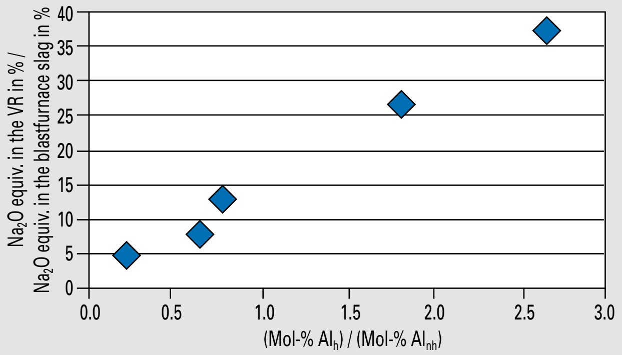


Fig. III-9: Relationship between the relative dissolved alkali content (Na_2O equivalent) of the blastfurnace slags and the ratio of the aluminium portions of the blastfurnace slags bound and not bound by the hydrotalcite

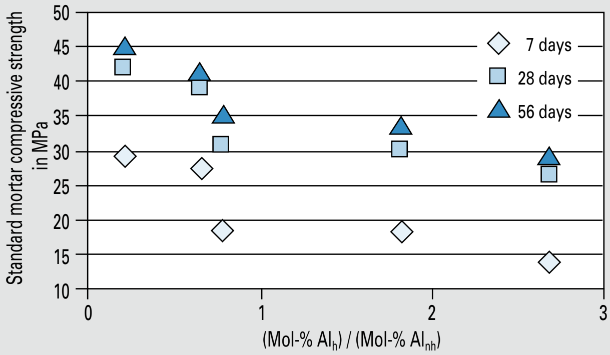


Fig. III-10: Relationship between the standard mortar compressive strength (EN 196-1) of blastfurnace cements and the ratio of the aluminium portions of the blastfurnace slags combined and not combined by the hydrotalcite

content. The gypsum content of cements A and B after 16 hours is significantly lower than that of the other blastfurnace cements (**Fig. III-7**) since the increased ettringite formation uses up dissolved sulphate, thus promoting gypsum decomposition. Accordingly, the gypsum content present in cements C and D after the same hydration period is higher than that of the two cements mentioned before. Moreover, cements C and D are nearly identical in terms of their gypsum content. These cements further conformed with regard to the standard cement compressive strength after 7 and 28 days of hydration.

The role of magnesium and aluminium

The observations described above have conveyed a new picture of the significance of the chemical reactions the blastfurnace slags undergo during the hydration of the corresponding blastfurnace cements. Water is absorbed by the blastfurnace slags. It penetrates the blastfurnace slag glass structure and releases highly soluble constituents, such as alkalis, from the blastfurnace slag glass. The quantity of alkalis being released from the vitreous structure penetrated by water is proportional to the water penetration depth. Magnesium obviously characterises the reactivity of the blastfurnace slags with water (see above). Publications state that magnesium is preferably incorporated into the hydrotalcite-type phase $[Mg_4Al_2(OH)_{14} \cdot 3\,H_2O]$ together with aluminium. Only part of the aluminium contained in the blastfurnace slags (Al_h) is used up in this dominant reaction. Like with other glasses, the aluminium portion not consumed (Al_{nh}) is available for reactions inhibiting glass corrosion, which impede the formation of the hydrotalcite-type phase. Using the chemical formula for the hydrotalcite-type phase $[Mg_4Al_2(OH)_{14} \cdot 3\,H_2O]$ in mol%, the corrosion-inhibiting aluminium portion can be calculated to mol% Al_{nh} = mol% Al_{total} – 0.5 mol% Mgtotal. It decreases continually from HS A to HS E (**Fig. III-8**).

As a consequence, the thickness of the corroded glass layer and thus also the quantity of alkalis released does not only depend on the quantity of water absorbed, but is more in particular proportional to the ratio of the aluminium portion that is combined in the form of the hydrotalcite-type phase (mol% Al_h = 0.5 mol% Mg_{total}), and the aluminium portion that is still available for the formation of corrosion-inhibiting reaction products (mol% Al_{nh}) after the formation of hydrotalcite (**Fig. III-9**).

Cement standard compressive strength is, however, proportional to the mol% Al_h / mol% Al_{nh} ratio in only 4 of the 5 blastfurnace cements. This relationship does not apply to blastfurnace slag HS C (**Fig. III-10**).

The corrosion-inhibiting aluminium portion in blastfurnace slag C might have been reduced by the formation of other compounds. This corrosion-inhibiting aluminium portion actually available cannot be determined directly. It can, however, be bound in the wake of dominant chemical reactions, such as ettringite formation. In

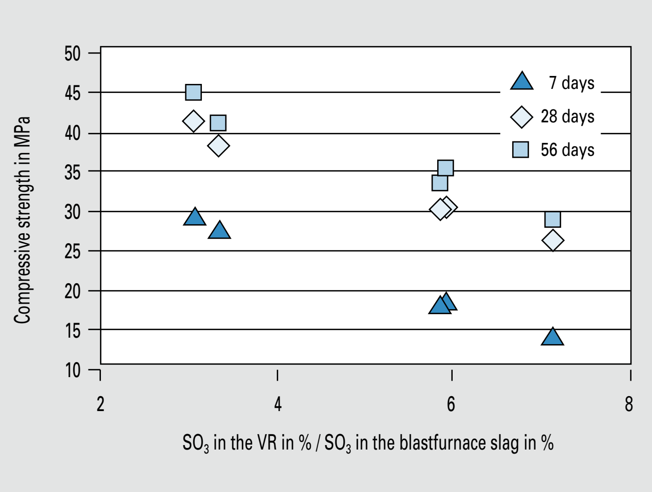


Fig. III-11: Relationship between the dissolved sulphate portion in the suspension filtrate of the blastfurnace slags and the standard cement compressive strength pursuant to EN 196 Part 3

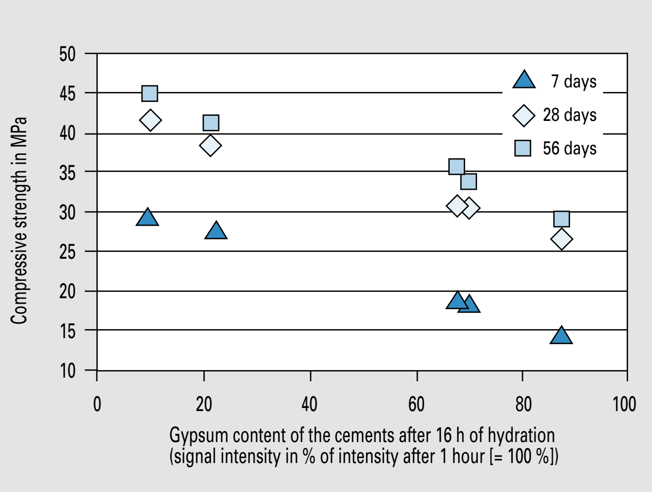


Fig. III-12: Relationship between the gypsum content of the blastfurnace cements after 16 h of hydration and the standard cement compressive strength according to EN 196 Part 1

the case of a blastfurnace slag with a higher aluminium portion available, the portion of sulphur that is not oxygenised and not bound in ettringite, for example, would have to be particularly low. The standard compressive strength of cement is inversely proportional to the (soluble) sulphur portion available in the blastfurnace slags then, which can serve as an indirect indicator of the aluminium portion actually available. This correlation actually applies to all 5 blastfurnace slags (**Fig. III-11**).

The sulphur contained in the blastfurnace slags is almost exclusively present as sulphide. To allow its being bound in ettringite, it must be oxidised first to form sulphate. The oxidation converting sulphide to sulphate is a chemical equilibrium reaction, which is boosted when the sulphate formed is consumed as a result of ettringite formation. Even when HS A and HS B are in their original state, needle-shaped ettringite can be found on their particle surfaces. The higher release of hydrogen sulphide owing to lower sulphide oxidation during the suspension of HS D and HS E is attributable to the lower aluminium proportion available in these blastfurnace slags. In the blastfurnace cements investigated, by contrast, sulphate in the form of gypsum and anhydrite was available to a markedly higher extent. In case of an increase in the formation of ettringite with the excess aluminium of the blastfurnace slags which is not required for the formation of hydrotalcite-type phases, the sulphate consumption in the blastfurnace cements investigated has to differ. The striking differences between the blastfurnace cements as far as ettringite formation after 16 hours of hydration in particular is concerned are reflected very clearly in the gypsum content of the blastfurnace cements after the same hydration time. Indirectly, this ettringite formation and the gypsum consumption clearly show the differences in the availability of aluminium in the various blastfurnace cements as well. The decomposition of a defined gypsum quantity in the blastfurnace cements investigated tallies very well with the standard compressive strength of the cements after 7, 28 and 56 days (**Fig. III-12**).

The binding of sulphate in ettringite, which acts as an indirect indicator for determining the aluminium portion available in the 5 blastfurnace slags, allows to establish a linear relationship between the reactivity of *blastfurnace slags* and the compressive strength of the corresponding *blastfurnace cements*.

Impacts of the phosphate contents on cement properties

Since the ban on feeding meat and bone meal and animal fat, which is effective for an indefinite period in Germany, was adopted at the end of 2000, some 750 000 t of meat and bone meal and some 370 000 t of animal fat have had to be disposed of annually. In the year 2003, some 452 000 t of that total were utilised as secondary fuels in cement manufacture.

The utilisation of meat and bone meal in the clinker burning process generally implies a higher phosphate input. The experience with product quality gained in practical application is largely favourable if the phosphate content in the cement clinker falls significantly short of 1 wt.%. Up to now, knowledge of the effects of higher phosphate contents on clinker mineralogy and thus on the setting behaviour and the strength development of cement was inadequate. The Research Institute of the Cement Industry therefore carried out a research project aimed at determining the fundamental working mechanisms of phosphate beyond the empirical values hitherto known.

Clinkers having a representative composition and phosphate contents of up to 8.0 wt.% P_2O_5 were burnt at the laboratory. In this process, the influence of the phosphate content on the sequence of the chemico-mineralogical reactions in relation to temperature was observed. In a next step, cements were manufactured from the clinkers and investigated with regard to their product properties. In addition to applying the usual standardised cement testing methods, particular emphasis was placed on realistic testing conditions. Interest thus also focused on the influence of temperature on cement hydration and strength development as well as the interaction with commercially available superplasticisers.

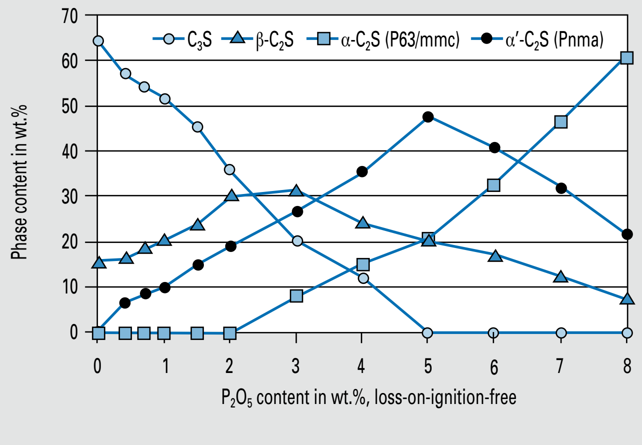


Fig. III-13: Content of silicate-nature phases in laboratory-made clinkers as a function of the phosphate content

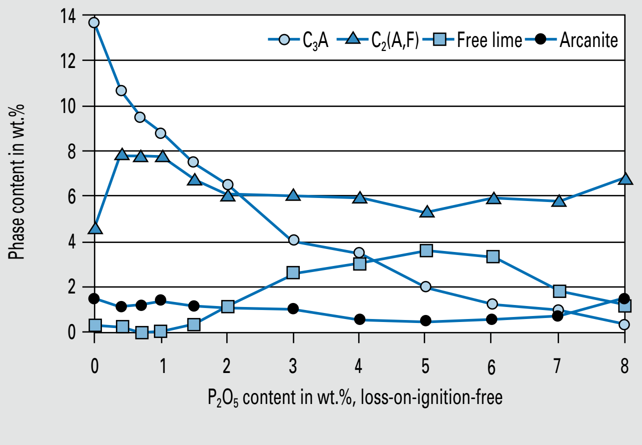


Fig. III-14: Content of additional phases in laboratory-made clinkers as a function of the phosphate content

Impact of phosphate on clinker composition

The investigations showed that phosphate takes an active part in the reactions occurring during clinker burning and shifts the stability limits of individual phases. Besides, it is so mobile as to be detected in largely even distribution throughout the cross section of the clinker granules even though it is supplied from outside. In the clinker burning process, the phosphate is first fixed by calcium in the form of hydroxyl apatite, which gets unstable at higher temperatures, reacting with silicon to form an isomorphous mixture made up of dicalcium silicate and tricalcium phosphate (C_2S-C_3P) first, which can be mixed with α-C_2S continuously. If the CaO supply is sufficient, this isomorphous mixture containing phosphate can react further to form alite containing phosphate. The viscosity of the clinker melt is diminished as a result of phosphate input, which is conducive to alite growth. As phosphate input increases, C_2S-C_3P isomorphous mixtures having a structure of α'-C_2S and α-C_2S are formed (**Fig. III-13**). These compounds allow over-stoichiometric incorporation of calcium. At phosphate contents exceeding 2 wt.% P_2O_5, the free lime content therefore rises slightly at first (**Fig. III-14**), but decreases again at phosphate contents > 5 wt.% as the share of α'-C_2S and α-C_2S grows. The share of aluminium incorporated in the dicalcium silicates is higher than that in the alite, which diminishes in line with a surge in phosphate input. On balance, the matrix phases thus decrease, with the C_3A portion being reduced in particular (Fig. III-14). The phases containing aluminate remain free of phosphate.

Influence of phosphate on product properties

The effects of a rising phosphate input into the clinker on product properties was determined using laboratory-made cements containing clinkers with P_2O_5 contents of up to 2.0 wt.%. At up to about 1.0 wt.% P_2O_5 in the clinker, early strength decreases slightly at first as a result of the reduced contents of alite and C_3A. It decreases more markedly as the phosphate content gets higher. The reduction in the alite content and the ensuing loss in early strength can be counteracted by raising the lime standard in the clinker. 28-day strength increases slightly up to 1.0 wt.% P_2O_5 and drops back to the original level of the phosphate-free reference cement by the time a P_2O_5 content of 2.0 wt.% is reached. As a result of the decline in the C_3A portion, the demand for sulphate required to ensure optimum setting behaviour decreases. If the sulphate supply remains unchanged, setting times increase initially. When the C_3A content drops further and the sulphate supply remains the same, this will lead to excess sulphatisation and the formation of secondary gypsum, which in turn shortens setting times. The investigations have shown that the incorporation of phosphate into the clinker does not primarily influence primary ettringite formation, but can impede strength development as a result of retarded formation of CSH phases. Phosphate was not found to have any influence on the effect of super-plasticisers. When polycarboxylate ether was used, for example, the effect on the hydration behaviour of the mixtures investigated was only slight both at 20 °C and at 8 °C. When, however, calcium lignin sulphonate was employed, which can have a retarding effect owing to its active ingredient, very low early strengths were observed at 8 °C. This is, however, not attributable to an interaction of the phosphate and the super-plasticisers, but simply to an additional reduction in early strength due to the phospate input into the clinker, which was observed also when no super-plasticiser had been used.

The investigations revealed that phosphate input of up to 1.0 wt.% does not have any adverse effects on clinker and cement properties. The demand for calcium, which rises as phosphate input increases, can, however, result in a decrease in the alite content in the clinker and in a reduction in the early strength of cement in particular. This influence can be diminished by raising the lime saturation factor.

Influence of the particle size distribution of main cement constituents ■

The properties of cements containing main constituents that were separately ground and subsequently mixed have been investigated systematically for some years. The main emphasis has been placed on cements containing 25, 50 and 75 wt.% blastfurnace slag (see Activity Report 2001-2003). As a rule, the cements were adjusted to a total

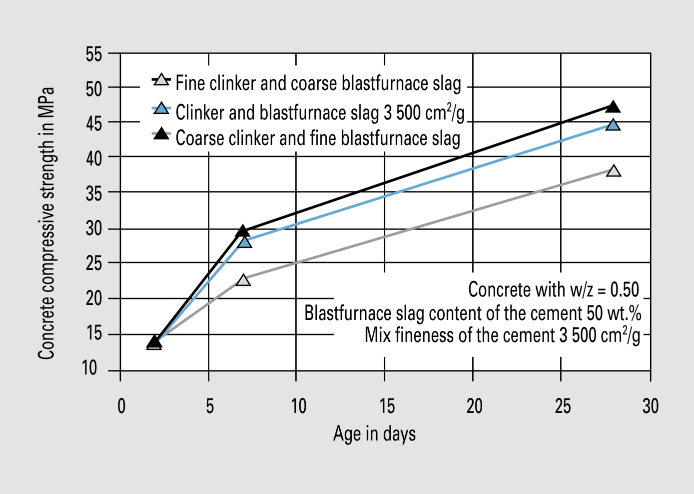


Fig. III-15: Strength development of concretes made from CEM III/A cements containing main constituents of varied fineness

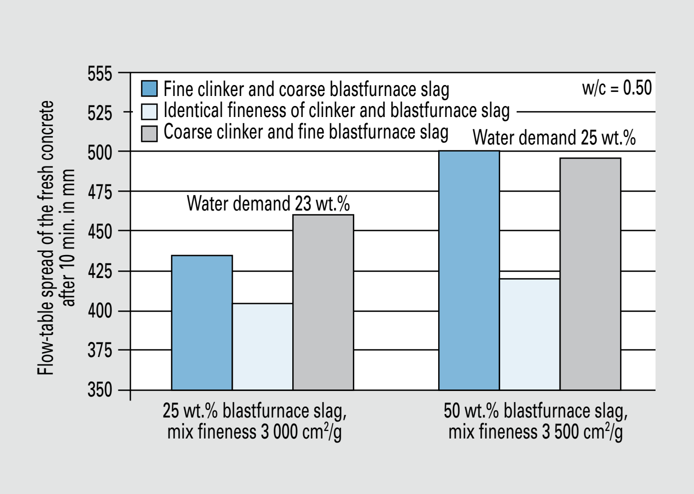


Fig. III-16: Fresh concrete consistency obtained when cements containing main constituents of different fineness are used

Tab. III-3: List of cements manufactured from one clinker and one blastfurnace slag

Cement	Blastfurnace slag content	Fineness of main constituents	RRSB slope of particle size distribution of the main constituents
CEM I	0	2 500 to 5 000 cm^2/g (including factory-made cements)	n = 0.8 to n = 1.0
CEM II/B-S*)	25 wt.%	3 000 and 4 000 cm^2/g	n = 0.8 to n = 1.0
CEM III/B*)	75 wt.%	3 000 and 4 000 cm^2/g	n = 0.8 to n = 1.0

*) Identical particle size distribution of the main constituents

sulphate content of 3.5 wt.% that consisted of 50% hardly soluble sulphate (anhydrite) and 50% readily soluble sulphate (total of SO_3 from clinker and from the hemihydrate added).

Cements containing blastfurnace slag with different finenesses of their main constituents

In the period under review, continuative investigations were carried out on cements of constant fineness but with substantial differences in fineness to be found in their main constituents. All the main constituents had a wide RRSB particle size distribution with a slope n = 0.8. It turned out that the early strength of CEM II/B-S cements with 25 wt.% blastfurnace slag and a fineness of the clinker/blastfurnace slag mix of 3 000 cm^2/g (according to Blaine) and CEM III/A cements with 50 wt.% blastfurnace slag and a mix fineness of 3 500 cm^2/g (according to Blaine), for example, could be influenced to a very small degree only. The results further highlighted that cements with a coarse blastfurnace slag content and a fine clinker content showed lower 28-day compressive strength values than cements containing fine blastfurnace slag and coarse clinker. Provided that cement fineness was constant, the water demand determined was almost unchanged in spite of variations in the fineness of the main constituents. The results obtained in standard mortar testing were confirmed upon application of these cements in concrete with a w/c ratio of 0.50.

It can be seen from **Fig. III-15** that the concrete compressive strength values after 7 and 28 days, respectively, were particularly low when the CEM III/A cement applied had been made of a coarse blastfurnace slag meal and a fine clinker meal. Furthermore, the combination of main constituents of different fineness also had an impact on the workability of the fresh concrete. The values of the flow measure determined 10 and 45 minutes after mixing of the concrete, respectively, were the higher, the larger the differences in the fineness of the main cement constituents had been set. Using CEM III/A cements (3 500 cm^2/g) as an example, **Fig. III-16** illustrates that the fresh concrete consistency obtained after 10 minutes was extra soft (F4) when the fineness of the main cement constituents differed significantly, and only soft (F3) when the fineness of the main cement constituents was identical. In the case of CEM II/B-S cement with 3 000 cm^2/g, the consistency obtained with different fineness of the main constituents was soft (F3), while only plastic consistency was obtained when fineness was identical (F2).

Relationship between the particle size distribution of cement and its 28-day compressive strength

Both the specific surface area and the slope of RRSB distribution determine the strength values of the cement. When only one grading parameter is changed, the effects on strength development can be assessed reliably. If the slope and the specific surface area are modified simultaneously by carefully directed adjustment of the grinding plants, the effects on strength development can be either intensified or compensated. For example, a reduction in the specific cement surface area can entail no impact whatsoever on standard strength, if it is accompanied by an increase in the RRSB slope of the particle size distribution of the cement. The investigations conducted in the period under review were aimed at identifying a definite relationship between the particle size distribution of a cement of constant composition and its 28-day strength which exists regardless of the slope and the specific cement surface area. The cements investigated and their parameters are listed in **Tab. III-3**.

Fig. III-17: 28-day compressive strength of cement as a function of the particle size at a transition value for the particle size distribution of 95% (X_{95})

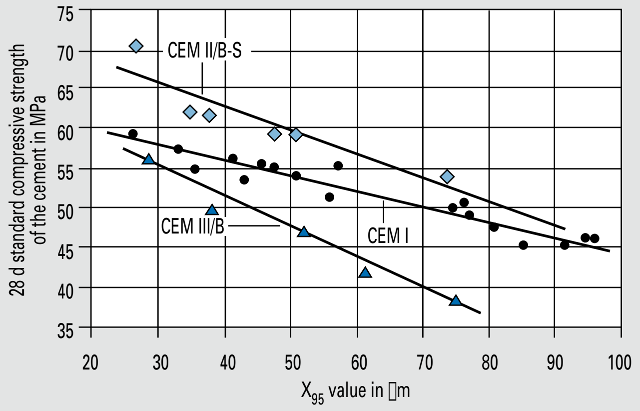
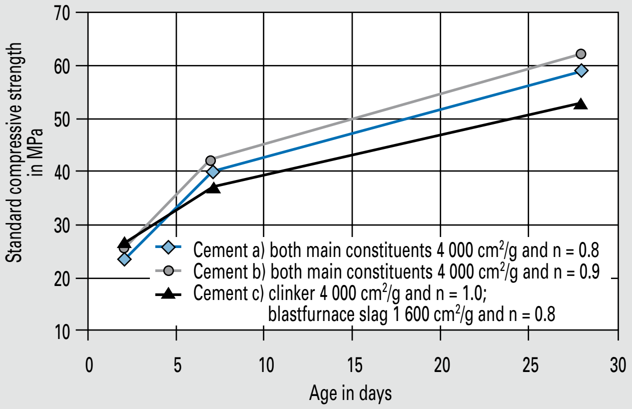


Fig. III-18: Strength development of CEM II/B-S cements with 25 wt.% blastfurnace slag



In **Fig. III-17** the 28-day compressive strength of CEM I, CEM II/B-S and CEM III/B cements was plotted against the particle size; the transition value being 95 % for each particle size distribution. This Figure includes laboratory-made and industrial-scale cements of different grinding fineness, RRSB slopes and compositions. One clinker exclusively formed the basis of the cements. The results yielded a good correlation. 28-day compressive strength is the lower, the higher the so-called X_{95} value is. The relationship obtained was nearly linear for each of the three cement types.

Investigations on optimising the 2- and 28-day compressive strength of cement

The X_{95} particle size lends itself as a controlled variable especially when the cements are ground separately and mixed subsequently. In this way the 28-day compressive strength of cement can be optimised separately, and the cements can thus be fine-tuned in the various ranges of their particle size distribution. A higher slope of that part of the distribution curve that is within the fine particle range is frequently desirable in order to attain a high reactive fines portion < 32 µm and thus increase early strength. In the coarse particle range, the curve would have to be somewhat flatter in order to raise the X_{95} particle size and thus limit the 28-day strength. This can be implemented successfully, for example, by mixing a fine clinker meal of narrow particle size distribution with a small quantity of coarse blastfurnace slag meal of wide particle size distribution. The investigations of other material combinations have not been finished yet.

Fig. III-18 illustrates the strength development of three CEM II/B-S cements with 25 wt.% blastfurnace slag. The cements were characterised by the same chemico-mineralogical composition, but by different granulometric properties. The main constituents of cement a) and the main constituents of cement b) had comparable particle size distributions. The discrepancy in strength between the two cements is attributable to the different RRSB slopes of n = 0.8 and n = 0.9, respectively. With the third cement c), by contrast, the particle size distributions of the main constituents clinker and blastfurnace slag deviated substantially. While the RRSB slope of the clinker was n = 1.0, the particle size distribution of the blastfurnace slag meal was fairly wide at n = 0.8. Moreover, the specific surface areas of the main constituents differed by more than 2 000 cm²/g. In comparison to cements a) and b), the narrow particle size distribution of the clinker allowed the early strength of cement c) to be increased by a total of 1 to 3 Mpa, although the fineness of the cement was lower. Besides, the 7-day and 28-day compressive strengths of cement c) were reduced in comparison to those of cements a) and b). This effect is primarily attributable to the influence of the coarse blastfurnace slag meal.

Cement fineness and reactivity

In addition to the influence of the specific surface area, the influence of the two main constituents was examined in numerous investigations of cements containing blastfurnace slag. The chemico-mineralogical composition of the clinkers and blastfurnace slags used can be seen from **Tab. III-4**.

Tab. III-4: Chemical analysis of the main constituents clinker and blastfurnace slag (loss-on-ignition-free)

Material no.	1	2	3	4	5	6
[wt.%]	Clinker	Clinker	Clinker	Blastfurnace slag	Blastfurnace slag	Blastfurnace slag
SiO_2	22.31	20.80	21.54	35.58	35.33	31.30
Al_2O_3	5.64	5.39	6.04	15.39	12.07	16.69
CaO	65.72	63.51	65.52	33.88	40.60	36.79
MgO	0.92	2.26	1.27	11.34	8.88	9.99
TiO_2	0.27	0.23	0.30	0.84	0.76	1.84
Fe_2O_3	2.41	4.04	2.66	0.59	0.38	0.50
Mn_2O_3	0.05	0.04	0.06	0.31	0.34	0.57
K_2O	0.90	1.15	0.96	0.88	0.44	0.37
Na_2O	0.30	0.26	0.14	0.42	0.31	0.40
$Na_2O_{\text{Äqu.}}$	0.89	1.25	0.77	1.00	0.60	0.64
SO_3	1.12	1.10	0.74	0.01	0.01	0.26
SG	97.40	68.19	73.43	Degree of sulphatisation		
KST	92.98	94.48	94.70	Lime standard		
C_3S	56.77	59.00	59.10			
C_2S	21.27	15.63	17.60			
C_3A	10.89	7.50	11.60			
C_4AF	7.33	12.39	8.20			
TM	2.34	1.33	2.27	Alumina module		
SM	2.77	2.21	2.47	Silicate module		

Fig. III-19 shows the strength development of the CEM II/B-S and CEM III/B cements made from clinker 3 and three different blastfurnace slags. The main constituents of each cement type were characterised by the same fineness and wide particle size distribution. Moreover, the fineness of the cements with a high content of blastfurnace slag was set higher at 4 000 cm^2/g than that of the cements with a low content of blastfurnace slag (3 000 cm^2/g). It becomes apparent from the Figure that the type of blastfurnace slag utilised had hardly any impact on the compressive strength at the age of 2 days. 2-day strength totalled 15 and 17 MPa, respectively, with the CEM II/B-S cements, and approx. 10 MPa with the CEM III/B cements. The dependence on blastfurnace slag reactivity turned out to be more pronounced with 7-day and 28-day strength, however. The strength differences between the material combinations measured at those points were considerable, ranging between 7 and 10 MPa.

Fig. III-20 represents cements made up of one blastfurnace slag and three different clinkers. Significant strength differences and characteristic strength developments were observed in the case of the CEM II/B-S cements containing a high clinker proportion. This phenomenon essentially reflects the different clinker properties. Strength differences of 5 to 10 MPa were measured at each testing age. Under the conditions described here, the predominant influence of clinker reactivity on the compressive strength of Portland slag cements could be reliably assessed on the basis of the strength development of Portland cements. Clinker reactivity had hardly any impact on the early strength of blastfurnace cements with a low clinker proportion, however, although the fineness of these cements was 1 000 cm^2/g higher. However, also the 28-day compressive strength of the CEM III/B cements was influenced only slightly by the clinker type used, so that maximum strength differences of 3 MPa occurred.

Influence of main cement constituents on alkalinity

A harmful alkali-silica reaction (ASR) can be prevented by using cements with a low effective alkali content. These so-called NA cements are standardised in DIN 1164 in Germany, their classification being based on the total alkali content. In general, NA cements basically cause a lowered amount of alkali being available in the pore solution of the hardened cement paste (effective alkali content), thus resulting in a corresponding reduction of the pH value.

While the effective alkali content of Portland cements rises in line with an increase in the total alkali content, the effective alkali content of cements containing several main constituents may deviate from their total alkali content to varying degrees. This can be traced back to the discrepancies in the solubility of the alkalis contained in the cement constituents on the one hand, and to the different alkali absorption by the reaction products on the other hand. As a consequence, the regulation according to which NA cements are classified on the basis of their total alkali content may in some cases lead to an exclusion of certain cements from use as NA cements due to their total alkali content, even though their effective alkali content is low.

Investigations

In order to be able to classify further cements as NA cements if applicable, it is necessary to determine their effective alkali content and to reliably predict it over long hydration periods. In this context, particular importance is conferred on the dynamic combination and dissolution processes of the alkalis in the hardened cement paste. However, knowledge of these processes was inadequate so far. This applies to cements with several main constituents in particular.

The Research Institute therefore conducted investigations to examine the influence of various blastfurnace slags, hard coal fly ashes and silica fumes on the effective alkali content of the cement. Pore solution investigations were conducted to gain an insight into the very phenomenon of how the alkalinity of the pore solution of hardened cement paste is changed by the utilisation of latent hydraulic or pozzolanic main cement constituents, respectively. Investigations of solid matter were to reveal, which chemico-mineralogical mechanisms are crucial for alkali binding and whether or how long, respectively, the bond is stable in the hardened cement paste.

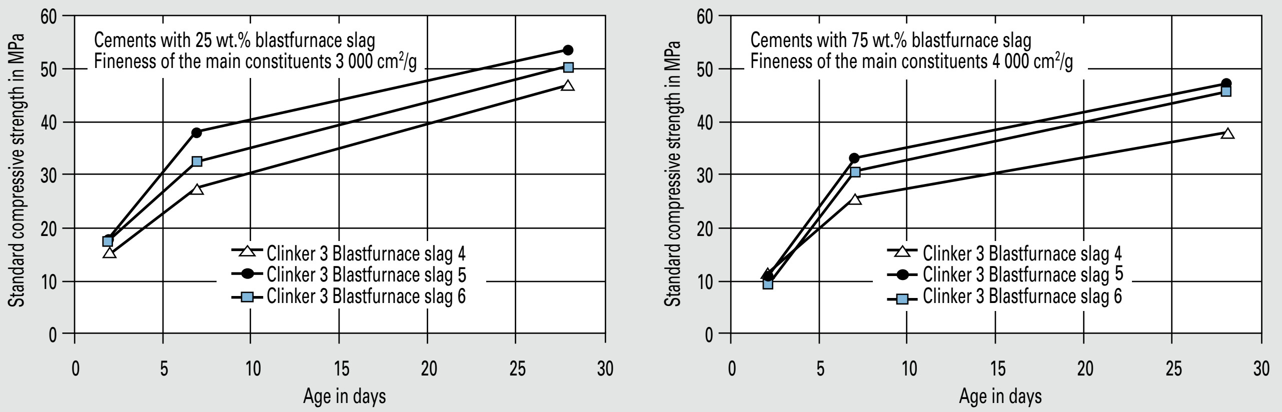


Fig. III-19: Comparison of the compressive strengths of CEM II/B-S and CEM III/B cements on the basis of the same clinker combined with 3 different blastfurnace slags; identical particle size distribution of the main constituents

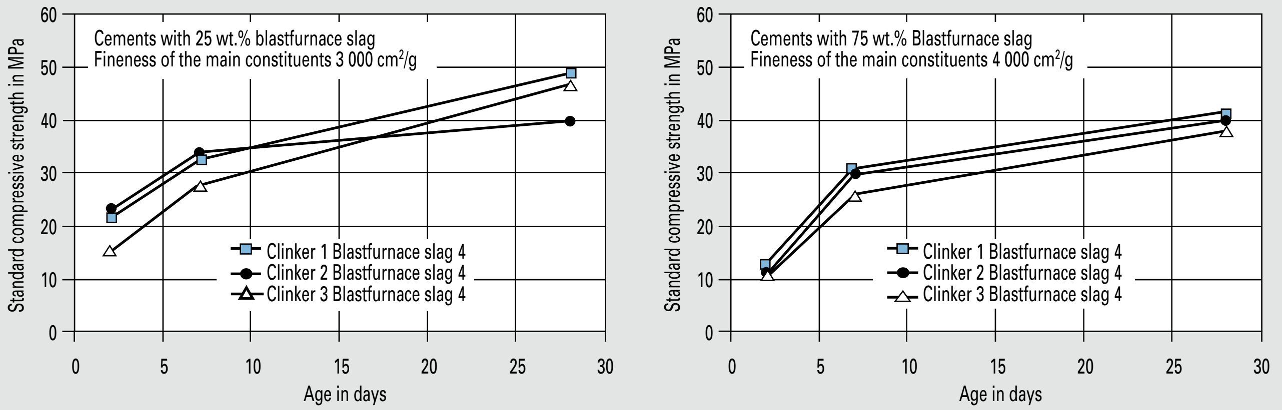
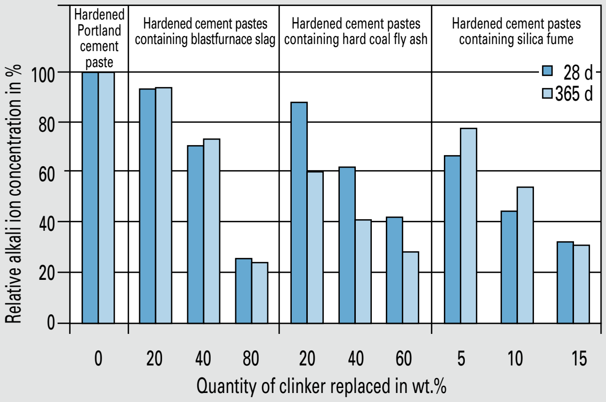


Fig. III-20: Comparison of the compressive strengths of CEM II/B-S and CEM III/B cements on the basis of the same blastfurnace slag combined with 3 different clinkers; identical particle size distribution of the main constituents

Influence of the main constituents on the alkalinity of the pore solution

The first step of the investigations consisted of manufacturing hardened cement pastes from different cements, which, however, each contained the same clinker. Blastfurnace slag, hard coal fly ash and silica fume were further main constituents. **Fig. III-21** illustrates the alkali ion concentration in the pore solution of the hardened cement pastes. All concentrations were put in relation to the alkali ion concentration in the hardened Portland cement paste. The Figure shows that a replacement of the clinker resulted in a decrease in the alkali ion concentration regardless of the main constituent used. The various cement constituents differ significantly in terms of their effectiveness, however.

Fig. III-21: Change in the alkali ion concentration of the pore solution caused by blastfurnace slag, hard coal fly ash and silica fume after different hydration periods



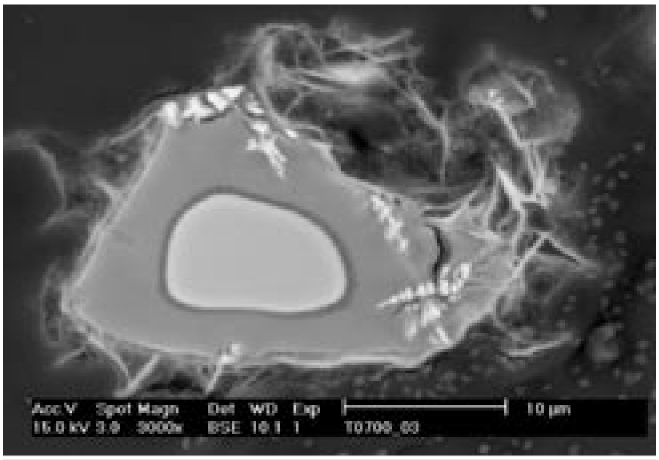


Fig. III-22: Reaction products of a blastfurnace slag stored in 10 mol potassium hydroxide. The unconverted core of the blastfurnace slag grain is surrounded by a layer of hydrotalcite-type phases and epitaxial growth of CSH and CASH phases.

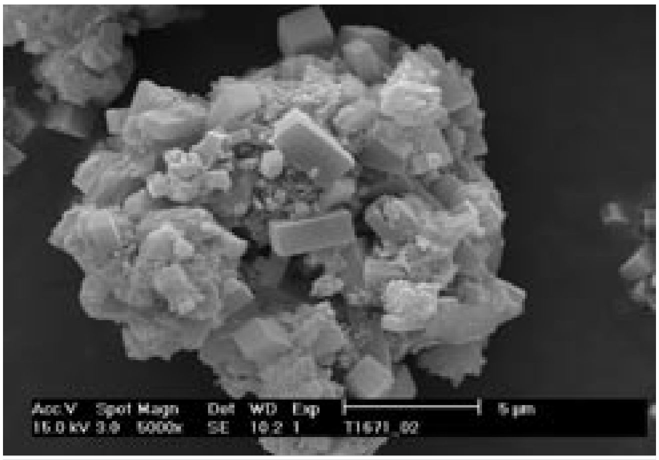


Fig. III-23: Reaction products of a fly ash stored in 10 mol potassium hydroxide. The fly ash ball is covered with aluminosilicates containing potassium (zeolites).

The alkali ion concentration in the hardened cement pastes containing blastfurnace slag does not decrease proportionally to the quantity of clinker replaced, but is reduced to a smaller extent. Part of the alkalis contained in the pore solution thus originates from the blastfurnace slags. Their share is, however, very small in comparison to the clinker. Due to this small share, however, a sizeable reduction in the alkali ion concentration cannot be observed until the blastfurnace slag contents exceed 20 wt.%. The investigations covered three blastfurnace slags with alkali contents ranging from 0.54 wt.% Na_2O_{eq} to 1.23 wt.% Na_2O_{eq}. The investigations yielded the result that all blastfurnace slags made similar contributions to the alkali content of the pore solution. Accordingly, the decisive factor for the effective alkali content of the cement is the alkali content of the clinker, and not that of the blastfurnace slag.

Up to a hydration time of 28 days, the influence which fly ash utilised in the cement has on the alkalinity of the pore solution is comparable to that of blastfurnace slags. Between 28 and 365 days, however, the alkali ion concentration is reduced substantially. The alkalinity of the pore solution after 365 days is lower than would have been expected on the basis of the reduced clinker quantity alone. As a consequence, also alkalis released during clinker reactions are incorporated in the reaction products.

A disproportionately high decline in the alkali ion concentration occurred when silica fume was utilised. The replacement of 15 wt.% clinker by silica fume resulted in a reduction in the alkali ion concentration to approx. 1/3 of the concentration found in the pore solution of the hardened Portland cement paste. As hydration progressed, the alkali ion concentration in the pore solution was found to increase in all hardened cement pastes containing silica fume. The release begins the earlier and is the more intense, the lower the silica fume content in the hardened cement paste is. The release of alkalis from hardened cement paste containing 5 wt.% silica fume, for example, begins as early as after 2 days. By contrast, the alkali ion concentration in a hardened cement paste containing 15 wt.% silica fume decreases continually up to a hydration time of 91 days. A release of alkalis was only observed after longer hydration times.

Causes of alkali binding

The binding of the alkalis in the different hardened cement pastes was investigated to identify the processes that influence alkali resources. Alkalis can generally be sorbed by the CSH phases. These phases account for the largest share of the solids phase in the hardened cement paste, thus constituting the most important combination partner for the alkalis. The binding capacity of the CSH phases changes in conjunction with their stoichiometric composition, however. As the calcium content in the phases decreases, their tendency to sorb alkalis increases. The CSH phases with the highest calcium content are formed during the reaction of the Portland cement clinker. When the clinker is replaced by the latent hydraulic or pozzolanic main constituents, respectively, which have a lower calcium content, the average Ca/Si ratio of the CSH phases in the hardened cement paste declines. The degree to which the Ca/Si ratio is reduced on average depends on the calcium content of the other main constituents apart from the clinker and their proportion in the cement.

Investigations were conducted to reveal whether alkali binding was restricted exclusively to the CSH phases or whether other alkali-binding phases were formed as well. To this end it was analysed which reaction products formed during the reaction of the blastfurnace slags and pozzolana in pure potassium or sodium hydroxide and in alkali hydroxide to which 30 wt.% $Ca(OH)_2$ had been added.

In addition to CSH phases, CASH phases (A = aluminium) and hydrotalcite-type reaction products (Mg-Al compounds) are formed during blastfurnace slag reactions regardless of the solution used. **Fig. III-22** shows the polished section of a blastfurnace slag particle the unreacted core of which is surrounded by a rim of hydrotalcite-type phases in the area of the original blastfurnace slag particle and epitaxial growth of CSH or CASH phases, respectively. Investigations of synthetically made hydrotalcites revealed that these phases are irrelevant for alkali binding. Thus, the binding of alkali both in hardened cement pastes containing blastfurnace slag and in hardened Portland cement pastes is restricted to sorption at the CSH or CASH phases.

In hardened cement pastes containing up to 40 wt.% blastfurnace slag, the Ca/Si ratio of the CSH phases is similar to that in the Portland cement, i.e. the alkali binding capacity in these hardened cement pastes is not higher than in hardened Portland cement paste either. The decrease in the alkali ion concentration of the pore solution of hardened cement pastes containing blastfurnace slag is thus chiefly attributable to the decline in clinker quantity and the ensuing lower release of alkalis from the starting materials. At blastfurnace contents of up to 20 wt.%, this leads to a drop in the alkali ion concentration that is only slight in comparison to hardened Portland cement paste, which is due to the contribution of the blastfurnace slag to the alkali content of the pore solution. The binding capacity of the CSH phases does not increase until the blastfurnace slag content exceeds 40 wt.%. As the quantity of CSH phases is lower at the same time, the overall binding of alkalis does not grow disproportionately in this case either.

The binding of alkalis in hardened cement pastes containing silica fume is exclusively restricted to sorption at CSH phases as well. The early onset of alkali binding is triggered by the rapid reaction of the silica fume with the alkalis dissolved in the pore solution. This process first leads to the formation of alkali-silica gel, which has a high affinity towards alkalis. As hydration progresses further, this gel can react with the $Ca(OH)_2$ separated during clinker hydration to be converted to CSH phases. Alkalis are released during conversion. In the long run, this reaction can result in an increase in the alkali ion concentration of the pore solution. The alkali-binding effect is thus limited in time.

Two effects promoting alkali binding occur when fly ash is used. For one thing, the reaction of fly ash, which begins after a hydration time of about 28 days, implies the formation of low-calcium CSH and CASH phases that can sorb alkalis to a higher degree. For the other, the dissolution of the fly ash glass may involve the formation of aluminosilicates containing alkali, which are referred to as zeolites (**Fig. III-23**). The stability of these phases depends on the availability of calcium. In the case of fly ashes to which $Ca(OH)_2$ was added during or subsequent to storage, zeolite phases were therefore detected on a small scale only. The principal reaction products detected were CSH and CASH phases instead.

Thus, the following reaction mechanism is conceivable for the alkali binding in hardened cement pastes containing fly ash. The dissolved fly ash glass first reacts with the immediately available alkalis from the pore solution to form zeolites containing alkali. Upon the influx of calcium, the zeolite compounds are converted to CSH and CASH phases, respectively. It depends on the quantity and stoichiometry of the phases formed whether this process entails a renewed rise in the dissolved alkali portion.

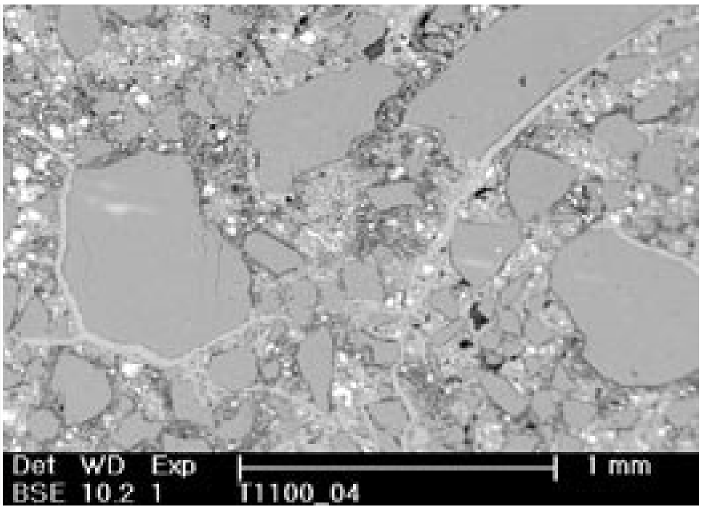


Fig. III-24: Scanning electron microscope image of a polished mortar section. The test mortar made from a CEM I-HS with w/c = 0.60 was stored in 4.4% sodium sulphate solution at 8 °C for one year. Cracks filled with gypsum extend crosswise through the structure and around the aggregate particles in particular.

The investigations show that the zeolitic alkali bond gains in importance as the fly ash proportion in the cement rises since the $Ca(OH)_2$ supply decreases due to the decline in clinker quantity. Even in the case of cements with a low fly ash content, it can, however, be safely assumed that the process converting zeolites to CSH phases takes place very slowly, if hydration time is long since the rate of diffusion of calcium is retarded by the growing consolidation of the pore structure.

Sulphate resistance ■

According to the concrete standard DIN 1045-2, certain mixes of cement and fly ash may be applied instead of highly sulphate resisting (HS) Portland or blastfurnace cements in case of sulphate attacks of up to 1 500 mg SO_4/l. For example, mixes consisting of 80 wt.% CEM I or 80 wt.% CEM II/A-LL and 20 wt.% hard coal fly ash can be utilised. Laboratory investigations on sulphate resistance carried out in the past revealed, however, that mortar samples made from such mixes containing fly ash frequently did not possess adequate sulphate resistance, especially at temperatures below 10 °C. The sulphate attack, which was initiated at the laboratory using sodium sulphate, caused massive damage by expansion, which was accompanied by subsequent thaumasite formation in part. These observations contrast with the experience gained in building practice, according to which hardly any damage occurred in concrete.

Extreme and realistic testing conditions

The sulphate resistance of cement/fly ash mixes was therefore purposefully investigated under varying laboratory conditions over the past years. In these investigations, a distinction was made between extreme testing conditions and realistic testing conditions. Extreme testing conditions imply very high sulphate concentrations (e.g. 30 g/l) in the test solution and high water/cement ratios (e.g. 0.60) for the test mortars. These conditions are applied in quick tests, which in Germany include the expert committee method (SVA method) and the Wittekindt method. Sulphate concentrations like these hardly ever occur in practical application, however.

The high sulphate concentration prevailing during the quick test method can result in expansion of the test pieces that does not conform to their behaviour in practical use. In these cases, the expansion under test conditions is not attributable to the formation of secondary ettringite, but to the formation of secondary gypsum (see **Fig. III-24**). The sulphate ions react with the calcium hydroxide generated during the hydration of calcium silicates. Both laboratory investigations and thermodynamic calculations show that this reaction can only take place at an adequately high sulphate concentration of several thousand mg/l. Gypsum is not formed at all at sulphate concentrations of up to 1 500 mg/l, however, and to a small extent only at concentrations of up to 3 000 mg/l.

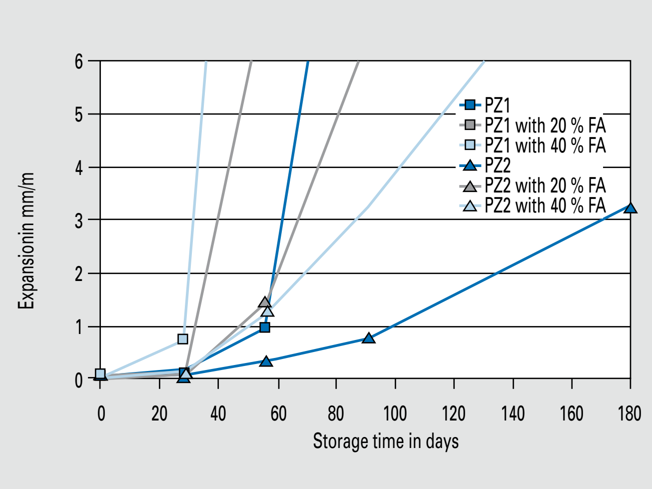


Fig. III-25: Expansion behaviour of flat mortar prisms tested in accordance with the Wittekindt method using 4.4% sodium sulphate solution and storage at 8 °C. PZ1 is a CEM I 32,5 R containing 11 wt.% C_3A, while PZ2 contains 8 wt.% C_3A. The fly ash was offset against the water/cement ratio with k = 1.

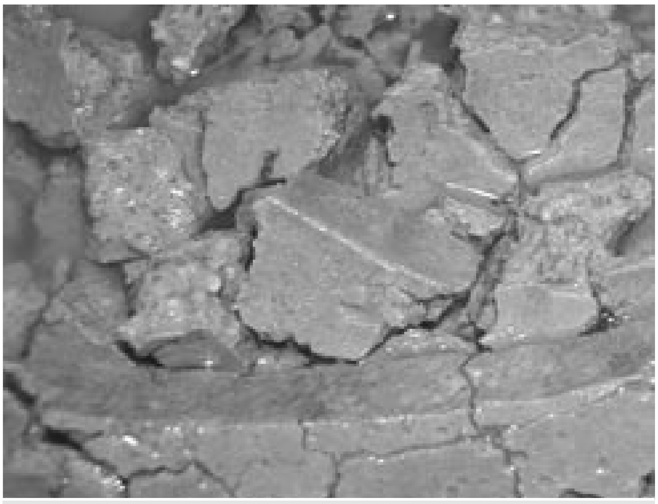


Fig. III-26: Flat mortar prisms made from a binder mix consisting of 80 wt.% CEM I 32,5 R and 20 wt.% FA (w/c = 0.60, k = 1) after 3-month storage in 4.4% sodium sulphate solution at 8 °C

Fig. III-27: Flat mortar prism made from a binder mix consisting of 80 wt.% CEM I 32,5 R and 20 wt.% FA (w/c = 0.60, k = 1) after 18-month storage in 0.22% sodium sulphate solution at 8 °C

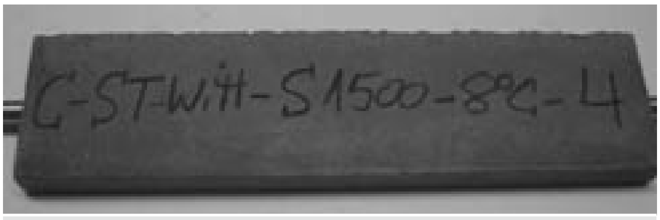


Fig. III-28: Flat mortar prism made from a binder mix consisting of 60 wt.% CEM I 32,5 R and 40 wt.% FA (w/c = 0.60, k = 1) after 18-month storage in 0.22% sodium sulphate solution at 8 °C

Test mortars containing fly ash

With cement/fly ash mixes in particular, a high sulphate concentration in combination with a low temperature has an adverse effect on sulphate resistance. For the most part, the flat mortar prisms expand strongly as early as after a few days (**Fig. III-25**) and frequently disintegrate within 2 or 3 months (**Fig. III-26**). This effect gets increasingly pronounced in line with a rise in the fly ash content. If, however, testing is performed at a sulphate concentration of 1500 mg/l or 3 000 mg/l, the sulphate resistance rises as the proportion of fly ash grows (**Figs. III-27** and **III-28**). This behaviour occurs regardless of whether a water/cement ratio of 0.60 or 0.50 for mortar production and an allowance factor of k = 1 or k = 0.4 for fly ash were chosen.

This behaviour can be explained as follows: At low temperatures, the pozzolanic reaction of the fly ash and thus the formation of hydrate phases required for a dense structure is retarded. Resistance to diffusion is not high, which is why sulphate ions penetrate to the interior of the microstructure, where they react mainly with the aluminate phases of the cement to form secondary ettringite, and with calcium hydroxide to form secondary gypsum, which are the two phases having an expansive effect. Since, however, diffusion also depends on concentration, the number of sulphate ions entering the structure is higher at a fairly high sulphate concentration than at a low concentration. Such an increased formation of expansive phases leads to an acceleration in damage inflicted to the microstructure. This behaviour gets the more pronounced the higher the content of fly ash is.

At low sulphate concentrations (e.g. 1 500 mg/l), secondary gypsum formation does not occur for one thing, and the diffusion of sulphate ions is considerably reduced owing to the low concentration gradient for the other. Less expansive secondary ettringite is generated. The pozzolanic reaction of the fly ash, which contributes to an increase in diffusion resistance although it takes place at a slow pace, comes to bear, resulting in higher sulphate resistance. In this case, too, it is true that the behaviour described is the more pronounced the higher the fly ash content is.

Physical and chemical sulphate resistance

In contrast to highly sulphate resisting Portland cements, cement/fly ash mixes do not possess any chemical resistance to secondary ettringite formation, however. The high sulphate resistance is exclusively attributable to an elevated physical sulphate resistance. Similar to blastfurnace cements, cements containing fly ash form phases during the hydration process which increase the diffusion resistance of the microstructure. As the diffusion resistance generally depends on the porosity of the microstructure, the water/cement ratio and the allowance factor k for fly ash have decisive influence on sulphate resistance as well. It becomes apparent from the flat mortar prism shown by way of example in Fig. III-27 that, at a water/cement ratio of 0.60 and an allowance factor k = 1, the corners and edges suffered damage attributable to the formation of expansive phases as early as after some months. Flat mortar prisms with a water/cement ratio of 0.50 and k = 0.4 displayed much higher sulphate resistance by comparison. Even after a sulphate attack of 18 months, hardly any damage was discernible (**Fig. III-29**).

Thaumasite formation

In addition to the mixes consisting of Portland cement and fly ash, it was the mixes of Portland-limestone cement and fly ash that interest focused on in particular. As a consequence of the limestone proportion, both expansive damage and a massive loss of cohesion in the microstructure due to thaumasite formation were observed in laboratory investigations. They were found to imply two correlations. The higher the proportion of fly ash was, the less thaumasite was formed, and the more severe initial expansive damage was, the more intense thaumasite formation was. When there was no expansive damage, virtually no thaumasite was formed. This behaviour can be traced back to two causes. For one thing, thaumasite is preferably formed from ettringite by rearrangement – the "indirect" way of formation. For the other, expansive damage increases the surface area accessible for a sulphate attack, allowing thaumasite formation to occur on a larger scale.

Fig. III-30 depicts the surface of a mortar prism made from a Portland-limestone cement/fly ash mix. The microstructure has lost cohesion as a result of thaumasite formation in places, which can be seen from the white reaction product on the otherwise grey structure. Thaumasite from the same prism is shown at large magnification in **Fig. III-31**. The crystals have the same needle-shaped, hexagonally-prismatic morphology as ettringite. Their chemical composition, however, shows the presence of carbon and silicon instead of aluminium, thus allowing their definite classification.

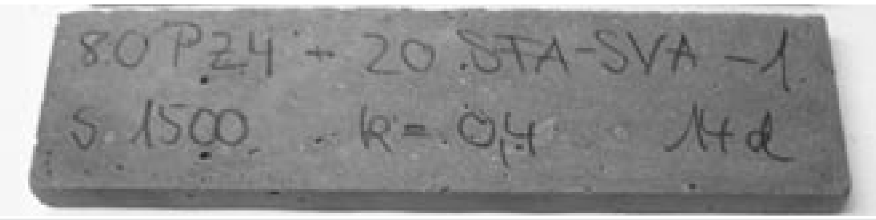


Fig. III-29: Flat mortar prism made from a binder mix consisting of 80 wt.% CEM I 32,5 R and 20 wt.% FA (w/c = 0.50, k =0.4) after 18-month storage in 0.22% sodium sulphate solution at 8 °C

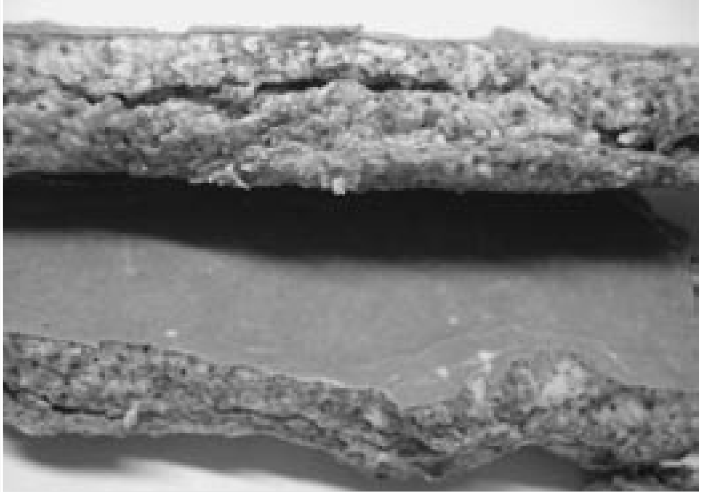


Fig. III-30: Mortar showing superficial loss of cohesion, after 2-year storage in 0.22% sodium sulphate solution at 8 °C; white areas show the formation of thaumasite

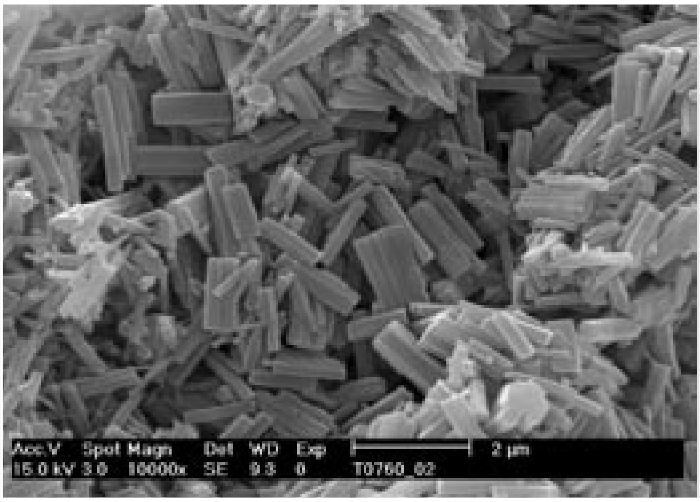


Fig. III-31: Scanning electron microscope image of thaumasite in a damaged mortar structure

Methods of testing

The evaluation of the numerous test results obtained at the Research Institute over the past years conveys the following picture of the testing methods. It is true that quick tests are adequate for differentiating various Portland cements on the basis of their chemical sulphate resistance. However, they cannot be expected to yield verifiable statements on the sulphate resistance at low temperatures of cement/fly ash mixes, as it is not only the chemical sulphate resistance that is important in the case of cements containing fly ash.

There is presently no testing method that allows to definitely and thus safely assess the sulphate resistance behaviour of cement/fly ash mixes in particular within a test period of a few weeks only. The shortcomings of the testing methods are also reflected in the fact that it has to date been impossible both at national and at European level to develop a standardisable method of testing. Against this backdrop, an expert panel of the German Committee for Reinforced Concrete (DAfStb) has continued discussing the topic of testing methods. The more recent findings are to be taken into consideration in this process as well.

Chromate – analytics and long-term stability of chromate reducing agents

All manufacturers of cement and cementitious preparations have had to comply with the specifications of the European Chromate Directive 2003/53/EC since January 17, 2005. Accordingly, a cement or a cementitious preparation must not contain more than 0.0002% (equivalent to 2 ppm) water-soluble chromate relative to the mass of dry cement. A harmonised European testing method has to be available to allow this water-soluble chromate to be determined.

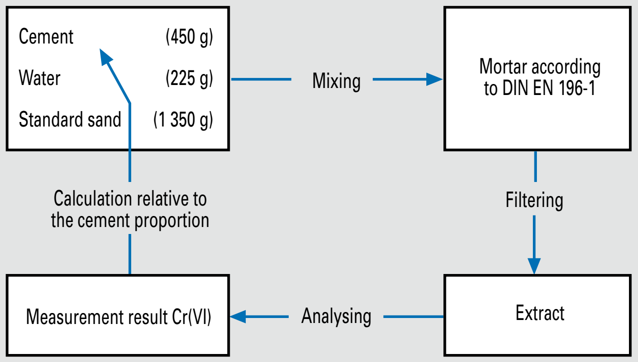


Fig. III-32: Schematic representation of the planned reference test method according to prEN 196-10

The European Commission assigned the mandate to develop a European test standard for the determination of water-soluble chromate in cements and cementitious preparations to the CEN/TC 51. Task Group CEN/TC 51/WG 15/TG 2, which was assigned this task, submitted a draft standard after a mere 18 months of intensive work.

This draft is, however, not expected to be finally adopted as EN 196-10 until the end of 2005. The European Commission recommends using the present draft standard as a basis for determining the water-soluble chromate in cements and cementitious preparations until then.

European method for chromate testing

Following intense discussion of the national methods for determining the water-soluble chromate in cement that had already been introduced in Europe, TG 2 elaborated the scheme for a harmonised Europe-wide testing method. According to this method, the scenarios for the release of chromate from cementitious preparations are to be simulated as precisely as possible, with practical applications being given due consideration. Accordingly, chromate determination is to involve the testing of cement in its various forms of application, i.e. mortar, concrete and other cementitious preparations. The new test standard consistently provides for testing to be performed on mortar in accordance with DIN EN 196-1. The water/cement ratio (w/c = 0.5) applied in this extraction method thus corresponds to practical cement application, which is not the case with the method pursuant to the Technical Rules on Hazardous Substances (TRGS 613) (w/c = 4). Basically, the determination of the water-soluble chromate in the aqueous filtrate of the mortar is similar to that laid down in the test specification that is applied in Germany and described in the Annex to TRGS 613 (**Fig. III-32**). The use of elemental bromine to take account of reducing substances is to be avoided by means of an optimised analysis procedure.

The extraction of the water-soluble chromate proportion of a cement by producing a standard mortar pursuant to EN 196-1 allows to correctly describe the exposure situation arising during cement application, if the skin should get in contact with the cementitious product after water addition in spite of the protection measures recommended. This is the only way of obtaining an evaluation of cement in terms of its water-soluble chromate content that is geared to practice, i.e. correct and fair.

Cementitious preparations

The determination of the water-soluble chromate content in cementitious preparations is similar to that of cements. Preparations are first suspended in water and subsequently filtered. Then the dissolved chromate in the aqueous extract is determined. Cementitious preparations may still be too dry after water addition to allow extraction of a quantity of filtrate that is sufficient for the chemical analysis of the water-soluble chromate. In these cases, the water/cement ratio has to be increased to the extent required for extracting a sufficient quantity of filtrate.

However, the extracts obtained from cementitious preparations rather often display milky cloudiness that may disturb analysis according to prEN 196-10 significantly or even render it impossible. Recommendations for the analysis of cementitious preparations are listed in an Annex to prEN 196-10.

Testing method can be improved

According to the new European method prEN 196-10 for testing water-soluble chromate in cements and cementitious preparations, the water-soluble chromate is determined using the so-called diphenyl carbazide method (DPC method). The dissolved chromate oxygenises diphenyl carbazide to diphenyl carbazone. In this process, the hexavalent chromium [Cr(VI)] in the chromate is reduced to trivalent chromium [Cr(III)]. Diphenyl carbazone and Cr(III) combine to form a deeply red-violet complex [DPC-Cr(III)], the concentration of which is determined by spectrophotometry. The formation of this complex presupposes a lowering of the pH value to a range between 1 and 2. This reduction of the pH value, however, results in an increase in the oxidation capacity of the hexavalent chromium. As a consequence, oxidisable compounds cannot reduce the chromate content of the analysis solution until these pH values reduced for the purpose of chemical analysis have been reached. This would lead to deficiencies in findings. Such oxidisable compounds therefore have to be oxydised already before the pH value is lowered. In the German (TRGS 613) or Danish (DS 1020) analysis specifications, this is accomplished by boiling the analysis sample with bromine water.

The handling of poisonous elemental bromine is unpopular, subject to restrictions or even outright banned in many countries. In the analysis specification of prEN 196-10, the application of an oxidation step is to be circumvented by adding the diphenyl carbazide prior to acidification and precise adjustment of the analysis sample pH to a value between 2.1 and 2.5.

Oxidation is necessary and useful

Comparison tests carried out on different European cements to determine chromate pursuant to prEN 196-10 (without oxidation) yielded unexpected results. The analysis results subdivided the laboratories which participated into two groups, one of which obtained higher results at fairly the same level, while the other measured lower results that ranged at a very uniform level as well. When the laboratories applied analysis methods including oxidation, all got results at a higher level. Outliers occurred in all cases. At some laboratories, the use of oxidising agents thus hardly made any difference, while it made a major difference at others.

The Research Institute of the Cement Industry was looking for an explanation for this phenomenon. It was observed that not all cement extracts which were processed according to prEN 196-10 (pH = 2.1 to 2.5) exhibited the typical red-violet coloration of the DPC-Cr(III) complex. In some cases, the test solution was red instead of red-violet. To check this observation, which had been made by visual inspection, the UV/VIS spectra of a pure chromate solution and a cement extract, both of which had been processed in accordance with prEN 196-10, were compared with each other (**Fig. III-33**). In the chromate solution, only the expected DPC-Cr(III) complex absorbs with an absorption maximum at a wavelength of about 540 nm. In the processed cement extract, by contrast, a solution component absorbs with an absorption maximum at a wavelength below 350 nm additionally (generating yellowish colour). If, for example, a cation other than Cr(III) forms this yellowish complex with the diphenyl carbazone, this reaction is at the expense of the concentration of the DPC-Cr(III) complex. The consequence would be a deficiency in the findings of hexavalent chromium (see above). The occurrence of this additional yellow coloration cannot be safely reproduced in all test solutions of one and the same extract. The tiniest variations in the analysis procedure according to prEN 196-10 may be liable to generate this additional yellow coloration. Such competing reactions with an influence on colour did not occur in chromate analyses conducted at a pH value below 2. A reduction of the pH value below 2, however, requires a prior oxidation step. These observations may furnish the explanation for the two groups of results obtained in the international proficiency investigations (see above) on the water-soluble chromate content in different European cements.

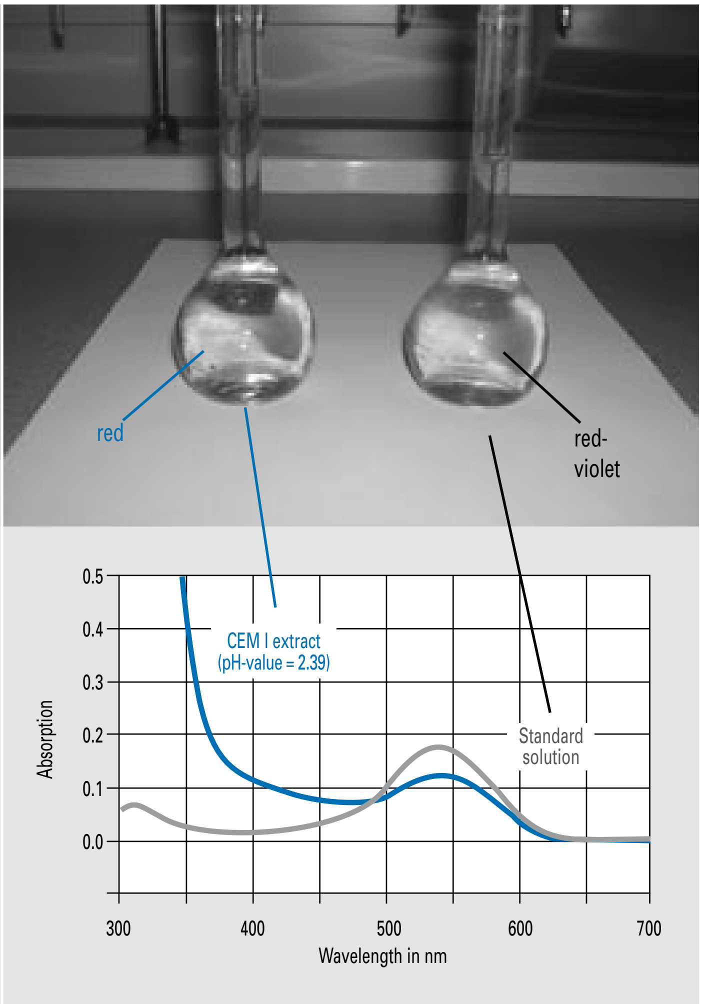


Fig. III-33: UV/VIS spectra of a calibration standard with hexavalent chromium and an aqueous cement extract, both of which were pretreated for spectrophotometric chromate determination in accordance with prEN 196-10

Chromate determination in cementitious preparations

Performing an oxidation step prior to lowering the pH value for chromate analysis is advantageous for the investigation of cementitious preparations as well. The aqueous extracts of tile adhesives, fillers and some other cementitious preparations display milky cloudiness. This cloudiness is attributable to organic additions, and its elimination requires considerable preparative efforts – provided that it is possible in the first place. Chromate analysis, however, presupposes an absolutely clear analysis sample as the cloudiness leads to unspecific absorption during spectrophotometric measurement, thus resulting in too high analysis results. If, however, the extract is heated with a suitable oxidation agent first, the organic additions are modified in such a way as to be easily filtered or decanted. The cloudiness no longer causes any problems then.

Economic production control

The analysis specification prEN 196-10 is highly geared to practice in terms of chromate extraction. It is this very extraction step, however, that is very labour- and cost-intensive when it comes to frequent routine analyses of the water-soluble chromate in cements and cementitious preparations. Many manufacturers of cement and cementitious preparations therefore wonder whether there is a more economic alternative test method for routine applications. Alternatives for the step of chemically analysing the water-soluble extract of a cement or cementitious preparation do exist. Determination can be carried out by ion chromatography or automated redox titration, for example, instead of spectrophotometry, yielding the same result. Even a non-specific chromium analysis by AAS, ICP-OES or ICP-MS is sufficient in many cases. There is, however, no real alternative to the time-consuming and costly extraction step laid down in prEN 196-10 since the extraction process is decisive for the successful dissolution of the chromate reducing agent and thus for the success of reduction, too. A different method would therefore not yield the same result as the reference method. This is, however, the very requirement an alternative method has to meet. The extraction of the water-soluble chromate by producing a standard mortar according to prEN 196-1 furnishes

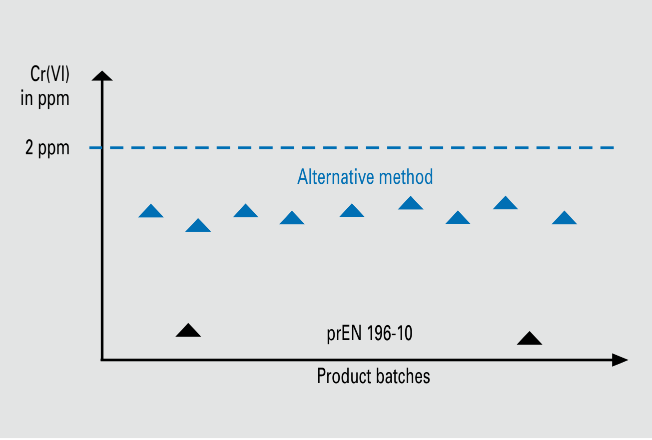


Fig. III-34: Simplified procedure for the routine testing of water-soluble chromate as part of the production control for cements and cementitious preparations

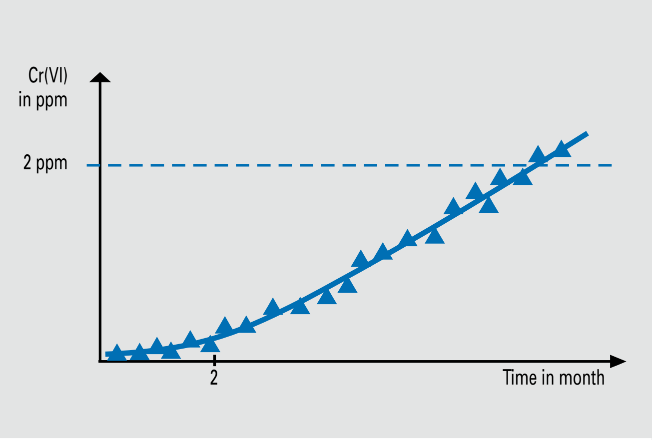


Fig. III-35: "Efficiency decay curve" showing the success and the durability of the chromate reduction measures taken by cement manufacturers

realistically low results. However, the reference method does not always have to be applied in the routine testing of water-soluble chromate as part of the production control of chromate-reduced cements and cementitious preparations. The extraction and the analysis may, for example, also be conducted in accordance with the simpler process described in the Annex to TRGS 613. Pursuant to previous experience, however, the analysis results thus obtained range at a higher level than those yielded by the reference method of prEN 196-10. If, however, the analysis results obtained according to TRGS range below the limit value of 2 ppm, the chromate contents analysed in accordance with prEN 196-10 will safely be below 2 ppm as well (**Fig. III-34**). In this way, the routine analysis of water-soluble chromate can be integrated into factory production control in a more economic manner.

Durability of chromate reduction

The various reducing agents for chromate in cement currently utilised in the cement industry boast different advantages. The reduction of bagged cements in accordance with the "industry-wide regulation" has been primarily accomplished by adding ferrous sulphate compounds in the form of granulates so far. The crystal water contained reacts with the cement to form a capsule of cement hydration products. Although this capsule reduces the (passive) solubility of the compounds, it also conserves the core of the ferrous sulphate particles, protecting it from further ageing and de-activation. When the cement sample is suspended in accordance with TRGS 613 or when the cement is processed, the encapsuled particles are comminuted mechanically, which accelerates their dissolution. This conservation of the chromate reducing agent also enhances the durability of the reducing effect. If, however, the chromate reducing agent is added to the cement not as granulates, but in fine-grained form, a conserving hydrate layer is formed around the particles of the chromate reducing agent as well, but the mechanically aided dissolution of the reducing agent is possible to a limited extent only. Such a fine-grained structure of the reducing agent is obtained when it is ground together with the cement or the cement components. This process of cement grinding also generates higher temperatures, which accelerate and intensify the release of crystal water from the chromate reducing agent and thus its passivation. For that reason, the cement industry has increasingly used tin(II) sulphate when the chromate reducing agent is metered in this way. This is a material free of crystal water. The costs incurred for the use of tin(II) compounds are, however, significantly higher than those for reducing agents based on ferrous sulphate. The Research Institute is therefore currently conducting trials on ferrous sulphates low in crystal water. The trials are to clarify whether these compounds can be of any help in reaching a compromise between technically simple metering by intergrinding, and adequately durable reducing efficacy. Initial results of these investigations show that, in practical application, the evaluation of the reducing effect of these ferrous sulphates with a lower water content strongly depends on the test methods applied, i.e. on the suspension process for chromate testing in particular. Pursuant to the new, practice-geared European method in prEN 196-10, the efficiency of these chromate reducing agents is good. By contrast, the test results obtained in accordance with TRGS 613 pretend lower efficiency.

For manufacturers of cements and cementitious preparations, the verification of effective chromate reduction in their products is crucial for the warranty period. Appropriate storage is of particular importance in this context. To describe the efficiency and durability of chromate reduction under suitable storage conditions, the efficiency in relation to storage time can be determined. If constancy both of dosage and effectiveness of the chromate reducer is given, either once or, preferably, at regular intervals a product sample can be taken, stored properly and be analysed regularly beyond the warranty period. The results can be visualised in a diagram (efficiency reduction curve) and put in relation to the limit value of 2 ppm to be observed (**Fig. III-35**). This representation constitutes a simple way of demonstrating the development with time of the chromate content from the time of reduction.

Measuring and testing methods ■

ESEM

The Environmental Scanning Electron Microscope (ESEM) is chiefly employed in two areas of application. For one thing, microstructures and hydrate phases forming microstructures, respectively, are pictured directly by means of secondary electrons. The investigations are performed on fracture surfaces of samples that are as fresh as possible, and serve to gain understanding of the processes taking place

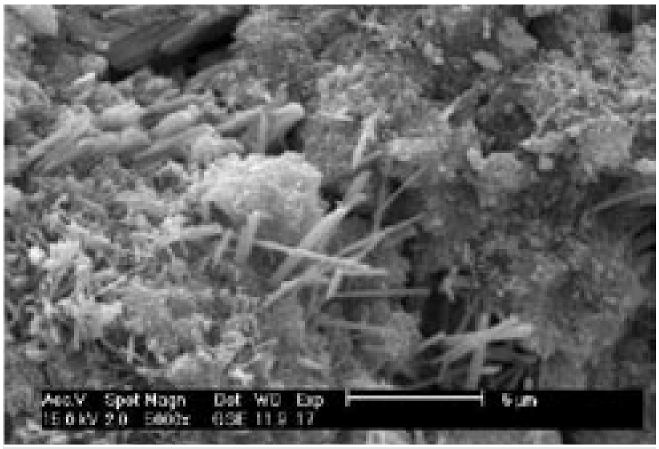


Fig. III-36: Secondary electron image of a fracture surface of mortar showing longish ettringite crystals and densely intergrown CSH phases

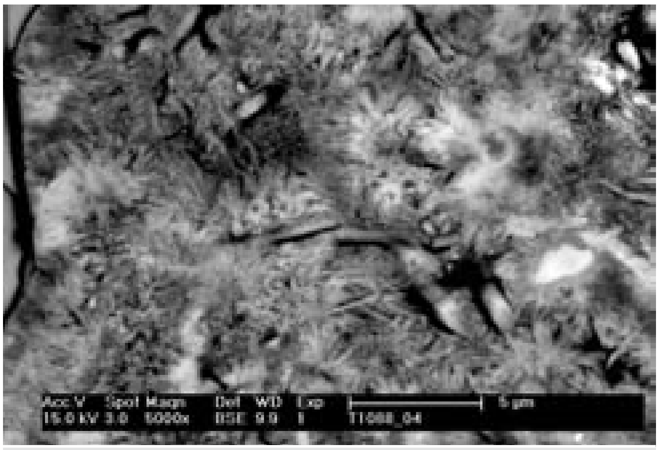


Fig. III-37: Backscattered electron image of a polished mortar section sample. The fibrous crystals of the CSH phases predominate. Occasional ettringite needles are discernible as well. The dark areas between the crystals are capillary and gel pores filled with resin.

during the stiffening, setting and hardening of hardened cement paste, mortar and concrete. The most emphasis was placed on evaluating the topological and morphological microstructure of the crystalline components. **Fig. III-36** serves as an example. It has to be taken into account that the surface of fracture within the structure preferably runs through fault zones, e.g. areas of higher porosity.

For the other, questions relating to the evaluation of cement clinkers are dealt with. Just like light microscopy investigations, this process requires polished clinker sections. However, the surfaces are not etched, but microscopised immediately. The backscatter electron detector takes pictures of the polished sample surface, which are subsequently evaluated in combination with the associated microanalytical investigations (spot analyses, line scan or mapping by energy-dispersive X-ray detector) (see Activity Report 2001-2003).

The investigations of hardened cement pastes, mortars and concretes carried out on polished samples has been gaining in importance recently. The aim behind this is to make statements not just on the quality, but also on the quantity of the phase composition and its distribution. Surfaces of fracture are rather unsuitable for this purpose, however. Given the undefined nature of the surface, quantitative element analyses are very inaccurate. For that reason, only plain polished samples are eligible for this kind of requirements. The preparation of the polished sections involves difficulties, however, especially as far as samples hydrated for a short time only – at an age of a few hours or days – are concerned. The hydrate phases are still soft, and the discrepancy in strength to the constituents not converted is very large. The methods for preparing such samples were optimised only recently. Very time-consuming processing is required to obtain a high-quality sample surface with as little relief as possible. The hydrated structure must first be dehydrated by drying and subsequently soaked with a very fluid epoxy resin, which has to be able to penetrate even capillary and gel pore areas without influencing the hydrate phases. The surface is levelled in several polishing steps, which may take up to several hours. In the end, a diamond grain size of ¼ µm is applied. As a result, a sample surface is obtained that does not present any undesired topographic contrasts and requires only a very thin carbon or metal coating to lend itself to investigation under a scanning electron microscope in uncharged state. **Fig. III-37** highlights the capacity of the method. In addition to the fairly coarse ettringite needles, the fine structures of the fibrous CSH crystals are discernible as well in the backscatter electron image at 5000-fold magnification.

Heat of hydration

Since January 2004, the harmonised European standards have provided for two reference methods for determining the heat of hydration of a cement: the solution method according to EN 196-8 on the one hand, and the semi-adiabatic method, which is also called Langavant method, according to EN 196-9 on the other hand. DIN EN 196-8 has replaced DIN 1164-8 (11/1978), which was the standard previously applicable in Germany. Although both the solution method and the semi-adiabatic method have become reference methods now, virtually only the solution method has traditionally been applied for determining the heat of hydration in Germany. The semi-adiabatic method has hardly any significance in Germany, which is utterly different in France, for example.

The differences between DIN EN 196-8 and DIN 1164-8 are slight and only relate to partial steps of the procedure. The principle of measurement has remained unchanged. It specifies that the heat of solution of unhydrated cement and cement hydrated for 7 days under standardised conditions shall be determined in an acid mix. The heat of hydration is calculated from the difference between the heat of solution values. The method has been proven for decades. Since, however, the reference method is very labour-intensive on the one hand and is considered not to be uncritical from an industrial safety point of view, there is a quest for an alternative method. This is because the samples are dissolved in a mix of hydrofluoric acid and nitric acid. As hydrofluoric acid is counted among the particularly hazardous substances, more and more works laboratories refrain from performing the solution method during factory production control. The heat of hydration is then determined by an alternative method, in most cases by means of isothermal heat flow calorimetry.

The Research Institute possesses an isothermal heat flow calorimeter (Type TAM Air) since mid-2003. At first, the results obtained from solution calorimetry were compared to those of heat flow calorimetry

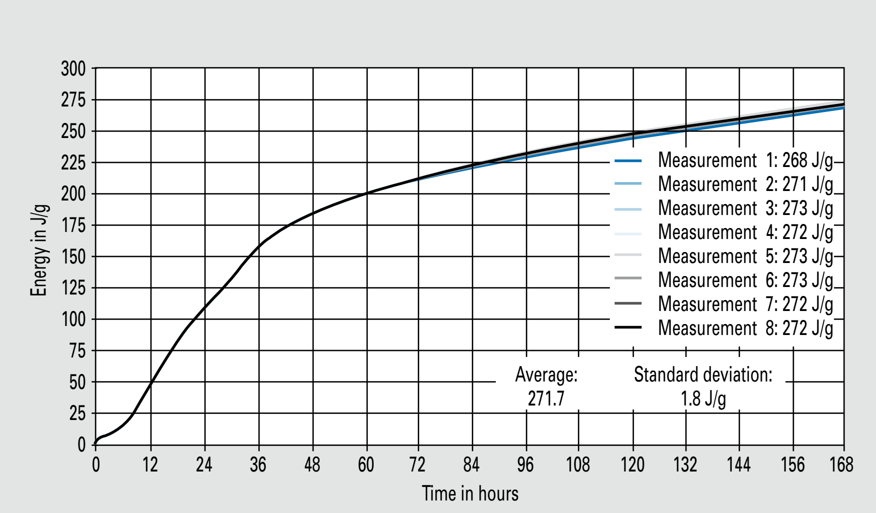


Fig. III-38: Determination of the heat of hydration of a CEM III/A 32,5 N-NW/NA by means of a heat flow calorimeter (TAM Air). The standard deviation of 8 measurements totals 1.8 J/g and corresponds to 0.7% of the measurement result in relative terms.

Fig. III-39: TAM Air heat flow calorimeter with 8 independent channels equipped with admix titration cells

in extensive comparison tests. Proceeding from these results, it has to be checked whether heat flow calorimetry can be introduced as an alternative method for determining the heat of hydration, thus replacing the reference method in day-to-day analysis. Moreover, heat flow calorimetry is also being applied because it does not only furnish the value of the total heat quantity released. Much rather, it additionally reveals the course of heat release, which allows to derive specific information on the hydration behaviour of the cement.

The heat flow calorimeter of the Research Institute is equipped with 8 independent calorimetry channels and can be operated with an accuracy of ± 0.02 K at a temperature range between 5 and 60 °C. According to previous experience, the instrument yields measurement results of very high reproducibility. In the case of standard cement with a typical heat of hydration release of 200 to 300 J/g after 7-day hydration, the standard deviation of the measurement results totals about 2 J/g (**Fig. III-38**). All 8 calorimetry channels are equipped with so-called admix cells. These are mixing cells provided both with a stirring apparatus and titration syringes (**Fig. III-39**). The cement is input into the mixing cell. Water and other liquids are added via the syringes as required, as soon as all the components in the calorimeter have been brought to the right temperature. This allows to prevent a disadvantage inherent in calorimeters that do not provide for cement and water being mixed in the apparatus. If mixing is effected outside the calorimeter, the initial heat release is not recorded by the instrument and thus missing from the overall mass balance. Moreover, the heat flow calorimeter and the use of admix cells allow to investigate the influence that admixtures and their time of addition have on the course of hydration. **Fig. III-40** depicts the effect of different retarding admixtures on the heat release of a Portland cement.

The Research Institute carried out various investigations to examine whether heat flow calorimetry lends itself as an alternative method. All cements scheduled to undergo low-heat testing were investigated both by means of solution calorimetry and heat flow calorimetry for a limited period. The measurement results are plotted next to each other in **Fig. III-41**. It meets the eye that the measurement values of heat flow calorimetry exceeded those obtained by solution calorimetry by an average of about 12% in the case of blastfurnace cements containing blastfurnace slag. By contrast, the results for Portland cements tallied well. For that reason, the deviations are assumed to be attributable to the blastfurnace slags. Additional investigations, which are still under way, are to identify the exact causes.

An international interlaboratory test on cement calorimetry initiated by the university of Lund in 2003 also was to serve to examine whether heat flow calorimetry was eligible as an alternative method. The Research Institute participated in this interlaboratory trial, applying isothermal heat flow calorimetry together with 18 other institutes and solution calorimetry together with 2 other institutes. The investigations were carried out on a Portland cement and a blastfurnace cement. The results of heat flow calorimetry yielded both good reproducibility and good comparability. A comparison of the methods showed that the measurement results for the Portland cement tallied well, but those for the blastfurnace cement did not. Since, however, only 3 laboratories performed solution calorimetry, the statistical significance of the results is low in comparison to that of heat flow calorimetry. For that reason, the Research Institute initiated a national comparison test at the end of 2004, in which 18 laboratories applying the heat flow calorimetry method and 10 laboratories applying solution calorimetry are participating. In addition to that, 6 different cements are being examined. The results are to be available in the spring of 2005 and serve as the basis for the sought validation of isothermal heat flow calorimetry as an alternative method.

X-ray fluorescence analysis

The spectrometric process of X-ray fluorescence analysis has long since been established as an investigation method applied to determine the main and secondary chemical constituents of cement. It has proved its worth in the process control of cement manufacture and in quality assurance within the scope of factory production control and third-party inspection. In contrast to wet chemical analysis, X-ray fluorescence allows several chemical elements to be determined in one analysis process from the same specimen.

At the Research Institute of the Cement Industry, X-ray fluorescence analysis can be performed using pressed powder pellets or fused pellets. The preparation method chosen depends on the nature of the sample and on the elements to be determined. Volatile or oxidisable components can only be fully determined when the samples have not undergone prior thermal treatment, i.e. when pressed pellets are used. With non-volatile components, the measuring accuracy can be enhanced by applying fused pellet preparation. This consists of mixing the sample with a fluxing agent at a suitable ratio, for example 1:10, and fusing it at 950 °C. Cooling at an adequate rate subsequently results in the vitreous setting of the homogeneous melt. In this way, matrix effects caused by the grain boundaries of the particles in a pressed pellet are eliminated. Moreover, the dilution of the melt minimises the mutual influencing by the fluorescence intensity of different elements. As a consequence, a great number of substances of different composition can be analysed with the same calibration.

A CEN working group is concerned with incorporating X-ray fluorescence analysis into the series of cement testing standards. The standard on X-ray fluorescence analysis is scheduled to be completed in 2005. In addition to the description of the process per se, the classification of X-ray fluorescence in relation to the chemical reference methods standardised to date is an essential constituent of the standard. The Research Institute is intent on standardising X-ray fluorescence analysis not as a new reference method, but as an alternative method to be adopted in addition to the existing methods. In case of arbitration, primary parameters that can be determined gravimetrically or volumetrically and on which most wet chemistry processes are based, are preferable to indirect parameters, which include spectrometric measurement data, from an analytical perspective.

X-ray diffractometry

X-ray diffractometry allows the immediate determination of crystalline constituents.

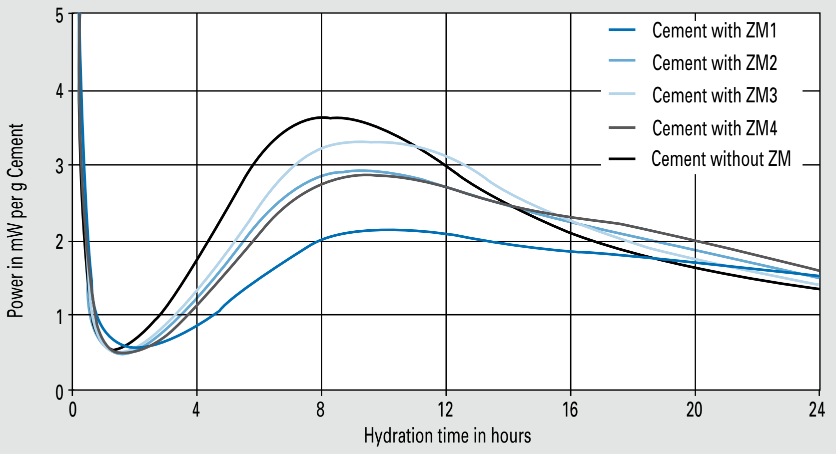


Fig. III-40: Influence of 0.5% admixture (ZM1 to ZM4) on the hydration behaviour of a Portland cement during the first 24 hours

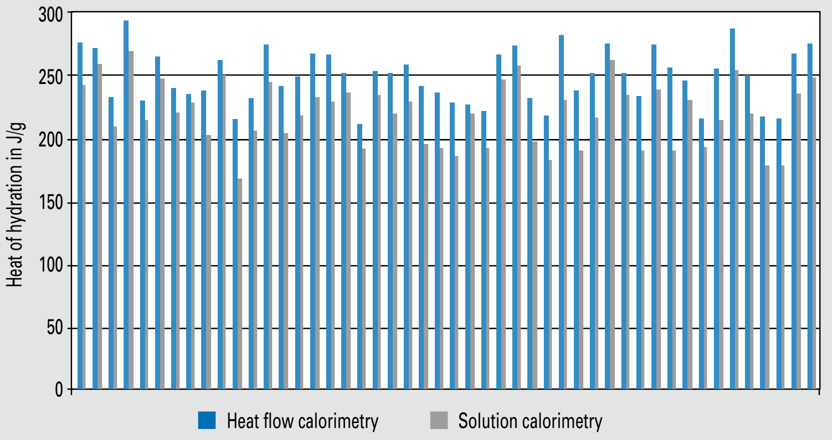


Fig. III-41: Comparison of the determination of heat of hydration by the solution method and by isothermal heat flow calorimetry (TAM Air) based on 48 cement samples

At the Research Institute, X-ray diffractometry is applied to characterise substances which are associated with the manufacture and application of cement in different ways. The spectrum ranges from qualitative and quantitative clinker investigations via the determination of hydration products as far as pigment testing according to DIN EN 12878.

Rietveld refinement has evolved into a high-performance method in the quantitative evaluation of X-ray powder diffractograms. The phase contents for clinkers and Portland cements calculated on the basis of Rietveld refinement are usually more reliable than the Bogue values calculated on the basis of chemical composition.

The increasing use of the Rietveld method in cement works as well as in research and development facilities gave rise to the requirement to have both Rietveld refinement itself and the underlying measuring method of X-ray diffraction validated as an analysis method. For that reason, an interlaboratory test was initiated with the aim of recording the status quo of implementation of the Rietveld method in the cement industry and presenting possible solutions to problems that arise in general. After the first part, which consists of analysing a clinker and a Portland cement, is completed, the interlaboratory trial is scheduled to be extended to include, among other things, testing the quantification of cements with several main constituents. In this context, the Research Institute has been developing methods based on Rietveld refinement that allow even vitreous constituents, such as blastfurnace slag, to be quantified.

The knowledge of all phases present in the sample investigated and of their crystalline structures is a fundamental precondition for successful Rietveld refinement. It has proved worthwhile in the determination of clinker and Portland cement to treat a divided sample of the substance investigated with methanol and salicylic acid in order to dissolve out the calcium silicates. The additional measurement of the residue allows an adequately reliable identification and subsequent quantification of the further clinker phases remaining.

Furthermore, it is crucial for the correctness of Rietveld refinement to take into account texture effects induced by preparation. Preferred orientations of the individual crystals in the sample that are not taken into consideration adequately can result in deviations of several wt.% with regard to the phase contents. In principle, Rietveld refinement allows for the reproduction of texture effects using suitable mathematical models. The choice of an appropriate set-up of measuring instruments constitutes a further possibility of eliminating this source of error. In transmission samples, prepared as capillary or flat specimens, the preferred orientation of anisotropic particles is by far less pronounced than in pressed samples.

Conversely, the observation of texture effects occurring during the common measuring set-up according to Bragg-Brentano allows to roughly estimate crystallite sizes. Based on the example of a clinker, **Fig. III-42** illustrates the influence of the preferred orientation of alite. The reflex at 32.3 ° (2 theta) in particular is considerably more intense in the textured specimen than in the specimen without texture. The preferred orientation causing this phenomenon is attributable to a coarser structure of the alites due to an extended sintering zone in the rotary kiln. The reflex width taken as a measure for crystallite size in other cases is overlaid by other influencing variables in this case. These include geometrical effects and the incorporation of foreign ions.

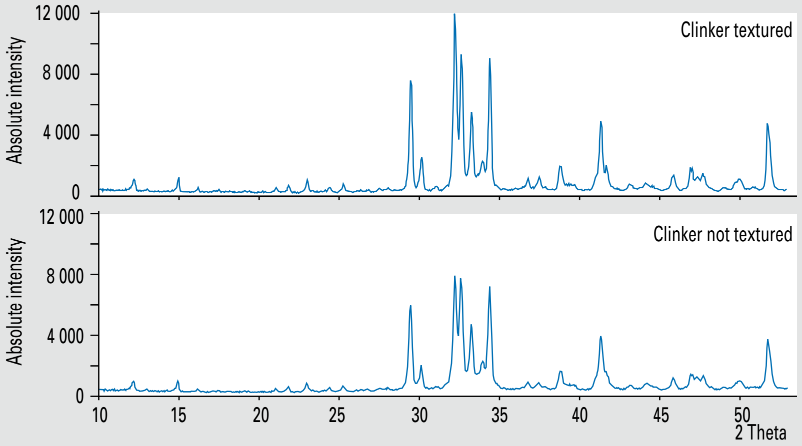


Fig. III-42: X-ray powder diffractograms of a cement clinker with and without prefered orientation of alite

Technical approvals

When construction products deviate from standards and other technical regulations, their application in the domain governed by building supervisory authorities presupposes national technical approval issued by the German Institute for Building Technology (DIBt). In individual cases, the responsible building supervisory authority may grant its consent instead. The investigations required for the technical approval of hydraulic binders and concretes are carried out – amongst others – by the Research Institute of the Cement Industry.

CEM II/B-S-NA cements with an alkali content exceeding 0.70 wt.% (Na_2O equivalent) are an example for cements approved by the building inspectorate. The approvals are based on investigations conducted by the Research Institute.

Not all the cements that conform to the DIN EN 197-1 and DIN 1164 standard series can be used for concrete according to DIN 1045-2 without restrictions, as no experience in construction practice and no scientific investigations have been available to date for some of them. According to DIN 1045-2, Portland-composite cements CEM II/B-M (S-LL) for example may only be applied for concrete not exposed to any risk of corrosion or attack (exposure class X0), and for foundation and internal components (XC1, XC2). If the scope of application is to be extended to include additional exposure classes, the DIBt must have issued a technical approval for application. The investigations needed for these approvals are conducted by the Institute as well after thorough counselling of the applicants. In the period under review, some German cement manufacturers developed new CEM II-M cements. The first national technical approvals have already been granted.

IV

Quality surveillance and quality assurance of cement

The quality surveillance and quality assurance of cement and cement-type binders still constitute one of VDZ's core competences. The identity of VDZ's quality surveillance organisation, however, changed profoundly in the last decade. Most binders are inspected in accordance with harmonised European standards now. The transition from quality surveillance, which was rather nationally geared, to quality assurance, which has a European orientation, was effected both regarding regulations and the conditions underlying surveillance. Accordingly, the internal structures of VDZ' quality surveillance organisation were adjusted consistently and tailored to international aspects over the past years. This process was continued in the period under review. The main emphasis was placed on the further professionalisation of certification services and the adoption of a more variable system for the billing of services.

The number of binders certified and inspected hardly changed in the period under review. Some 540 binders from 64 works were inspected in accordance with statutory regulations. The number of binders additionally inspected according to regulations under private law in compliance with agreements concluded with foreign bodies increased slightly. The areas of approval were extended slightly again in the period under review. Conducting inspection in accordance with EN 197-2, the European standard for conformity evaluation of cement, and the associated operating procedures has undoubtedly proved its worth. EN 197-2 now also serves as a model for corresponding conformity evaluation rules for additions. In the wake of the implementation of the European chromate directive, specifications regulating the inspection of the water-soluble chromate content were drawn up for the first time in the period under review.

The certification body for management systems FIZ-Zert, which was established in 1998, was re-accredited in the period under review. While certification was exclusively restricted to quality management systems in the past, it encompassed the certification of environmental management systems and the verification of CO_2 emissions for the first time in the period under review.

The essential product and test standards in the domain of cement standardisation have been completed by now. Activities are therefore focused on completing the existing standards. The new or revised versions, respectively, of as many as 4 harmonised European cement and binder standards and as many as 6 test standards were completed in the period under review. This has been the first time that harmonised European specifications governing cements with low heat of hydration have been in effect. Moreover, the most important test standards for cement were revised 15 years after they were first published. To take account of worldwide developments, standardisation activities will be more closely coordinated between the European committee CEN/TC 51 and the ISO committee TC 74 in the future.

Mortar consistency testing

VDZ's quality surveillance organisation

VDZ was founded more than 125 years ago to standardise the testing and evaluation of the quality features of cement. Accordingly, the testing, inspection and certification of cements and cement-type binders to meet the protective goals set by the state building regulations or according to the Construction Products Law are some of VDZ's constitutional functions. For this purpose the association operates the quality surveillance organisation as a testing laboratory, inspection body and certification body (PÜZ body).

Over the past 10 years in particular, the character of the surveillance organisation changed considerably. Prompted by the shifts in the European regulations and the adaptation of internal structures required, the transition from rather nationally geared "quality surveillance" to modern product certification of stronger European orientation was implemented during that period. The re-orientation of the Research Institute resulted in a significant change in the income structure over the past years. Joint work is increasingly bankrolled by external research funds and by income the VDZ realises from services rendered for its members. For that reason, the consistent professionalisation of certification services, too, was paramount in the period under review. The changeover of the billing system allowed to allocate costs in accordance with their origination to a higher degree, and to adopt a more variable system for the billing of services. Over the past years, the Research Institute created the preconditions for services being rendered efficiently and reliably in an overall environment of growing requirements.

Regardless of these changes, the quality surveillance organisation continues to be one of VDZ's core competences and constitutes a major pillar of joint research. The comprehensive pertinent data base that the Research Institute has compiled over many years is the prerequisite for the association's successful activities. VDZ was only able to give competent answers to many questions regarding building practice and also to questions of cement standardisation because the corresponding cement data of nearly all German cements was at hand at the Research Institute. This data can be processed in anonymous form and utilised for scientific evaluations.

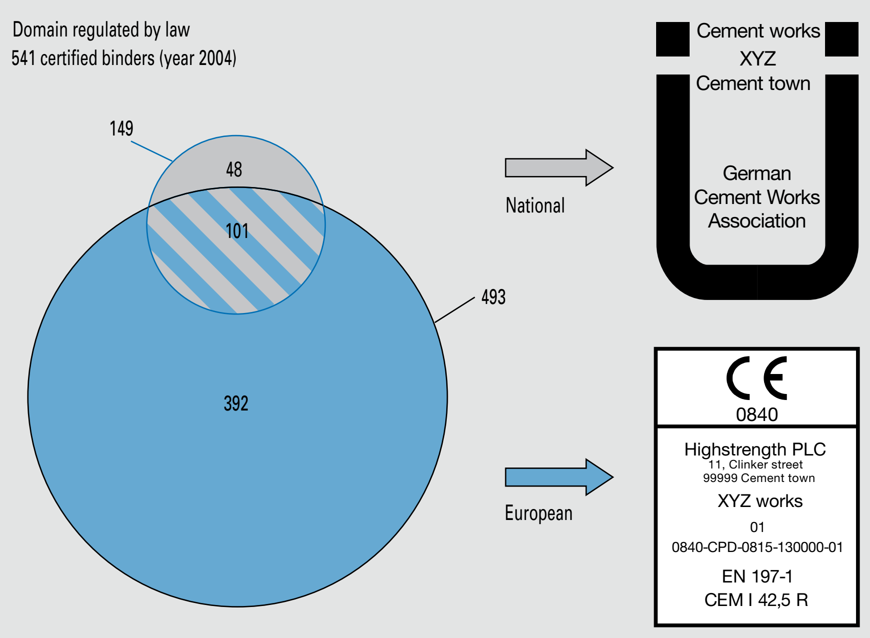


Fig. IV-1: Cements in the domain regulated by law that were certified by VDZ's quality surveillance organisation

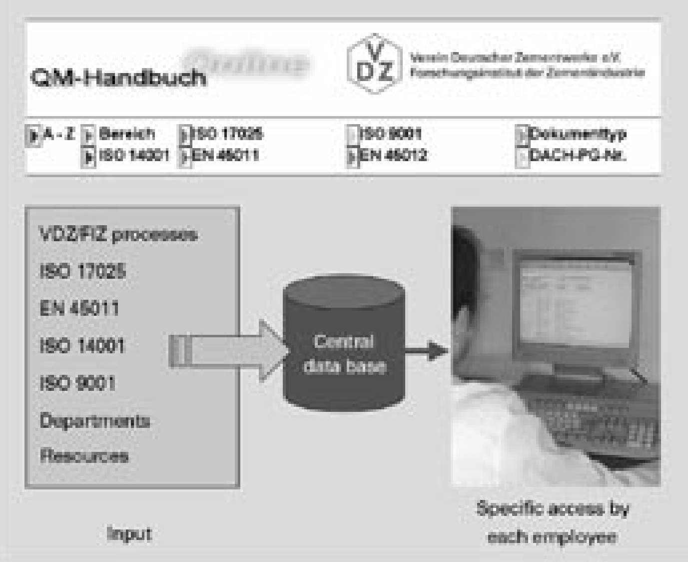


Fig. IV-2: The EDP-backed in-house management system of VDZ / FIZ

Approval and accreditation

VDZ's quality surveillance organisation exercises its functions as a testing laboratory, inspection body and certification body in the domain regulated by law. Approval covers the state building regulations (LBO) on the one hand, which are applicable at national level. Conformity of construction products with the state building regulations is indicated by attaching the national conformity mark (Ü mark). Moreover, VDZ's quality surveillance organisation is notified according to the German Construction Products Law, which implements the EU Construction Products Directive, and is registered in Brussels as certification body No. 0840. Conformity with harmonised European standards and regulations is indicated by attaching the CE marking. The introduction of the first harmonised cement standard EN 197-1 in the year 2001 triggered a major shift in the key activities performed by VDZ's quality surveillance organisation. As can be seen from **Fig. IV-1**, just under 85% of the binders subject to the domain regulated by law have been certified in accordance with European regulations by now. Categories overlap in the case of cements with special properties, which are certified pursuant to the national "supplementary standard" (Restnorm) DIN 1164-10 and simultaneously meet the requirements of European standard EN 197-1.

VDZ's quality surveillance organisation additionally obtained accreditation as a product certification body under private law according to EN 45011 in 2002 although this is not required by law. In addition to that, all relevant laboratory tests were accredited in accordance with ISO 17025. To that effect, a lean, computer-aided in-house management system was instituted, which complies with the specifications of 4 different conformity attestation standards (**Fig. IV-2**). The intention behind this was to subject the quality surveillance organisation to regular and independent external inspection and thus to evaluation criteria which are applicable to other certification bodies in Europe.

Approval by the competent building supervisory authorities covers cement-type binders, concrete additions and admixtures as well as cementitious mixtures within the scope of both standards and building inspectorate approvals (**Tab. IV-1**). VDZ's quality surveillance organisation primarily certifies cements and cement-type binders. In order to offer a services range that is highly attractive for clients, however, the areas of activity and approval were gradually extended and supplemented by additional construction products. An application for approval to be supplemented and extended to include further construction products, respectively, was filed in the period under review as well.

Third-party inspection of cement according to statutory regulations

Tab. IV-2 presents an overview of the cements and hydraulic binders which VDZ's quality surveillance organisation certified and inspected, respectively, in the year 2004. 541 binders, including 505 (93%) cements, were inspected in accordance with statutory regulations (**Fig. IV-3**). The figures also cover 13 cements from 8 foreign works. In addition to that, VDZ's quality surveillance organisation issued certificates of conformity according to DIN 1164 for 2 cements on the basis of third-party inspection by a foreign inspection body. The number of binders audited has increased by a total of 9 since 2002. As a consequence of works closures, the number of works inspected declined to 64, as against 68 in 2002. An average of 8.4 binders was inspected per works (**Fig. IV-4**).

Tab. IV-I: Areas where VDZ's quality surveillance organisation is approved as a testing laboratory, inspection body and certification body for construction products

Construction products	Technical regulation(s)	Conformity attestation level	
		BPG	LBO
Binder			
common cement	DIN EN 197-1	1 +	
cement with special properties	EN 197-4	1 +	
	EN 14216	1 +	
	DIN 1164-10, -11		ÜZ
calcium aluminate cement	EN 14647	1 +[2]	
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[4]		ÜZ
Concrete additions			
type I additions (e. g. pigments)	EN 12878	2 +[2]	
type II additions (fly ash, silica fume)	EN 450-1	1 +	
	EN 13263-1	1 +[2]	
trass	DIN 51043		ÜZ
single pigments	DIN EN 12878		ÜZ
pigments as delivered	DIN EN 12878		ÜHP
fly ash	DIN EN 450		ÜZ[5]
other concrete additions	Approval[4]		ÜZ
Concrete admixtures			
	EN 934-2, -3, -4	2 +	
	DIN V 18998		ÜHP
	Approval[4]		ÜZ
Aggregates			
	EN 12620	2 +	
	EN 13055-1	2 +	
	EN 13139	2 +	
Masonry mortar			
	EN 998-2	2 +	
Cementitious mixtures[6]			
grouting mortar	DIN EN 447		ÜZ

BPG: Construction products law LBO: State building regulations ÜZ: conformity certificate

[1] Not relevant in building authority terms, attestation level corresponds to ÜZ
[2] Harmonised European standards are not available yet
[3] Applied for
[4] If production process, composition or properties deviate substantially from the standard
[5] Until the harmonised European standard takes effect
[6] Requests for further applications have been filed

Tab. IV-3 summarises the number of domestically produced cements inspected by VDZ's quality surveillance organisation as well as the corresponding domestic dispatch quantities for 2004 compared to 2002 (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 certified has increased by 20 to 492 since 2002. The figures include 401 cements from 49 works in the old federal states, and 91 cements from 7 works in the new federal states. Moreover, 12 domestic and foreign depots operated by manufacturers were included in the inspection, and samples were taken of a total of 26 cements dispatched from there.

For the first time since 1995, a significant rise in the share of Portland cement CEM I in the dispatch quantity was recorded, which was accompanied by a drop in the

Tab. IV-2: Overview of the cements and hydraulic binders inspected and certified by VDZ's quality surveillance organisation in 2004

Binder	Standard /regulation	Scope	Type of certification	Certification body	Inspection body	Number of binders	Number of works
Cement	EN 197-1	EU	Statutory	VDZ	VDZ	494	64
	DIN 1164[1]	Germany					
	DIN 1164	Germany			Others	2	2
	Approval	Germany			VDZ	11	6
	ZTV Beton	Germany		-	VDZ	56	39
	BRL 2601, NEN 3550	Netherlands	Under private law	BMC	VDZ	96	25
	TRA 600, PTV 603, NBN B 12	Belgium		VDZ	VDZ	33	14
	Reglement NF	France		AFNOR	VDZ	22	8
Masonry cement	DIN 4211	Germany	Statutory	VDZ	VDZ	24	19
	BRL 2603	Netherlands	Under private law	BMC	VDZ	5	3
Hydraulic road binder	DIN 18506	Germany	(Statutory)	VDZ	VDZ	12	10

[1] Upon request additional EC certificate of conformity according to EN 197-1 or additional certificate of conformity according to DIN 1164

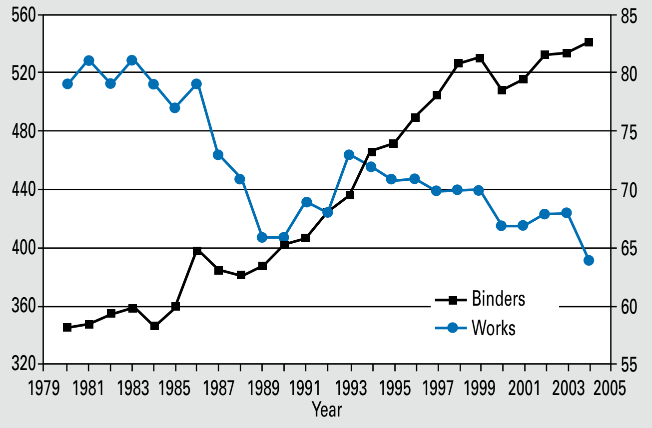


Fig. IV-3: Trend of binders and works audited by VDZ's quality surveillance organisation

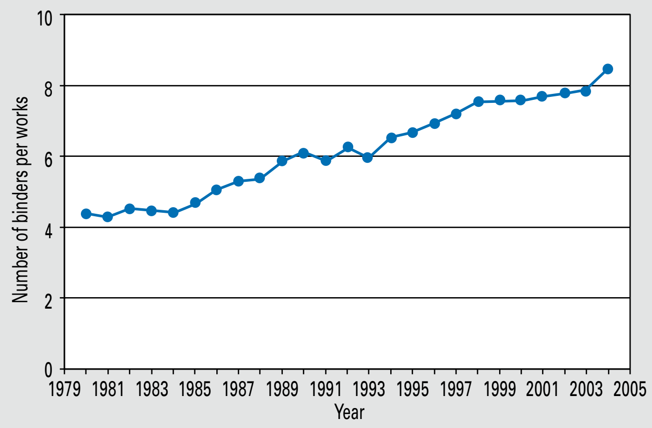


Fig. IV-4: Average number of binders inspected per works for the works inspected by VDZ's quality surveillance organisation

dispatch quantity proportion of blastfurnace cement CEM III. On the other hand, the number of Portland cements certified decreased, while that of blastfurnace cements increased. A further striking tendency was a marked shift in the share in dispatch quantities at the expense of the cements of strength class 32,5 and in favour of the cements of strength classes 42,5 and 52,5, respectively.

56 cements approved for use in concrete pavements were inspected in 2004 as well. VDZ's quality surveillance organisation further inspected 24 masonry cements to DIN 4211, of which 5 related to the classification MC 12,5, and 12 hydraulic road binders to DIN 18506 in 2004.

Third-party inspection of cement according to voluntary regulations

Bilateral agreements between VDZ's quality surveillance organisation and the corresponding Belgian, French and Dutch inspection bodies on the mutual recognition of testing, inspection and certification activities have existed for many years. They relate to the third-party inspection pursuant to voluntary regulations beyond the scope stipulated by law. VDZ's quality surveillance organisation performs the supplementary tests and inspections required at the German manufacturers' sites upon consultation with the corresponding foreign body. This allows to avoid additional works visits and inspections, which in turn reduces the costs accruing for cement manufacturers. In the period under review, an additional agreement was concluded with the Dutch certification body Stichting BMC, according to which the Research Institute can perform inspection activities for Dutch customers as a subcontractor of BMC.

VDZ's quality surveillance organisation is currently inspecting 96 cements and 5 masonry cements in accordance with Dutch evaluation criteria (BRL) additionally; the certificates are issued by BMC.

To obtain the Belgian BENOR marking, a total of 12 instead of 6 audit testings per year has to be conducted. Furthermore, there are additional requirements for the final set and the screening rejects of cements.

Tab. IV-3: Number of domestic cements certified by VDZ's quality surveillance organisation in 2004 (2002)

Cement	Number of cements				Share in (domestic) cement dispatch in wt. %			
	32,5	42,5	52,5	Total	32,5	42,5	52,5	Total
Portland cement CEM I	62 (70)	86 (87)	57 (57)	205 (214)	23.0 (23.5)	28.3 (24.5)	7.3 (5.9)	58.6 (53.9)
Portland-composite cement CEM II	85 (83)	42 (39)	14 (12)	141 (134)	22.1 (24.9)	7.5 (5.8)	1.4 (1.3)	31.0 (32.0)
Blastfurnace cement CEM III	97 (92)	39 (25)	7 (5)	143 (122)	8.3 (11.2)	1.9 (2.4)	0.2 (0.2)	10.4 (13.8)
Pozzolana cement CEM IV	2 (2)	- (-)	- (-)	2 (2)	0.0 (0.2)	- (-)	- (-)	0.0 (0.2)
Composite cement CEM V	- (-)	- (-)	1 (-)	1 (-)	- (-)	- (-)	0.0 (-)	0.0 (-)
Total	246 (247)	167 (151)	79 (74)	492 (472)	53.4 (59.8)	37.7 (32.7)	8.9 (7.4)	100.0 (99.9)
Cements with high early strength	138 (144)	101 (107)	48 (48)	287 (299)	44.7 (49.3)	30.9 (27.6)	7.4 (6.3)	83.0 (83.1)
Cements with normal early strength	108 (103)	66 (44)	31 (26)	205 (173)	8.7 (10.5)	6.8 (5.1)	1.5 (1.2)	17.0 (16.9)
Cements with special properties (low heat, high sulphate resistance, low alkali)	70 (80)	34 (30)	5 (3)	107 (113)	No information			

Several parts of NBN B 12 specify requirements for cements with special properties. VDZ's quality surveillance organisation is currently certifying and inspecting 33 cements according to Belgian regulations additionally.

There are regulations governing the issuance of the NF marking in France. They require 12 audit testings to be performed per year. An agreement with the French certification body AFNOR holds that VDZ's quality surveillance organisation should act as a subcontractor of AFNOR to perform audit testing and works visits at German cement works. VDZ's quality surveillance organisation is currently testing and inspecting 22 cements from 8 works which are labelled with the NF mark.

Further construction products

VDZ's quality surveillance organisation still places the main focus of its work on the testing, inspection and certification of cement and cement-type binders. However, an increasing number of other inspection orders is being executed, too. For example, the quality surveillance organisation tested and inspected 30 pigments, among other materials, in the period under review. Employees of the Research Institute were also involved in completing the pigment standard DIN EN 12878 in all language versions. The final adoption as a harmonised standard is scheduled for 2005. Moreover, various contract tests, such as suitability testing of grouting mortar or testing pursuant to ASTM, were carried out.

Proficiency testing

The European standard for conformity evaluation of cement EN 197-2 stipulates that testing laboratories in charge of executing audit testing take part in regular proficiency tests. The requirement of regular participation in proficiency tests also derives from the accreditation of the Research Institute's testing laboratories pursuant to ISO 17025. In its capacity as an approved testing laboratory for cement according to NEN 3550, the Research Institute's laboratory has taken part in weekly proficiency testing of a Dutch reference cement since 1988. The tests are organised by Stichting BMC and evaluated 4 times a year. There is a meeting of the pilot laboratories once a year where the results of the proficiency testing and the causes of possible differences in the test results are discussed. VDZ's testing laboratory also participates in the cement proficiency testing carried out every year by the Association Technique de l'Industrie des Liants Hydrauliques (ATILH), in which some 180 test laboratories regularly take part. Numerous other inter-laboratory tests, especially with member works, are carried out every year in order to detect possible sources of error at an early stage.

Testing laboratory

Every year, the laboratories of the Research Institute test about 3 500 binder samples as part of audit testing, contract testing and proficiency testing. Given an average of approximately 10 properties to be tested, this amounts to some 35 000 individual tests. Given such a high sample throughput, efficient test processes are essential on the one hand; on the other hand, a consistent standard and high quality of testing must be ensured.

Physical testing is carried out in a testing laboratory that was refurbished completely in 1996 and has been optimised and supplemented continually since then. The high degree of standardisation of testing procedures allowed to ensure consistent testing quality in spite of changes in staff. Chemical tests are performed in the cement chemistry department of the Research Institute. The activities in this field also included preparations aimed at significantly increasing the number of heat of hydration measurements executed (cf. Chapter III). As a consequence of the changeover to the European standards for LH cements, the frequency of audit testing rose from the previous two times to six times per year. Planned optimisation measures relate to the adaptation of the test methods to the specifications of the new EN 196 and to the incorporation of the data base into the interdisciplinary LIMS system (cf. Chapter 0).

Quality assurance

Since April 2001, standard cements labelled with the CE marking can be put into circulation on the European domestic market without any restrictions. They are inspected in accordance with EN 197-2, the European standard for conformity evaluation. A CEN report and interpretations by the notified bodies, which create the basis for uniform application of the conformity evaluation standard by different bodies in Europe, have been adopted additionally. Thus, an integral set of regulations governing the implementation of conformity evaluation is available, which is not the case for many other construction products. The experience gathered with the application of these regulations to date is favourable in every respect.

Conformity evaluation of other construction materials

The phrasing of the standard for conformity evaluation EN 197-2 provides for its scope of application not being restricted to standard cements according to EN 197-1, but also covering further cements. For example, further product standards for cements with special properties and a standard for masonry cements were adopted in the period under review, which are included in the scope of EN 197-2 (cf. section on "standardisation" below). The conformity attestation process stipulated is system 1+, which is the highest possible level of attestation laid down in the Construction Products Directive (**Tab. IV-4**). The systems 2+ and 2, respectively, which do not provide for product certification, are stipulated for hydraulic sub-base binders and building lime at European level.

Like cements, reactive additives are subject to system 1+. In the period under review, a conformity evaluation standard for fly ash, EN 450-2, was completed, a corresponding standard for silica fume – EN 13263-2 – is undergoing the voting procedure, and a third one for granulated blastfurnace slag – EN 15167-2 – is being elaborated. All these three conformity evaluation standards are largely identical to EN 197-2. Specific differences primarily relate to the interpretation of the term "works" and to process control. Moreover, harmonised standards for admixtures and aggregates were completed in the period under review.

Tab. IV-4: Systems of conformity attestation according to the EU Construction Products Directive and associated standards for the conformity evaluation of concrete constituents

System	Attestation of conformity	Functions of the approved body	Standard for conformity evaluation	Concrete constituents
1 +	Certification by certification body	Third-party inspection *including* testing of spot samples	EN 197-2	Cement[1] Masonry cement
			EN 450-2	Fly ash
			EN 13263-2[3]	Silica fume
			EN 15167-2[3]	Granulated blast-furnace slag
1		Third-party inspection *without* testing of spot samples	-	-
2 +	Declaration of conformity by manufacturer	Initial inspection and *regular inspection*	EN 934-6	Admixtures
			EN 13282[3]	Road binders
			EN 12620 et al.[2]	Aggregates
			EN 12878	Pigments
2		*Initial inspection* only	EN 459-2	Building lime
3		Initial testing only	-	-
4		-	-	-

[1] Standard cement, cement with special properties, high-alumina cement

[2] In case of high safety requirements, otherwise system 4

[3] Standard is undergoing voting procedure or being prepared

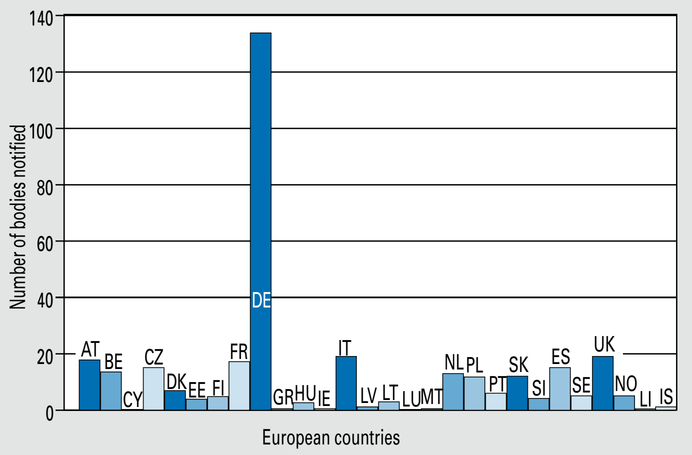


Fig. IV-5: Number of bodies aproved according to the Construction Products Directive in Europe

Cooperation of notified bodies

It can be seen from **Fig. IV-5** that there are some 335 notified bodies in Europe now, which were approved each for the scope of the EU Construction Products Directive by the authorities of the member countries. More than 130 of them are located in Germany. In view of this large number of bodies coming from areas where utterly different traditions and experiences prevail, the harmonised interpretation and application of the standards and regulations is important. At the instigation of the EU Commission, the notified bodies are to organise their mutual cooperation themselves. To that purpose, various committees were set up at European level. VDZ's quality surveillance organisation is involved in the work of the Advisory Group of the notified bodies, in the associated committee mirroring this group, and in Sector Group 02 "Cement, Concrete, Mortar, Aggregates".

In the period under review, Sector Group 02 worked out interpretations on the product standards for building lime, admixtures, aggregates and masonry mortar. It further discussed the question of the extent to which the European interlaboratory tests for cement conducted by the approved bodies can be coordinated or possibly even replaced by one single European interlaboratory test. Among other topics, the Advisory Group discussed questions of organisation, details regarding the exchange of experiences between the various bodies, guidance papers issued by the EU Commission, horizontal documents and construction product-specific interpretations as well as questions relating to CEN and EOTA. In the short time since the panel was founded, such a plurality of interpretations on questions of conformity evaluation encompassing more than one product has been elaborated that individuals can hardly keep track of them any more. In the associated national panel which mirrors this group, the status of the national accreditation law was debated as well. It is to be hoped that this law will allow to accomplish better coordination of the domains covered and not covered, respectively, by statutory regulations, and that it will entail lower expenditure and higher international acceptance.

Tab. IV-5: Differences in the legal areas for the conformity evaluation of cement according to EN 197-2 and the compliance evaluation of chromate-reduced cement according to prEN 196-10, Annex A

Standard	EN 197-2	prEN 196-10, Annex A
Evaluation	Conformity (conformity evaluation)	Compliance (evaluation of compliance)
Scope	EU construction Products Directive 89/106/EWG	EU Chromate Directive 2003/53/EC
Protection target	Safety[1)]	Industrial health and safety
Requirement for	Hardened concrete	Fresh concrete
Public authority	Building supervisory authorities	Industrial health and safety authorities
Conformity evaluation	CE (notified bodies)	?

[1)] 6 essential requirements (stability, fire protection, health, safety in use, noise protection, thermal insulation)

Compliance surveillance for chromate

The European chromate directive took effect on January 17, 2005. It lays down limit values for the water-soluble chromate content in cement. A European test method – prEN 196-10 – for chromate determination was elaborated, which is presently available as a draft standard. The analytical steps of the test method are described in detail in Chapter III.

All questions pertaining to evaluating the compliance of the chromate content are regulated in an annex to prEN 196-10, which forms part of the standard and is similar to the conformity evaluation standard for cement EN 197-2 in many aspects. The main reason for compiling a separate document was the fact that different legal areas are concerned (**Tab. IV-5**). Conformity evaluation according to EN 197-2 within the scope of the EC Construction Products Directive belongs to the area of responsibility of the building supervisory authorities, while industrial health and safety authorities are in charge of evaluating compliance with the water-soluble chromate content. The distinction between these concepts, which is indicated by the use of the terms “conformity” and “compliance” in the English version, cannot be translated into German adequately.

Similar to EN 197-2, the draft standard comprises specifications on factory production control by the manufacturer, on the functions of a certification body possibly called in, on the compliance criteria, on the evaluation of compliance, and on the measures to be taken in case of non-compliance. Manufacturers have to make sure that the permissible chromate content is complied with as part of their factory production control. To that effect, their works quality manual has to comprise a description of the associated process control, in particular with regard to the use of the reducing agent, the tests conducted, and other measures. Using a sample of finished cement, they have to prove at least once a month that the permissible chromate content is observed. The effectiveness of the reducing agent can be reduced as storage time gets longer. For that reason, proof must not be furnished immediately after sampling, but when the shelf life declared by the manufacturer is expiring. The cement sample has to be stored in completely airproofed containers beforehand.

Certification of management systems

Product certification is subject to statutory regulations and mandatory. By contrast, the certification of management systems is entirely voluntary. Moreover, the degree of itemisation required and the methods of evaluation differ. Product certification places greater emphasis on controlling compliance with specifications regarding contents. System certification, by contrast, rather has the features of a dialogue and chiefly serves to optimise a system in terms of formal requirements. The methods for establishing such systems and for describing the relevant processes in manuals and other documents are basically the same, however. For that reason, the specific requirements for factory production control on the one hand and for management systems according to ISO 9001 or ISO 14001 on the other hand are commonly incorporated into a single, so-called “integrated” management system.

The common features of and specific differences between product and system certification were intensely discussed in conjunction with the establishment in the mid-90ies of EN 197-2, the first conformity evaluation standard for cement. In order to take advantage of possible synergies between product certification performed by VDZ’s quality surveillance organisation and the certification of quality management systems according to ISO 9001, the decision to set up a certification body for management systems, FIZ-Zert, was taken then. FIZ-Zert was first accredited by the umbrella organisation for accreditation (TGA) under private law in 1998. Five years after it was first granted accreditation for quality management systems according to ISO 9001, FIZ-Zert now was re-accredited in the period under review.

The range of subjects relevant for the companies has shifted since FIZ-Zert was first accredited. The experience and routine in the handling of integrated management systems gathered by now suffice to meet both the requirements for factory production control according to EN 197-2 and for quality management systems according to ISO 9001. On the other hand, the issue of environmental protection in cement manufacture has been getting ever more important for the cement manufacturing companies (cf. Chapter II). In the period under review, FIZ-Zert therefore created the internal preconditions enabling it to certify also environmental management systems according to ISO 14001. FIZ-Zert’s re-accreditation for quality management systems in 2003 was accompanied by its first-time accreditation for the certification of environmental management systems according to ISO 14001. Thus, integrated QM/EM systems can now be certified as well. **Fig. IV-6** illustrates the implementation of a system audit at a cement works by way of example.

Questions relating to CO_2 emissions trading have been gaining in importance for the cement industry (cf. Chapter II). In the

Fig. IV-6: Conversation between the works' quality management system representative and the external auditor

year 2004, the CO_2 emissions of all cement works with clinker production had to be verified in accordance with the Law on Trading Greenhouse Gas Emissions for the first time. FIZ-Zert was involved in the verification process at a total of 28 production sites of cement works and lime works.

Standardisation

The European cement standardisation committee CEN/TC 51 was founded more than 30 years ago. This step was triggered by an EU initiative aimed at lifting trade barriers that existed because the EU member countries had different regulations and standards. In many years of meticulous work, the uniform testing specifications of the EN 196 standard series were worked out and tested in interlaboratory trials first. Preparations for EN 197-1, the product standard for standard cements, were started at the same time. The standardisation mandate provided for all cements categorised as traditional and proven in Europe being included. The compilation of the conformity evaluation standard EN 197-2 was commenced in the early 90ies. Since the completion of EN 197-1 and -2 at the turn of the millennium, harmonised specifications for standard cements have been applicable in Europe. Since then, cements labelled with the CE marking can be traded without any restrictions in all EU countries. Restraints on application merely result from restrictions laid down in the respective concrete standards, which are still nationally oriented in spite of the completion of EN 206 (cf. Chapter V). Further standardisation work is currently focusing on the completion of the existing product and conformity evaluation standards. As outlined below, TC 51 finalised either new or revised versions of as many as 4 harmonised European cement and binder standards and 6 test standards in the period under review.

The worldwide standards organisation ISO, in which 146 countries are involved, published test specifications for cement as well. These are virtually identical with the European standards, which is due to the fact that the European committee CEN/TC 51 has overall responsibility for the standardisation of cement according to ISO. It has to be taken into account that ISO standards serve as guidelines, while CEN standards are mandatory. Given the close connection to the work of ISO, Asian countries – particularly China, Japan and Korea – professed heightened interest in intensifying cooperation at the latest CEN/TC 51 meeting for the first time. About two thirds of global cement output is currently produced in Asia; this corresponds to almost 4 times the quantity produced in the whole of Europe. China alone accounts for a share of approx. 42% of global cement output. Its cement output is thus about 24 times higher than that of Germany. To take account of global trends, closer cooperation with the ISO committee TC 74 was agreed upon at the latest meeting of CEN/TC 51. Japan in particular did crucial pioneering work in standardising X-ray fluorescence analysis as a testing method. It was therefore agreed to take this standard as an opportunity to cooperate more closely for the first time.

LH cement

The work relating to harmonised European standards for cements with low heat of hydration was completed in the period under review. It can be seen from **Tab. IV-6** that 3 European standards dealing with cements with low heat of hydration appeared with an issue date of August 2004. The requirements for standard cements with low heat of hydration are comprised in an A1 amendment of DIN EN 197-1. The heat of hydration requirement of < 270 J/g corresponds to the previous German specifications. This additional property is, however, now indicated by the letters LH (for low heat of hydration) instead of NW in German.

EN 197-4 exclusively covers the standardisation of blastfurnace cements. They differ from standard cements in terms of early strength requirements. The low early strength is indicated by the letter "L". These cements can be classified as LH cements as well. EN 14216 deals with cements with very low heat of hydration (VLH). All VLH cements are assigned to strength class 22,5 and must not exceed a heat of hydration of 220 J/g. These cements can primarily be applied in massive structural elements. **Tab. IV-7** summarises the new strength classes for cement introduced by EN 197-4 and EN 14216.

Cements with high sulphate resistance

Neither the attempts to develop a European, "performance"-oriented method for testing sulphate resistance, nor the attempts to specify uniform prescriptive criteria for standardising highly sulphate resisting cements have been crowned by success so far. A European draft standard for cements with high sulphate resistance was last rejected by a requisite majority in 2001. All standardisation activities were subsequently suspended for the time being. On the other hand, the EU Commission is pressing for the course of action pursued in the treatment of cements with high sulphate resistance to be standardised to a higher extent in Europe. The large discrepancies in the specifications governing pozzolana cements in the individual EU countries in particular have prevented a viable compromise from being reached so far (cf. also Chapter III). For that reason, a European research programme was initiated in the period under review to scrutinise damage mechanisms more closely. It is, however, becoming evident as early as now that it will not be possible to develop a generally applicable performance test method in the foreseeable future. TC 51 therefore decided

Tab. IV-6: Standards for cements with special properties completed in the period under review

	Standard	Issue	Cement / binder	Type of binders		Strength class	Additional classes
				Number	Designation		
European	DIN EN 197-1+A1	08/2004	Common cement with low heat of hydration	27	CEM I CEM II CEM III CEM IV CEM V	32,5 N/R 42,5 N/R 52,5 N/R	LH (≤ 270 J/g)
	DIN EN 197-4	08/2004	Low early strength blast-furnace cement	3	CEM III	32,5 L 42,5 L 52,5 L	LH (≤ 270 J/g)
	DIN EN 14216	08/2004	Very low heat special cement	6	VLH III/B VLH III/C VLH IV VLH V	22,5	VLH (≤ 220 J/g)
National	DIN 1164-10[1]	08/2004	Common cement with special properties	27	CEM I CEM II CEM III CEM IV CEM V	32,5 N/R 42,5 N/R 52,5 N/R	HS (highly sulphate resisting) NA (low effective alkali content)
	DIN 1164-11	11/2003	Cement with short setting time				FE (early setting) SE (fast setting)
	DIN 1164-12	6/2005	Cement with a higher proportion of organic constituents				HO (high proportion of organic additions)

[1] Substitute for DIN 1164:2000

to make a new try to standardise the essential cements with high sulphate resistance at European level on the basis of prescriptive criteria, which is conducted in parallel to said research activities.

The input data required is furnished by a CEMBUREAU survey on the market shares in the individual EU member countries. Cements with high sulphate resistance hold a market share of just over 5% in Europe. These are mainly CEM I and CEM III cements which are produced in most countries and between them hold a market share of approx. 70% (**Fig. IV-7**). Although highly sulphate resisting CEM IV cements are manufactured in two countries only, they account for a relative market share of 18%. Moreover, a few countries have laid down specifications for CEM II and CEM V cements with high sulphate resistance.

Further European cement standards

In the period under review, prEN 14647, the standard on calcium aluminate cement, was completed and the voting procedure for its adoption as a harmonised European standard was initiated. The standard comprises an annex of explanatory notes indicating the criteria to be taken into account when calcium aluminate cement is used in

Tab. IV-7: Strength classes of cement

Strength class	Standard	Compressive strength in MPa			
		Initial strength		Standard strength	
		2 days	7 days	28 days	
22,5	DIN EN 14216	-	-	≥ 22.5	≤ 42.5
32,5 L	DIN EN 197-4	-	≥ 12	≥ 32.5	≤ 52.5
32,5 N	DIN EN 197-1	-	≥ 16		
32,5 R		≥ 10	-		
42,5 L	DIN EN 197-4	-	≥ 16	≥ 42.5	≤ 62.5
42,5 N	DIN EN 197-1	≥ 10	-		
42,5 R		≥ 20	-		
52,5 L	DIN EN 197-4	≥ 10	-	≥ 52.5	-
52,5 N	DIN EN 197-1	≥ 20	-		
52,5 R		≥ 30	-		

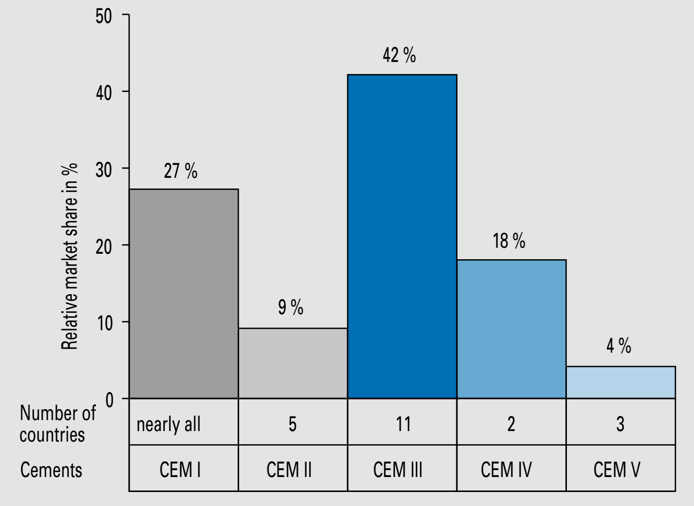


Fig. IV-7: Relative market share of highly sulphate resisting cements in Europe

Tab. IV-8: Status of the test standards elaborated by CEN/TC 51

Method for cement testing	Standard	Applicable version	Status
Strength determination	EN 196-1	2-2005	-
Chemical analysis of cement	EN 196-2[1]	2-2005	
Determination of setting time and soundness	EN 196-3	2-2005	
Pozzolanicity of pozzolanic cements	EN 196-5	2-2005	
Determination of fineness	EN 196-6	12-1989	First revision, preparation for CEN/ISO survey
Methods of cement sampling and sample selection	EN 196-7	12-1989	
Heat of hydration – solution method	EN 196-8	10-2003	-
Heat of hydration – semi-adiabatic method	EN 196-9	10-2003	
Determination of the water-soluble chromium(VI) content of cement	prEN 196-10	2-2005	CEN survey
Chemical analysis using X-ray fluorescence	EN 196-2.2	-	Work in progress
Methods for determining the C_3A content in cement	Open	-	Being considered
Quantitative determination of constituents	CEN report[2]	-	Publication in 2005
Determination of the total organic carbon content of limestone	EN 13639	07-2002	-
Hardened concrete testing – resistance to freeze-thaw – Part 9: scaling	prCEN/TS 12390-9	-	Ready for formal vote as CEN/TS
Hardened concrete testing – resistance to freeze-thaw – Part 10: internal structural damage	prCEN/TR 15177	-	CEN technical report is completed Publication in 2005
Determination of the influence of cement on leaching from hardened mortar and concrete	EN yyy	-	Not started yet

[1] Revised version of EN 196-2 also comprises specifications of EN 196-21 “Determination of the chloride, carbon dioxide and alkali content of cement” applicable previously

[2] Replaces ENV 196-4

concrete and mortar. This is to ensure that the particular properties of calcium aluminate cement are taken into consideration when it is applied. Regardless of that, the bodies of the building supervisory authorities and the standardisation organisations agree that calcium aluminate cement still has to be excluded from use in load-bearing structural elements in Germany.

The first revision of EN 197-1, the standard for common cements, is scheduled to be carried out in 2005. The basic structure of the standard is not to be modified; changes are to be restricted to minor updates. CEN/TC 51 further decided to draw up a European standard for super-sulphated cements, as these cements are occasionally applied in Europe.

National “supplementary standard” (Restnorm) DIN 1164

Cements with special properties continue to be covered by the national “supplementary standard” (Restnorm) DIN 1164. It no longer consists of 1 part, however, but comprises 3 parts now. A Section 10, which replaces the 2000 issue of DIN 1164, merely describes the additional requirements for cements with high sulphate resistance (HS) and low effective alkali content (NA). The specifications for cements with low heat of hydration (NW) were replaced by those for LH cements included in EN 197-1. Standard cements having HS or NA properties still need to be marked and inspected in accordance with DIN 1164. Cements according to DIN 1164-10 basically comply with all the specifications of DIN EN 197-1.

Product developments in the cement industry have shown that some of the cements with special properties are not covered by existing standards. Up to now, these cements required building authority approval, which was costly and time-consuming. As experience with these cements has been gathered for many years now, cements with reduced setting time and cements with a higher proportion of organic additions (HO) have been standardised in Section 11 and Section 12, respectively, of DIN 1164. Section 11 distinguishes between cements with early setting properties (FE cements) and fast setting cements (SE cements). Apart from their setting behaviour and their content of additions, respectively, these cements conform to DIN EN 197-1. DIN 1164-11 does not impose any restrictions with regard to cement types. However, the building supervisory authorities intend to restrict the application of SE cements, citing as a reason that the experience available to date is limited to Portland cements. From the Research Institute’s point of view, however, there are no technical or building practice reasons that justify such a restriction and thus the exclusion or Portland composite cements in particular.

Binder standards

The work on DIN EN 413-1, the harmonised European standard for masonry cement, was completed in the period under review. The standard, which was published with an issue date of May 2004, has replaced the national standard DIN 4211 applicable previously. As large parts of the European sub-base binder standard had been integrated into DIN 4211 as early as in 1995, the modifications to be implemented were slight. The fact that masonry cements MC 22,5X are standardised as well now is one of the major new features. These masonry cements do not contain any air-entraining agents. 10 years after test standard EN 413-2 was first published, its revised version appeared. Among other things, the speed of load application during strength tests, the test methods for setting and water retention capacity, and the calibration process for the air-entraining device were modified, and the values for the accuracy of the various test methods were added.

The national standard for "Hydraulic road binders" – DIN 18506 – was last revised in 2002. This process involved the incorporation of major portions of the corresponding European pre-standard ENV 13282. The process of converting the European pre-standard to a harmonised European standard was initiated in the period under review. In accordance with different traditions prevailing in Germany and France in particular, 2 types of road binders are to be differentiated. For one thing, road binders with high early strength are to be included, which do not differ substantially from standard cements in terms of their hardening characteristics. For the other, road binders with very slow hardening properties, which are characterised on the basis of strength after 56 days, are to be included. As full-scale application of the test methods according to EN 196 will presumably not be possible with the latter, the methods will have to be modified accordingly.

Tab. IV-9: Comparison of the setting test method according to DIN EN 196-3 as specified in the 1994 and 2005 versions

Amendments	EN 196-3	
	1994 issue	2004 issue
Relative air humidity in the laboratory room	At least 65%	At least 50%
Shape of Vicat ring	Conical, also cylindrical if verification is available	Conical or cylindrical
Manufacture of cement paste	Also using drinking water, for example, if verification is available	Distilled or de-ionised water
Measurement of standard stiffness	240 s	(240 ± 10) s
Measuring point for standard stiffness	(6 ± 1) mm	(6 ± 2) mm
Time interval in cement paste production	90 / 15 / 90 s	90 / 30 / 90 s
Specimen storage	Moisture box	Under water
Storage temperature	(20 ± 1) °C	(20.0 ± 1.0) °C
Measuring point for initial setting time	(4 ± 1) mm	(6 ± 3) mm
Confirmation measurement of final set	Not required	2 further measurements at a different point

Testing standards

The establishment and revision of testing standards for cement still constitutes an essential function of CEN/TC 51. **Tab. IV-8** summarises the status of the various test standards.

15 years after the physical and chemical test methods EN 196-1, -2, -3 and -5 were first published, their revised versions were published in the year 2005. The revision of the standards was started just under 10 years ago. Proceeding from the experience gathered by then, a large number of detail items were reviewed and adapted if necessary, without changing the fundamental principles of the test methods. Among other things, the efforts to include the vibrating table in the standard as an alternative method for testing mortar compaction being equivalent to the CEN jolting table were successful. Moreover, some details with regard to conducting the setting test were modified (see **Tab. IV-9**). As difficulties regarding compliance with the stipulated moisture content of the ambient air occurred time and time again in practical application, a general changeover to underwater testing was effected.

The two test standards for determining heat of hydration, i.e. the heat of solution method according to EN 196-8 and the semi-adiabatic method according to EN 196-9, were published in the period under review. In accordance with the specifications of the respective product standards, the test results obtained after 7 days in the case of EN 196-8 and after 41 hours in the case of EN-196-9 are equivalent (cf. also Chapter III). Moreover, a European test method for determining the water-soluble chromate content was elaborated. Since the European chromate directive took effect on January 17, 2005, this method had to be completed and tested in interlaboratory trials under enormous time pressure. The details of the draft standard are described in detail in Chapter III, and the annex on conformity criteria that forms part of the standard is dealt with in the section on "Quality assurance" of this Chapter. The work on standardising the X-ray fluorescence analysis process, which is routinely applied in chemical analysis at many works, was intensified in cooperation with ISO/TC 74 in the period under review (see Chapter III).

V

Concrete constituents and technology, concrete engineering

Portland-composite cements have increasingly been gaining in importance as the cements works have to make a contribution to reducing CO_2 emissions. This can be achieved primarily by using cements in which the clinker portion is reduced and the share of other main constituents, such as blastfurnace slag, fly ash or limestone meal, is increased. The objective pursued by the Research Institute's work is to optimise these cements in such a way as to enable their application without restrictions in all areas of concrete construction.

Some research projects are still concerned with preventing a harmful alkali-silica reaction (ASR). Damage partly attributable to an alkali-silica reaction occurred at a few concrete pavements after a service life of 6 to 10 years. Based on the investigations it had carried out, VDZ gave recommendations regarding the alkali content of road paving cements.

The interaction of cement and admixtures constitutes a further key topic of the research conducted by the Concrete technology department. The investigations cover the new generation of super-plasticisers, shrinkage reducing admixtures and air entraining agents.

The results of scientific work were published in lectures and reports, and immediately found their way into standardisation work. Employees of the Institute made a major contribution to this work, particularly as far as the compilation and introduction of new standards in the field of concrete was concerned. An A1 amendment to DIN 1045-2 was published in time before the transition period from the old to the new generation of standards expired, rendering DIN EN 206-1 and DIN 1045-2 the only standards that may be applied for new structures. Moreover, mention must be made of the cooperation in the compilation of several guidelines by the German Committee for Reinforced Concrete (DAfStb) and in regulations issued by the Research Association for Roads and Traffic (FGSV).

LTU Arena in Düsseldorf during the construction phase

Portland-composite cements

The use of Portland-composite cements enhances the ecological efficiency of concrete construction as the clinker content of these cements is lower than that of Portland cements. The utilisation of other main constituents allows to reduce the CO_2 emissions during cement manufacture in particular. Projected to the annual domestic dispatch of the German cement works, which totals some 30 million t (average from 1999 to 2003), a 5% decline in the average clinker proportion, for example, would allow to reduce annual CO_2 emissions by more than 1 million t. This presupposes, however, that these cements are largely comparable to Portland cements in terms of their construction properties and their inclusion in the set of regulations.

Preconditions set by standards and areas of application in building practice

To estimate the future potential of new cements, it is useful to have a look at the share of the cements dispatched in Germany subdivided by their area of application in building practice. **Tab. V-1** roughly summarises these figures for the year 2000. A distinction is made between the categories of common building construction, civil and underground engineering, traffic areas and other applications. The breakdown highlights that some 50% of the cements manufactured in Germany are used to produce ready-mixed concrete for internal and external components to be employed in common building construction, i.e. in the construction of residential and commercial buildings. 14% of cement dispatch is used to produce precast elements for building construction. The domestically dispatched cements applied in civil and underground engineering account for a share of about 12%, while some 19% of the cements are employed in the manufacture of concrete products for traffic areas and in concrete road construction. The remaining dispatch share of 8% is used in unreinforced concrete.

Tab. V-1: Areas of application and share in domestic dispatch of German cements in %

Area of application	Structures	Cement strength class	Cement type	In-situ concrete	Factory-made concrete
Various applications	Unreinforced concrete	32,5 N/R	CEM I CEM II CEM III CEM IV CEM V	8	-
Common building construction (including mortar and floor screeds) Residential construction	Internal components (protected from freezing)	32,5 N/R 42,5 N/R	CEM I CEM II CEM III	47	14
Commercial building construction	External components				
Civil and underground engineering	Bridges, tunnels, hydraulic engineering and marine structures, pipes	52,5 N/R 42,5 N/R 32,5 N/R	CEM I CEM II CEM III	9	3
Traffic areas	Paving blocks, quarries	52,5 N/R 42,5 N/R	CEM I CEM II CEM III	-	16
	Roads, airfield surfaces, ballastless track	32,5 R	CEM I CEM II CEM III	3	-

The cements with several main constituents assigned to strength class 32,5 which have been manufactured in Germany to date comply with all the major requirements for the production of in-situ concrete – irrespective of whether it is ready-mixed or site-mixed – for common building construction. The strength development of these cements is fast enough for common manufacturing processes. The concretes made from these cements are adequately protected against steel corrosion in concrete induced by carbonation and chloride. They further possess freeze-thaw resistance that is adequate in the climate conditions prevailing in central Europe. In-situ concrete for civil engineering structures, such as tunnels or bridges, is usually made from cements of higher strength classes, i.e. mostly from Portland cement CEM I these days. CEM II and CEM III cements can, however, be applied in this area, too, and have conquered growing market shares. The domain of common building construction including residential construction and commercial building construction thus represents an essential market segment. If new cements meet the requirements for these areas of application, large market segments can be opened up for these cements.

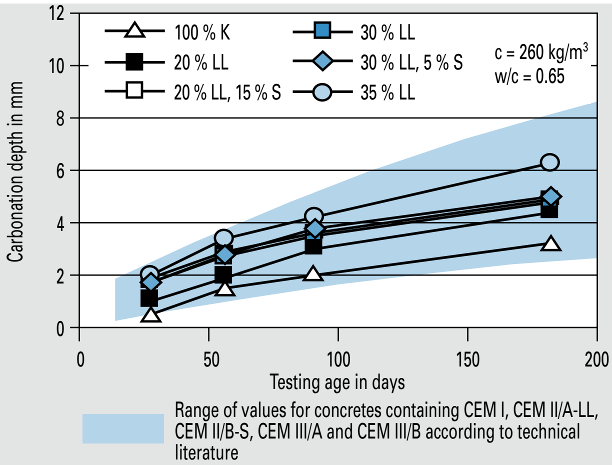
In principle, all cements in accordance with DIN EN 197-1 and DIN 1164 lend themselves to the production of concrete according to DIN EN 206-1 and DIN 1045-2. With regard to the durability of the concretes made from these cements, however, differences induced by the cement type used have to be taken into account depending on the area of application. The concrete standards lay down correspondingly different application rules depending on the exposure class that a structural element is to be classified in. Furthermore, the application of several CEM II cements not used in Germany before, such as Portland-limestone cements with limestone contents of up to 35 wt.% (CEM II/B-LL) and Portland-composite cements with up to 35 wt.% blastfurnace slag and limestone (CEM II/B-M (S-LL)), is also subject to restrictions. These restrictions relate to application in structural elements exposed to freeze-thaw and chloride attack in particular (exposure classes XS, XD, XF). When such cements are to be applied in areas for which their use is not permissible according to the concrete standard, a national technical approval has to be obtained. This is the case with new CEM II-M cements developed by some German cement manufacturers. The first technical approvals for such CEM II-M cements were granted last year. As these cements increasingly prove themselves in practical application, which is substantiated by the data base compiled as part of research projects, the necessity of such approvals can be dispensed with by modifying the application rules accordingly. Given this scenario, the Research Institute carried out investigations to extend the data base for concretes made from new Portland-composite cements. These chiefly consisted of determining the parameters relevant to durability that Portland-limestone cements with limestone contents of up to 35 wt.% (CEM II/B-LL) and Portland-composite cements with up to 35 wt.% blastfurnace slag and limestone (CEM II/B-M (S-LL)) possess. Further investigations will centre on Portland-fly ash cements with up to 35 wt.% siliceous fly ash and Portland-composite cements CEM

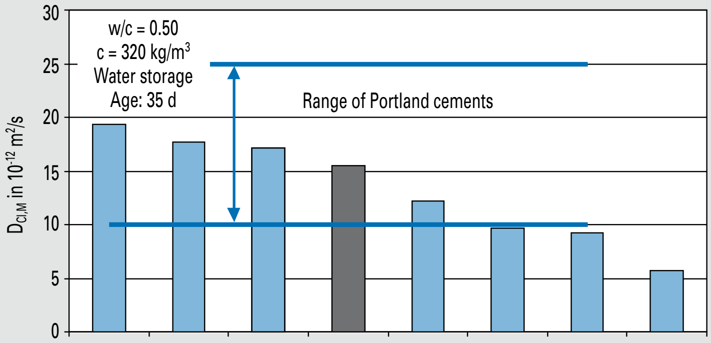
II-M (V-LL) and CEM II-M (S-V) of different compositions.

Durability of concretes made from Portland-composite cements

Comparative durability investigations of concrete presuppose that the concretes possess a comparable strength level as a parameter for similar microstructure formation at the time of testing, which is usually after 28 days. For that reason, Portland-composite cements should have a comparable 28-day compressive strength, which ranges between 44 and 48 MPa in the area of practical relevance for German cements of strength class 32,5 R. The fineness of the main cement constituents Portland-cement clinker, blastfurnace slag and limestone therefore had to be varied in such a way as to ensure that the strength level indicated was roughly matched when the composition of the cements varied. The strength development, the porosity and the pore size distribution, the carbonation, the resistance to chloride penetration and the resistance to freeze-thaw with and without de-icing salt of the mortars and concretes made from these cements were investigated. The composition of the mortars and concretes was geared to the limit values for the composition of concrete according to the exposure classes of DIN 1045-2.

Fig. V-1: Development with time of the carbonation depths of concretes containing cements with different main constituents





Clinker in %	65	65	70	100	65	65	65	65
Blastfurnace slag in %	-	-	-	-	5	10	15	35
Limestone in %	35	35	30	-	30	25	20	-
f_{cm} in N/mm^2	52.2	43.7	46.0	56.7	53.4	49.6	50.8	57.0

Fig. V-2: Chloride migration coefficients $D_{Cl,M}$ of the concretes with w/c = 0.50 and c = 320 kg/m^3 under investigation

Carbonation

Fig. V-1 illustrates the development over time of the carbonation depths of some of the concretes investigated, which had the composition required for exposure class XC3. The range of values to be assumed according to technical literature for the cements CEM I to CEM III/B under the testing conditions prevailing in the present case is given in the Figure as well. These cements may be applied in all exposure classes for carbonation-induced reinforcement corrosion. It becomes apparent from the representation that the carbonation depths determined for concretes made from cements with up to 35 wt.% limestone were within the range mentioned above, although at 40 MPa the 28-day standard compressive strength of the cement with 35 wt.% limestone was fairly low. The same applied to the carbonation depths of concretes made from Portland-composite cements with up to 35 wt.% blastfurnace slag and limestone. The porosity of mortars made from Portland-limestone cements increases slightly as the content of limestone meal gets higher. The increase in the carbonation depth of the concretes made from cements containing limestone correlated with the rise in the proportion of pores > 0.1 µm of the corresponding mortars at the age of 28 days.

Resistance to chloride penetration

According to bibliographical reference, the use of up to 25 wt.% limestone does not substantially impair the resistance to chloride penetration. The resistance to chloride penetration of concretes made from Portland-limestone cement and having a limestone content > 25 wt.% was assumed to be slightly lower than that of concretes containing Portland cement. The results achieved here confirmed this assumption. **Fig. V-2** shows the chloride migration coefficients measured for concrete with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m^3 at an age of 35 days. Different laboratory-made cements were used to produce these concretes. At the same time, however, the chloride migration coefficient values determined for Portland-limestone cements with up to 35 wt.% limestone were found to be within the usual range of values for Portland cements and Portland cements with a high sulfate resistance given in publications ($D_{Cl,M}$ between approx. 10 and $25 \cdot 10$ -12 m^2/s). In concretes made from cements containing blastfurnace slag, the amount of capillary pores, which is decisive for essential transport processes, is reduced in favour of the gel pore volume, which is largely irrelevant for transport processes. When Portland-composite cements with up to 35 wt.% blastfurnace slag and limestone were used, the chloride migration coefficients therefore fell short of the coefficient of the Portland cement tested and exceeded that of the Portland-slag cement with 35 wt.% blastfurnace slag.

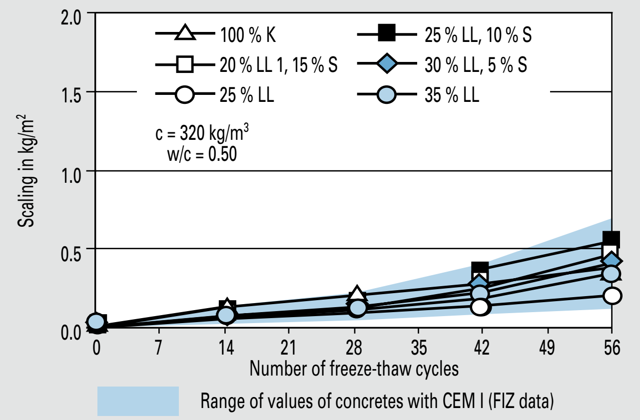


Fig. V-3: Scaling of concretes made using Portland cement and different Portland-composite cements – CF test

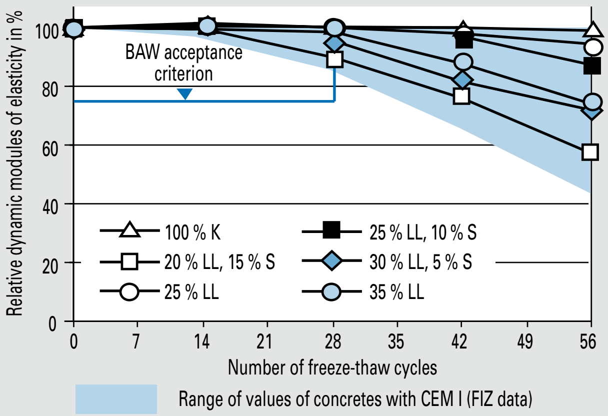


Fig. V-4: Relative dynamic modulus of elasticity of concretes with c = 320 kg/m³ and w/c = 0.50 made using Portland cement and different Portland-composite cements – CIF test (acceptance criterion of the Federal Waterways Engineering and Research Institute (BAW): 75% after 28 freeze-thaw cycles)

Resistance to freeze-thaw and freeze-thaw with de-icing salt

When damage is caused by freeze-thaw attack, a distinction is made between external and internal damage. External damage is visible as surface scaling. Internal damage to the microstructure can, for example, be ascertained by means of ultrasonic transit time measurement and the dynamic modulus of elasticity thus derived (see also the section on durability). The significance of a drop in the dynamic modulus of elasticity in terms of the concrete properties to be expected after exposure to freeze-thaw has, however, been clarified neither for laboratory-made concretes nor with regard to the durability of concretes in practical application so far. The modulus was determined as part of the investigations of new cements as well in order to gather experience and to compare it with figures quoted in publications as well as with acceptance criteria discussed in various bodies.

In the trials conducted, concretes with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m³ which were produced from the laboratory-made Portland-limestone cements with up to 35% limestone did not exhibit significantly higher scaling rates than concrete made from Portland cement even when water saturation was high in the CF test. A systematic influence of the limestone content was not discernible. This applied to the scaling of the concretes made from Portland-composite cements with up to 35 wt.% blastfurnace slag and limestone, too (**Fig. V-3**). The relative dynamic moduli of elasticity of these concretes determined by the CIF method are shown in **Fig. V-4**. Differentiation in terms of the limestone content is more pronounced here than it is with scaling. The testing of concrete according to the CIF method implies various acceptance criteria that will not be discussed here. The acceptance criterion of 75% after 28 freeze-thaw cycles laid down in the "Freeze-thaw testing of concrete" code of practice by the Federal Waterways Engineering and Research Institute was met by a wide margin by all concretes. On the whole, the relative dynamic elasticity moduli of the concretes made from Portland-composite cements were within the range of values obtained for concretes made from Portland cements. In the cube test method, the same concretes displayed virtually no change in the relative dynamic modulus of elasticity after up to 100 freeze-thaw cycles regardless of the cement used. This means that even after 100 freeze-thaw cycles, critical saturation was not reached in this test.

The influence of different Portland composite cements on the concrete's resistance to freeze-thaw with de-icing salt is depicted in **Fig. V-5**. The scaling behaviour of the concretes made from Portland-composite cements did not differ significantly from that of concrete containing Portland cement. The scaling rates of all concretes after 28 freeze-thaw cycles fell considerably short of the value of 1.5 kg/m³, which is generally used as acceptance criterion in this test.

Conclusions and outlook

According to the investigations conducted, also the Portland-composite cements with blastfurnace slag and limestone (CEM II/B-M (S-LL)) which have not been applied in Germany to date can be utilised in concretes of all exposure classes with regard to corrosion of the reinforcement induced by carbonation and chloride, and freeze-thaw attack with and without de-icing agent. To substantiate the investigation results on the resistance to freeze-thaw and freeze-thaw with de-icing salt of concretes made from Portland-limestone cements CEM II/B-LL, the Research Institute is carrying out supplementary investigations of limestones with a $CaCO_3$ content ranging between 75 and 90 wt.%.

Cement and admixtures

The use of concrete admixtures to control the properties of the fresh and hardened concrete is state of the art today. Some 90% of the concrete produced in Germany contains concrete admixtures. Overall, more than 550 concrete admixtures are presently available in Germany, which can be classified in 14 different functional groups. At approx. 70%, concrete plasticisers and super-plasticisers account for the lion's share.

The influence that concrete admixtures have on the hydration of cement is most often determined empirically and forms the subject of controversial discussions. There is still a substantial lack of scientifically

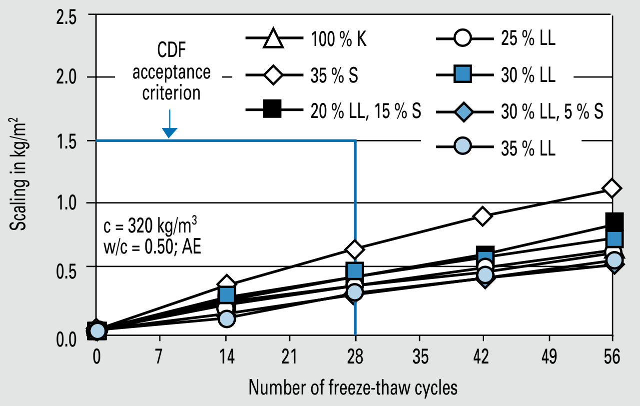


Fig. V-5: Scaling of concretes made using Portland cement and different Portland-composite cements – CDF test (acceptance criterion: 1.5 kg/m² after 28 freeze-thaw cycles)

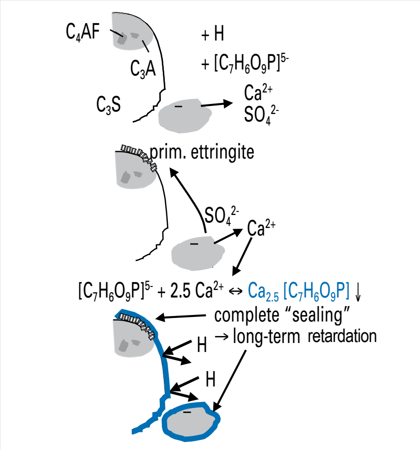


Fig. V-6: Influence of ESR on the hydration of Portland cement with optimised sulphate agents

founded understanding of the precise working mechanisms of some admixtures. This applies to long-term retarding admixtures, shrinkage reducing admixtures on the basis of polycarboxylate ether, and novel air-entraining concrete admixtures in particular, the function of which formed the subject of extensive investigations.

Long-term retarders (LTR)

LTR are organic retarding admixtures which, due to their composition, can severely inhibit the hydration of cement, in some cases for several days. In addition to their utilisation for fresh concrete recycling, LTR are used to retard the setting of shotcrete in case of long transport routes, and for mass concrete. The LTR approved as recycling aids in Germany primarily contain 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

A research project sponsored by the Federation of Industrial Cooperative Research Associations (AiF) and the Dyckerhoff Foundation systematically investigated the effects of LTR on the hydration of pure clinker phases, clinker and Portland cements. Investigations of pure clinker phases revealed that the extended set retardation is based essentially on blocking the hydration of the calcium silicates. LTR prevented the hydration of C_3S almost fully for up to 180 days. The addition of LTR resulted in increased phase conversion with pure C_3A and in reduced phase conversion with pure C_4AF. In the case of mixes consisting of C_3A and sulphate agent, the LTR led to a short-term acceleration in the formation of primary ettringite. The further course of hydration of C_3A and C_4AF, respectively, and the reaction of hemihydrate with water to form gypsum were retarded significantly. When the mixes of C_3A and sulphate agent additionally contained calcium hydroxide, all other hydration reactions except for primary ettringite formation were inhibited.

The investigations of Portland cements confirmed the results obtained from the investigations of pure clinker phases. With Portland cements with optimised sulphate agents, the long-term retardation of the hydration of the calcium aluminates and calcium silicates was always accomplished as planned. When the supply of calcium sulphate was too low, the addition of LTR strongly accelerated the hydration of C_3A, which resulted in particularly fast stiffening and setting. The further strength development was, however, strongly impeded since the lower-reactivity calcium silicates were retarded at the same time. The working mechanisms of the LTR in case of addition to a Portland cement that were derived from the test results are shown in **Fig. V-6**. It schematically depicts the cross section of a clinker particle and of sulphate agents ($C\overline{S}H_x$). In the alkaline medium of the pore solution, the PBTC splits off five protons and is present in completely dissociated form ($[C_7H_{11}O_9P]^{5-}$). Owing to the calcium and sulphate ions supplied by the sulphate agents, a thin layer of primary ettringite is formed on the surface of the calcium aluminates, which retards the further hydration of C_3A. Apart from that, the sulphate agent supplies an adequate quantity of calcium ions for the immediate formation of hardly soluble calcium phosphonate ($Ca_{2.5}[C_7H_6O_9P]$. The calcium phosphonate "seals" both the surfaces of the clinker particle and those of the sulphate agents not yet dissolved. The further penetration of water (H) and the further ion exchange, respectively, are impeded massively, which results in the planned extended retardation of hydration.

When the supply of sulphate agents in Portland cements is missing or too low (**Fig. V-7**), only small quantities of dissolved calcium are available. As a consequence of the calcium demand of the PBTC, the hydration of reactive clinker phases, such as C_3A, is briefly accelerated in these cases. The hexagonal calcium aluminate hydrates (CAH) which are then increasingly formed mostly lead to marked stiffening or setting. The calcium ions released during this short acceleration phase are fixed by PBTC. The hardly soluble calcium phosphonate thus produced coats the surfaces of the individual clinker particles in different ways. The surfaces of relatively slow-reacting clinker phases, such as C_3S and C_2S, which are largely free of hydration products when the hardly soluble compounds are formed, may be covered with a largely closed coating of calcium phosphonate. Surfaces partly covered with hydration products already, such as those of the C_3A, possess a fairly large specific surface area. The quantity of calcium phosphonate formed is usually not sufficient to fully "seal" these areas. As water penetration and ion exchange cannot be

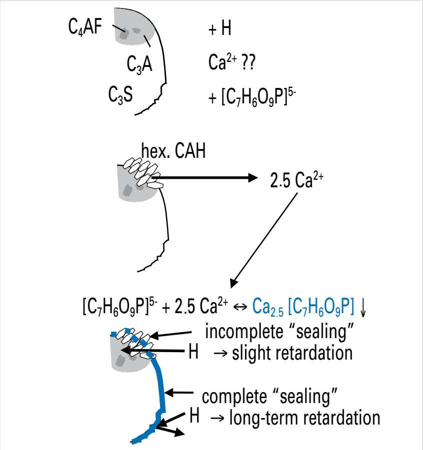


Fig. V-7: Influence of LTR on the hydration of Portland cements without optimised sulphate agents

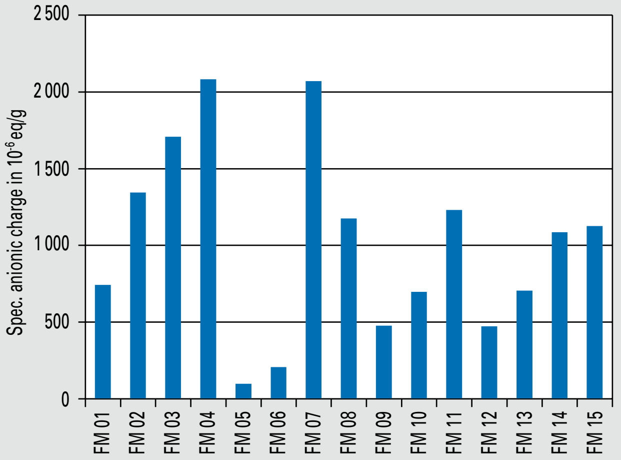


Fig. V-8: Specific anionic charge of 15 ordinary super-plasticisers based on PCE

inhibited completely, the hydration of these phases is only slightly retarded.

It became apparent that the sulphate optimisation of cements cannot be replaced by LTR, but that the formation of primary ettringite initiated by calcium sulphate and the provision of calcium ions constitute essential preconditions which ensure that the LTR works as planned. For that reason, sulphate-free cements, for example, are not suitable for purposeful long-term retardation.

Super-plasticisers

The manufacture of flow concrete and high-strength concrete presupposes the use of super-plasticisers. Synthetic organic polymers with carboxylic acid groups, such as polycarboxylate ethers (PCE), constitute an advance in the field of active ingredients contained in super-plasticisers. 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, the PCEs adsorb on the positively charged surfaces of the cement and other fine solids particles. The dispersing effect is largely attributable to the steric repulsion of the side chains. Variation of the length ratio of the main chain and side chains allows to adjust different properties, such as strong initial plasticising effect and/or extended workability of fresh concrete, each associated with either unchanged or retarded cement setting. Practical application shows that these super-plasticisers can be more sensitive to temperature variations, different cements or variations in cement composition than the classic super-plasticisers based on lignin, melamine and naphthalene sulphonate. This may for example result in a faster decrease of consistency, segregation, intensive bleeding or significant retardation of strength development. More profound understanding of the interaction of super-plasticisers and cement or concrete, respectively, is required to prevent such undesired reactions.

Fundamental investigations carried out as part of a research project sponsored by the AiF are aimed at determining the influence that the chemical structure of the PCE molecules and the chemico-mineralogical composition of ordinary cements have on the dispersion and the strength development of the pastes, mortars and concretes made from them. The essential parameters induced by admixtures and cement that may cause undesired reactions, such as rapid loss of workability or low early strength, are being recorded systematically. The structure or composition, respectively, that "robust" PCEs must have in order to plasticise the majority of ordinary cements as effectively as possible and as planned is to be identified.

The first main emphasis of the investigations consists of compiling a data base on the exact chemico-mineralogical composition of selected ordinary cements, and on the composition and molecular structure of ordinary PCEs. In addition to various PCEs and cements, also the margin of variation in different cement and super-plasticiser shipments will be analysed. Moreover, the composition of the pore solution of some cement pastes at an early age shall be added to the data base. The second main emphasis consists of systematically investigating the interaction of the ordinary PCEs and individual cements on the basis of cement/PCE mixes that are chosen in consideration of the data base established. In this way, the cement and admixture parameters responsible for optimum efficiency of the PCEs are to be determined. The influence that the molecular structure of the PCE molecules has on the dispersion, the effective period and the strength development of pastes and mortars made from model cements is to be investigated on the basis of purposefully synthesised PCEs having main and side chain lengths of different definition. To that end, rheological parameters, such as the yield value and the dynamic viscosity, as well as the zeta potential and the composition of the pore solution are determined.

In a first step, the chemical composition and the physical parameters of 15 ordinary super-plasticisers on PCE basis were investigated. The molecular structure was identified using NMR (Nuclear Magnetic Resonance) spectroscopy and GPC (Gel Permeation Chromatography), respectively, as well as through the determination of the specific anionic charge volume. Initial results of these investigations suggest that some of the 15 super-plasticisers contain nearly identical PCE molecules. The specific charge describes the actually effective charge of the main chain of the PCE molecule. **Fig. V-8** summarises the specific anionic charge volumes determined for the 15 super-plasticisers (FM). The charge of the PCE molecules range between about 80 and 2 070 charge equivalents per gramme of polymer. Sorption to positively charged cement surfaces of super-plasticisers with very low charge density is presumably markedly lower than sorption of super-plasticisers with a high specific anionic charge volume.

Determination of the zeta potential

The sorption of super-plasticiser molecules on the cement particle surfaces is investigated by measuring the zeta potential. In conjunction with rheological investigations it is examined whether the zeta potential allows to draw conclusions on the initial plasticising action and the duration of the plasticising effect of super-plasticisers.

The zeta potential is an electro-kinetic potential in the contact surface between the mobile and the rigid part of the double layer formed at the phase boundary between solids and aqueous solutions (**Fig. V-9**). The potential indicates the charge conditions on the particle surface. Up to now, it has only been possible to determine the zeta potential in highly diluted cement suspensions (w/c ~ 1 000) by means of measuring electrophoretic mobility, i.e. via the molecular velocity in an electric field generated. Given the high influence that the solids content and the ion strength, among other factors, have on the zeta potential, a transfer of the results to suspensions with w/c ratios common in practical use is highly incorrect.

Since September 2004 the Research Institute has had the possibility of determining the zeta potential of suspensions with a very high solids content (w/c ≥ 0.40) by means of a new electro-acoustic measuring method. The device consists of a probe that stimulates the molecules in the suspension to perform relative motions via an ultrasonic field (**Fig. V-10**). As a consequence the charged molecules form dipoles. The electric field generated is measured as a colloidal vibration current and converted to the zeta potential. The input data required are the density and the ultrasonic speed of the solid and the liquid phase, the particle size distribution, and the concentration. The temperature, the pH value and the conductivity of the respective solutions can be determined in parallel to the zeta potential. An automatic burette allows the stepwise addition of admixtures, for example.

By way of example, **Fig. V-11** illustrates the influence of super-plasticisers (SP) on melamine sulphonate (MS) and polycarboxylate ether (PCE) basis on the zeta potential of a cement paste. While the anionic super-plasticiser containing melamine sulphonate as an active ingredient causes the zeta potential to shift in a negative direc-

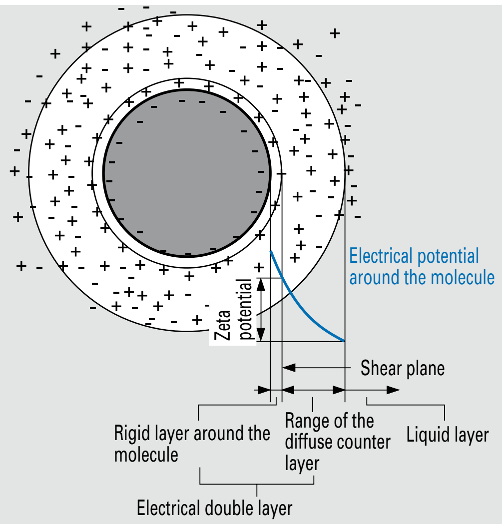


Fig. V-9: Schematic representation of the electrical double layer and the zeta potential

Fig. V-10: Probe for determining the zeta potential

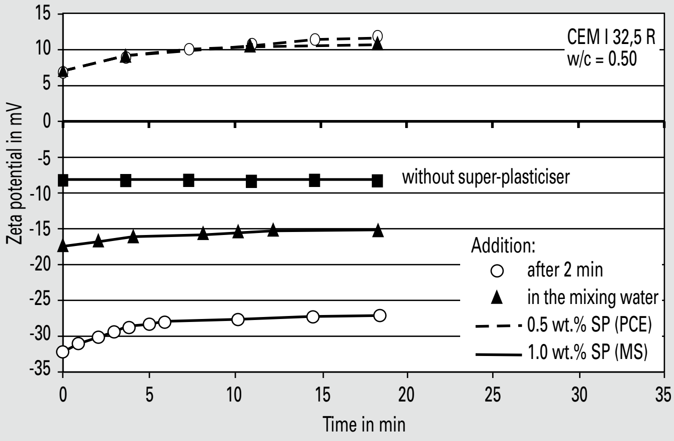


Fig. V-11: Influence of super-plasticisers on the zeta potential of cement paste, w/c = 0.50

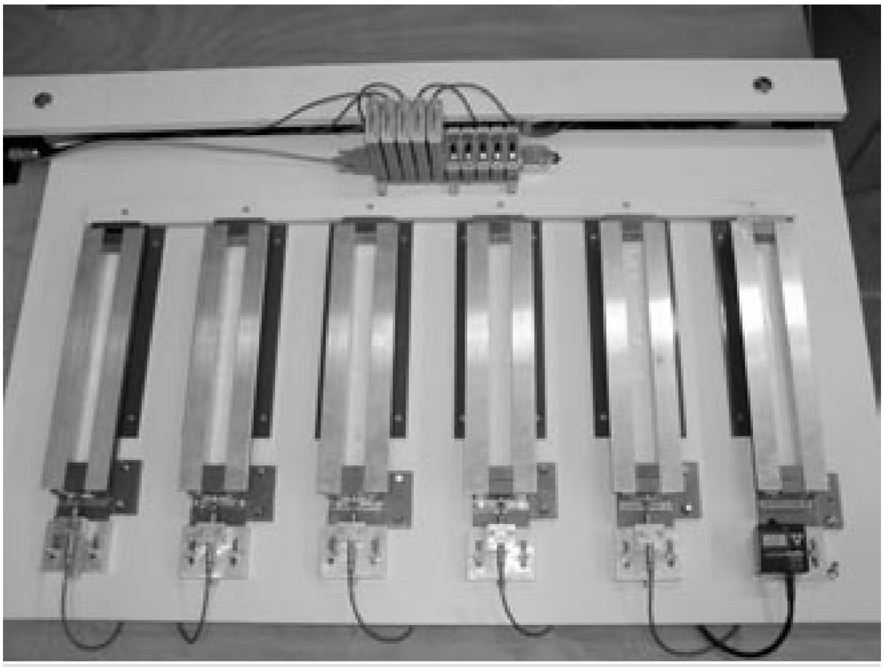


Fig. V-12: Test set-up for the continuous measurement of the autogeneous shrinkage of hardened cement paste

tion, the PCE shifts the zeta potential in a positive direction. Moreover, the influence of the time of addition is clearly discernible with melamine sulphonate. The zeta potential obtained in case of subsequent input is significantly lower than that obtained in case of immediate input.

Shrinkage reducing admixtures

Concrete shrinkage leads to deformations that may cause stress in structural elements in case of constraint. As a consequence, cracks (superficial cracks or separation cracks) that impair durability may occur. Shrinkage lowers the crack-proofness of large-surface structural elements, such as floor slabs, and of high-strength concrete components at an early age. Shrinkage is induced by changes in the moisture content of concrete, which change the interior forces in the microstructure of the hardened cement paste matrix as a consequence of the environmentally induced drying or self-desiccation of the concrete. This results in tensile stress, which causes the matrix to contract. Deformation is impeded by the aggregates to some degree.

Shrinkage Reducing Admixtures (SRA) were developed in Japan in the early 80ies to reduce concrete shrinkage. These have been in use also in Europe since about 1997. In Germany, shrinkage reducing admixtures have primarily been employed in floor screed works and in mortar applications so far. They are, however, presently not used in load-bearing structural elements made from concrete, reinforced concrete and prestressed concrete as general building inspectorate approvals for this type of admixture have not been issued yet.

Research results published to date show that the statements on the working mechanisms and effects of SRA are contradictory. This applies both to investigations of hardened cement paste and of mortar and concrete. There has previously been a lack of conclusive research results that explain the effects these admixtures have on the pore structure, the material parameters and the long-term behaviour of both hardened cement paste and concrete. The Research Institute is conducting investigations on the working mechanisms of shrinkage reducing admixtures as part of a research project sponsored by the AiF. This project is aimed at identifying the fundamental workings of shrinkage reducing admixtures as they interact with cement. On the basis of these results, the potential of shrinkage reducing admixtures can be estimated and taken advantage of to enhance the performance of the building material concrete.

Shrinkage reducing admixtures are water-soluble, surface-active agents. They primarily consist of higher alcohol, which reduces the surface tension of water. The decrease of shrinkage is usually considered to be caused by the reduction in surface tension. When quantities ranging between 10 and 20 wt.% relative to the water are added, the surface tension of the mixing water is reduced by up to 63%. Higher dosages do not reduce the surface tension of the aqueous solutions any further. Under building practice conditions, this saturation point is generally not reached. The application of shrinkage reducing admixtures diminishes the shrinkage of both standard concrete and high-strength concrete. The extent of reduction depends on the w/c ratio and the age of the concrete. The use of SRA in standard concrete was found to reduce shrinkage by up to 50%. At the same time, compressive strength and tensile strength decreased. The dosage and the chemical composition of the shrinkage reducing admixture are decisive influencing variables in this context.

The determination of the microstructure and hydration properties of hardened cement paste and mortar samples containing SRA is an essential part of the investigations carried out by FIZ. Moreover, interest particularly focuses on identifying both the share of the autogeneous shrinkage and of the drying shrinkage of hardened cement paste obtained when different shrinkage reducing admixtures are utilised. A measuring device allowing to determine the hygric deformation behaviour of conserved hardened cement paste samples stored nearly frictionless was developed to measure the autogeneous shrinkage at low w/c ratios (**Fig. V-12**). Measurement is continuous and starts about 6 hours after water addition. Initial results have shown that the overall shrinkage of hardened cement paste samples (w/c = 0.40) can be reduced by up to 50% by adding SRA at a quantity of about 2 wt.% relative to the cement.

Air entraining agents

Air entraining agents generating a large number of small, evenly distributed air voids with a diameter ≤ 300 µm in the fresh concrete have to be added to the concrete to achieve adequate resistance to freeze-thaw. In the hardened concrete, the air voids serve as an expansion space for reducing the pressure created when the pore solution freezes. Road paving concrete, which is exposed to severe attacks by de-icing salt in the winter, has to be made in the form of air-entrained concrete. Bridge caps and scraper tracks of sewage treatment plants constitute further examples of application.

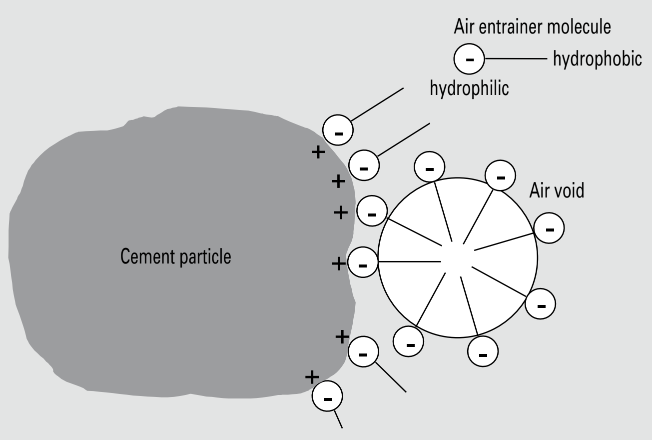


Fig. V-13: Sorption of the air entrainer molecules and adhesion of an air void to a cement particle

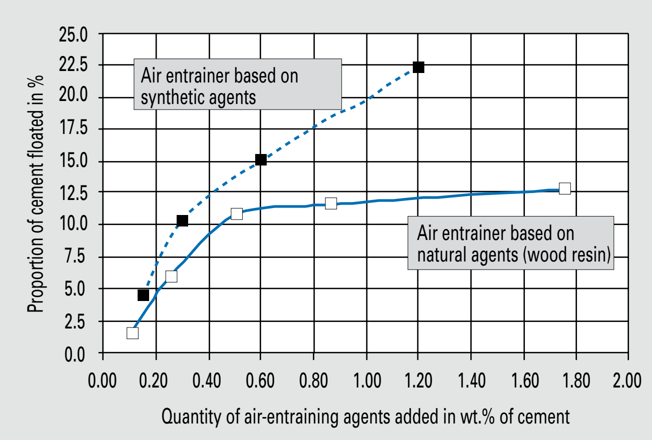


Fig. V-14: Proportion of cement floated as a function of the quantity added and the active ingredient basis of two ordinary air-entraining agents

Air entrainers belong to the surface-active agents also known as tensides. A feature all tensides have in common is their hydrophobic/hydrophilic molecular structure. They are made up of a covalent hydrophobic hydrocarbon chain and an hydrophilic polar carboxyl, sulphate or sulphonate group. The basic materials used for air entrainers are primarily soaps made from natural resin (wood resin); for a couple of years, synthetic active ingredients (e.g. alkyl polyglycol ether, alkyl sulphate or alkyl sulphonate) have been utilised increasingly as well. The active ingredients are applied separately or in combination.

The starting point from which the investigations at the Research Institute proceeded was damage that had occurred in the production of road paving concrete. The air void content of the hardened concrete was considerably higher than that of the fresh concrete in some cases. The Research Institute conducted initial investigations of six ordinary air entraining agents – three based on synthetic active agents, three based on natural active agents – to determine the cause of damage. The trial results showed that a substantial increase in air content can occur only if, as a consequence of too short mixing, an excessive quantity of air entrainer was metered during production in order to attain the desired air void content. In that case, the fresh concrete is supplied with air entrainer that is inadequately decomposed and activated. The air void content may increase if mixing energy is subsequently applied. No systematic influence of the type of active ingredient (synthetic or natural) on air void formation was detected.

As knowledge of the exact interactions of the active ingredient forming air voids, the mixing time and the quantity added is inadequate, the effort that has to be expended in initial testing and during construction work in order to avoid deficient applications is tremendous. A research project sponsored by the AiF is therefore determining the basic workings of active ingredients forming air voids upon interaction with cement. Two focal topics that are based on each other are being studied.

First of all, a data base including the active ingredients contained in ordinary air entrainers and their concentrations is compiled. To that end, the data on the air entraining agents currently available is gathered on the basis of information provided by manufacturers and literature research. As this information is frequently not accessible, own investigations are carried out additionally to determine the chemical composition of the admixtures by infrared spectroscopy. Moreover, their pH value, density, solids content and refractive index are identified. Using the data base thus established, various ordinary air entrainers are chosen on the basis of their active ingredients to carry out the planned investigations on the second key topic of "cement paste and mortar investigations". As the air entrainers often consist of a mix of different substances, pure chemical substances are included in the investigations as well.

A total of 10 substances (4 ordinary air entraining agents and 6 active ingredients) were selected. The sorption behaviour (sorption on cement / precipitation of the active ingredients from the pore solution / floatability of cement) of the substances generating air voids is investigated using cement paste, while mortar forms the basis for studying air void formation as a function of the type and quantity of the active ingredient added and of the mixing time. Supplementary trials are to serve to examine the combination of super-plasticisers and air entrainers as well.

The first flotation tests aimed at defining the sorption behaviour of the air entrainers were started. During the mixing process, the air entrainer molecules arrange around air bubbles, or the polar group of the molecule, which usually has a negative charge, is sorbed by positively charged areas of the cement particles (**Fig. V-13**). The adhesion of the air voids to the cement particles enhances the stability of the air voids in the fresh concrete. In the flotation test water, cement and air entrainer are mixed in a vessel and fine air bubbles are injected into the suspension. When air entrainer molecules are sorbed by cement particles, air bubbles can accumulate and rise to the water surface with the cement particles, where the foam produced is skimmed off over a constant period. When the foam has dried, the quantity of cement floated can be determined. **Fig. V-14** shows initial results by way of example. The investigations covered two ordinary air entraining agents on the basis of a natural and a synthetic active ingredient, respectively; the quantity added was varied. With the air entrainer based on synthetic active ingredients, the quantity of floated cement rises continually as the quantity added is increased. With the air entrainer based on wood resin, by contrast, the proportion of floated cement stops increasing once a certain quan-

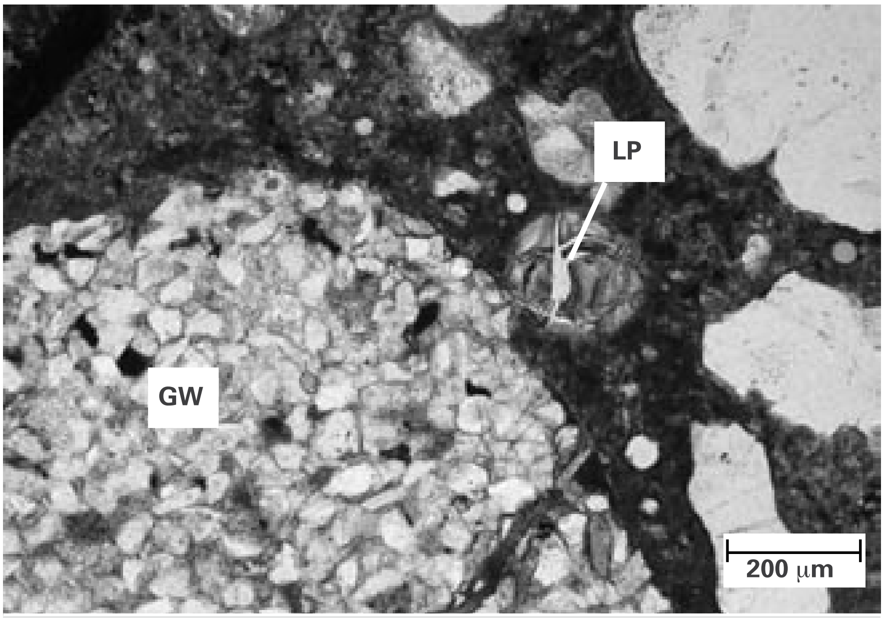


Fig. V-15: Polished thin section of a concrete containing a cracked greywacke particle (GW) and an air void filled with gel (LP); polished thin section was made after storage of the concrete in a 40 °C fog chamber

tity added is reached. The interactions to which these differences are attributable are to be determined. This phenomenon is presumably caused by the fact that the proportion of active ingredient dissolved in the suspension changes depending on the chemical composition of the air entrainer. With the air entrainer based on synthetic agents, a larger amount of the air entrainer molecules added remains dissolved. As a consequence, more air bubbles can be stabilised, which can in turn adhere to cement particles and hence increase the amount of floated cement.

Code of practice on air-entrained concrete

A revision of the "Code of practice for the manufacture and processing of air-entrained concrete" dating from 1991 was necessitated by the FIZ investigations, but also by the extension of the range of concrete constituents (e.g. new cements, admixtures and additions), the application of new mixing and placing methods, and the adaptation to new standards. The new version of the code of practice with the same title, which appeared in 2004, comprises advice for building practice aimed at ensuring the purposeful adjustment of the air void system. Among other topics, it deals with the choice of constituents, the composition, the production and processing, and the curing and testing of air-entrained concrete. In order to prevent a subsequent increase in the air content from occurring during construction work in the future, it is recommended to carry out more extensive initial tests in which higher quantities of air entrainer are added and the time of mixing is extended. If construction work is performed in summer, the fresh concrete temperature is to be raised to 30 °C during the test additionally.

Alkali-silica reaction ■

In an alkali-silica reaction (ASR), alkali-sensitive constituents in the aggregates react with the alkalis in the pore solution of the concrete to form an alkali silicate having water absorption tendency. The ensuing increase in volume causes swelling pressure which, depending on the type, reactivity, quantity and particle size distribution of the alkali-sensitive constituents, the effective alkali content in the pore solution and the supply of moisture, can damage the concrete microstructure and diminish concrete durability.

The investigations the Research Institute conducted in the period under review were aimed at measures allowing to prevent a harmful ASR. To that end, the development of test methods allowing to rapidly determine the sensitivity of aggregates to alkalis was continued. Moreover, the basis created for the development of further low-alkali cements was consolidated by carrying out analyses of pore solutions in particular.

Concrete road pavings

A few concrete road pavings were damaged by crack formation 6 to 12 years after they had been laid. The Research Institute of the Cement Industry closely examined the concrete used in the pavement. To determine whether an ASR had contributed to the damage, drill cores were taken from damaged and damage-free sections of the road pavings, stored in a fog chamber at 40 °C and subjected to expansion measurement. In addition to that, polished thin sections of the concretes were produced and assessed under the light-optical microscope (**Fig. V-15**). This revealed that involvement of an ASR in some of the damage cases could not be ruled out. It became evident in particular that with the "road" type loading case (intense external alkali supply and high dynamic stress), aggregates not cited in the alkali guidelines of the German Committee for Reinforced Concrete (DAfStb) so far can lead to disruption of the internal microstructure as a result of an ASR. These include greywackes from different areas of extraction (cf. Fig. V-15), quartz porphyry and recycled aggregates.

Prevention of a harmful ASR

When a harmful ASR cannot be prevented by using non-reactive aggregates, the alkalinity of the pore solution must be reduced by utilising low-alkali cements or pozzolanic additions. The mode of action that latent hydraulic and pozzolanic main cement constituents and concrete additions, respectively, have on the alkalinity of the pore solution were thoroughly investigated by the Research Institute (see Chapter III).

The swelling capacity of the alkali silicates produced during an ASR depends on their chemical composition. Sodium and potassium silicates display an inclination to absorb water and swell accordingly. Various observations have led to the assumption that the silicates formed from lithium show no swelling tendency in the concrete under certain preconditions.

Use of lithium

The effect of lithium was investigated in some tentative tests the Research Institute conducted using alkali-reactive aggregates from German deposits. Concretes were made from north German gravel and high-grade gravel chippings from the Upper Rhine region, respectively, using lithium nitrate and lithium hydroxide. Pursuant to publications, the molar ratio of lithium and the total of potassium and sodium in concrete should amount to 0.8 (lithium nitrate) or 1.0 (lithium hydrox-

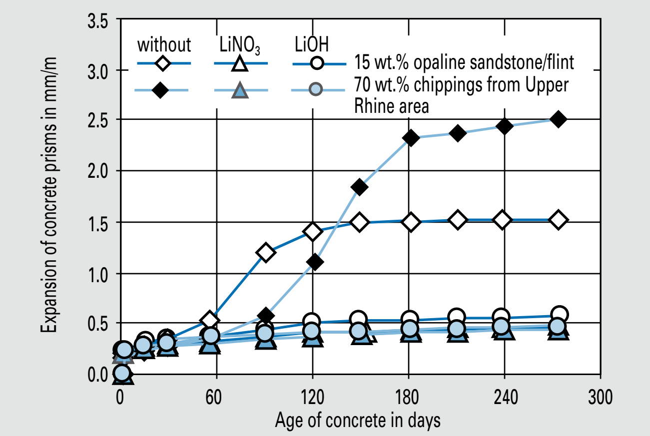


Fig. V-16: Effect of lithium nitrate ($[\text{Li}/(\text{Na}+\text{K})]_{\text{molar}} = 0.8$) and lithium hydroxide ($[\text{Li}/(\text{Na}+\text{K})]_{\text{molar}} = 1.0$) on the expansion of concrete bars (10 x 10 x 50 cm) with 500 kg/m³ CEM I 32,5 R (1.3 wt.% Na_2O_{eq}) and w/c = 0.55

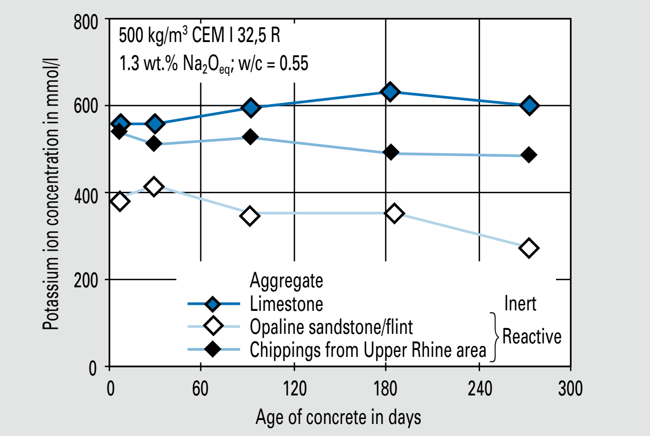


Fig. V-17: Influence of the aggregate on the potassium ion concentration of the pore solution during conserved storage in a 40 °C fog chamber

ide), respectively, when highly reactive aggregates are utilised. The quantity metered thus directly depends on the alkali content of the Portland cement used and on the cement content of the concrete. For investigation purposes, a Portland cement with Na_2O_{eq} of 1.3 wt.% (test cement) was used, and the concrete was prepared with 500 kg/m³ cement.

The phenomenologic behaviour of the concretes was studied on the basis of the expansion and the dynamic modulus of elasticity of 10 x 10 x 50 cm bars, and on the basis of the crack formation in a 30 cm cube. The use of lithium compounds significantly reduced the expansion of the concrete bars stored in the fog chamber at 40 °C in comparison to the bars made from a concrete without admixtures (**Fig. V-16**). Moreover, the concrete cubes did not exhibit any cracking when lithium had been used. The favourable effect of lithium compounds for this type of storage was thus confirmed. Long-term investigations of samples stored on the roof of the Düsseldorf Institute building are to reveal whether this result can be transferred to realistic ambient conditions.

Influence of lithium on the pore solution

The mode of action of lithium compounds was investigated by squeezing out pore solutions of concretes containing lithium and by determining their concentration of lithium, potassium and sodium. A comparison with the total alkali quantity input into the concrete via cements and admixtures shows that the binding of lithium to the hydration products or the alkali-silica gel is considerably better than that of sodium or potassium. Further basic research will be necessary, however, to identify the exact mode of action of lithium. Lithium compounds are currently not utilised in Germany due to their high price.

Effect of an ASR on the alkalinity of the pore solution

Knowledge of the point of time following concrete manufacture at which an ASR starts and of the quantity of alkalis from the pore solution that is consumed in this reaction has been inadequate so far. For that reason, the alkali content of the pore solution of concretes containing different aggregates (limestone, gravel with opaline sandstone and flint from north Germany, high-grade gravel chippings from the Upper Rhine region) was determined at different points of time. **Fig. V-17** illustrates that the potassium ion concentration in the pore solution of a concrete containing opaline sandstone and flint is markedly lower than that of concrete with inert limestone as early as after a few days. As a consequence of the high proportion of alkali-sensitive constituents, a correspondingly high quantity of potassium ions is combined in the ASR reaction products. The potassium ion concentration of concrete with high-grade gravel chippings from the Upper Rhine region decreases only slightly although the expansion of these concretes after storage in a 40 °C fog chamber was fairly large (Fig. V-16). A drop in the alkali ion concentration of the pore solution therefore does not allow to draw any conclusions about correspondingly severe concrete damage. The alkali ion concentration that is required to trigger a harmful ASR with different aggregates forms the subject of further investigations.

External alkali supply

Experience gained in road construction (“road” type loading case) indicates that external alkali supply in combination with freeze-thaw attack can trigger or intensify a harmful ASR when the aggregates contain constituents that react with alkalis. The exact correlations have not been clarified yet. A pertinent research project was initiated in cooperation with the Bauhaus university in Weimar. Concretes of different composition are exposed to attacks by freeze-thaw, by de-icing salt, and by a combination of freeze-thaw and de-icing salt. Subsequent damage that may possibly occur as a consequence of an ASR is studied by examining the expansion of the bars and the cracking of the cubes. In some cases, the concretes shall also be pre-damaged mechanically. The impact of different de-icing agents is examined. Furthermore, alkali profiles throughout the specimen cross section are established. In combination with microstructure investigations, this is to serve to evaluate the relationship between an attack by de-icing salt and an ASR.

Methods of testing

When an alkali-reactive aggregate has to be used because a non-reactive aggregate is not available for economic reasons, the evaluation of its sensitivity to alkalis constitutes a crucial prerequisite for the choice of appropriate measures aimed at preventing concrete damage. Test methods

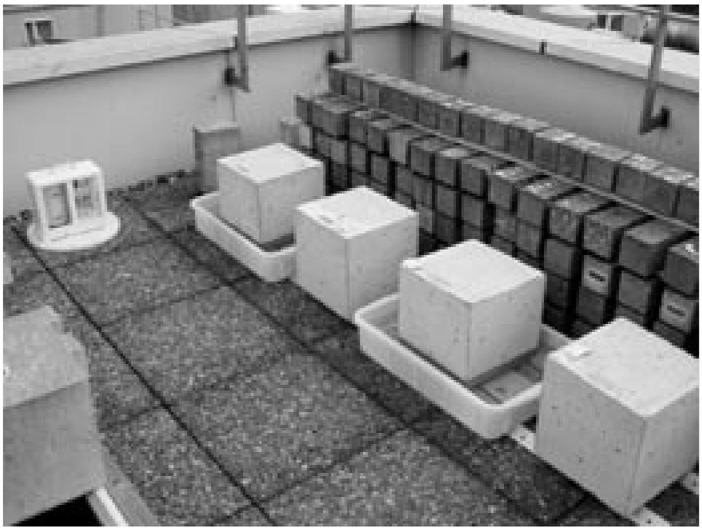


Fig. V-18: Dry and wet (footbath) outdoor storage of 30 cm cubes

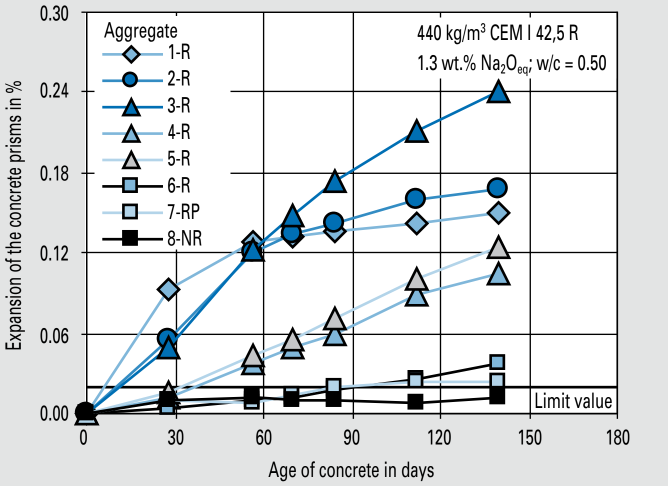


Fig. V-19: Expansion of concrete prisms (7.5 x 7.5 x 28 cm) containing different aggregates (R = reactive; RP = reactive with pessimum; NR = not reactive) during the 60 °C method of concrete testing (RILEM AAR-4)

for supranational application that allow to perform this evaluation have not yet been available in Europe. This is mainly due to the fact that experiences with a harmful ASR differ from country to country. There is a lack of investigation results that compare the behaviour shown by different aggregates in various test methods to their behaviour in practical use or under realistic conditions, respectively. This gap is to be closed by means of the EU-sponsored PARTNER project, in which 24 institutions – most of them from Western Europe – are involved. The goal of the project is to develop a uniform European testing system for evaluating the sensitivity of aggregates to alkalis.

Data on the west European aggregates known to be alkali-sensitive was gathered. It is to be published in an atlas comprising microscopic pictures of aggregate details as well as exact petrographical descriptions and information on the behaviour of the aggregates in construction practice. Of these aggregates, 22 were picked out for laboratory investigations. Upon determination of their parameters, their sensitivity to alkalis was examined using methods already available. Three petrographical analysis methods, one chemical method, two mortar tests, four concrete tests and field site tests are conducted, the results of which are compared to the experience gained in practice. Finally, interlaboratory tests are conducted to obtain statistical data on the comparability and reproducibility of the test methods.

In addition to petrographical investigations, the Institute has so far primarily carried out concrete tests and organised the field site tests (cf. **Fig. V-18**) in 8 different locations in Europe. These locations are representative of the cold moderate climate in north Europe with and without external alkali supply, the moderate climate in central Europe, and the warm climate in south Europe.

Fig. V-19 shows the expansion of concrete prisms (c = 440 kg/m^3, w/c = 0.50) that were made using reactive and non-reactive aggregates from European deposits. The specimens were stored at 60 °C over water in accordance with RILEM AAR-4. It can be seen that the expansion of all concretes with reactive aggregates that are shown exceeded the limit value of 0.02% as early as after some 90 days. In order to establish a connection with the experiences previously gained in Germany, concretes containing the same aggregates were tested according to Part 3 of the German alkali guidelines. These investigations have not been completed yet. The current status of the investigations suggests, however, that the 60° C test method seems to be more “rigid” than testing in the 40° C fog chamber.

Performance testing

It is necessary for economic reasons to be able to use alkali-reactive aggregates together with the regionally available cements and additions in the production of concretes that can be relied on not to suffer a harmful ASR. To that end, a performance test method is being developed that allows to quickly test regular concrete compositions for a potential harmful ASR. The 60 °C method mentioned above is already being applied for this purpose in France. The Research Institute has been testing different concrete compositions containing the aggregates known to be alkali-reactive in Germany as part of a project sponsored by the AiF. The results will be compared to the observations made over many years on different structural elements and on samples stored on the roof of the FIZ building under practical conditions. Initial results suggest that this method can at least be applied for dense aggregates.

Durability

Concrete structures must possess adequate durability, i.e. high resistance to environmental impacts, throughout their service life. In addition to the resistance to attack by freeze-thaw and freeze-thaw with deicing salt, this also implies the resistance to media attacking concrete, such as sulphatic water. The regulations currently in effect specify requirements for constituents (e.g. cement type, type of aggregate) and concrete composition (e.g. water/cement ratio and air content of the fresh concrete) for concretes exposed to aggressive environmental conditions with an impact on durability. These concrete technology specifications are based on many years of experience on normal-strength concretes

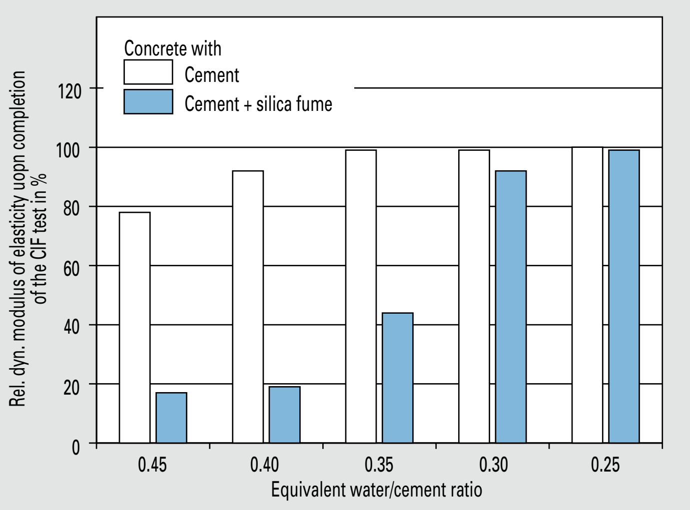


Fig. V-20: Relative dynamic modulus of elasticity of the concretes upon completion of the CIF test

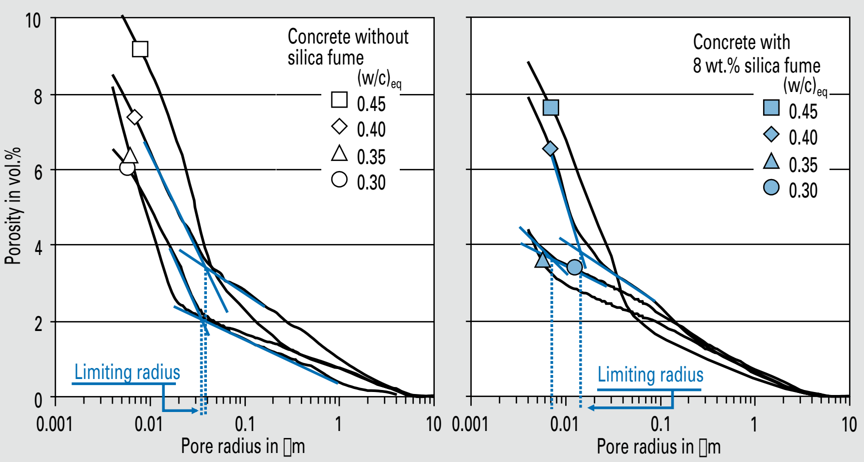


Fig. V-21: Porosity as a function of the pore radii of the concrete mortar matrix; left-hand side without silica fume, right-hand side with 8 wt.% silica fume

gathered in concrete construction. They ensure that the concretes are highly durable, provided that they have been processed and cured expertly.

Resistance to freeze-thaw and freeze-thaw with de-icing salt

When damage is caused by freeze-thaw attack, a distinction is made between external and internal damage. External damage is visible as surface scaling, which consists of small particles or thin layers being detached or flaked off from the concrete surface. De-icing agents usually intensify the damage. Internal damage to the microstructure is defined as progressive destruction of the concrete microstructure deeper inside. The 9% increase in the volume of water when ice is formed generates stresses if the expansion space (in the form of pores) in the microstructure is insufficient. When the stresses generated exceed the tensile strength of the concrete, the microstructure is damaged. This damage is not visible from outside at first, but can, for example, be ascertained by means of ultrasonic transmission time measurement.

Laboratory investigations of concretes without artificially entrained air voids that had been exposed to pure freeze-thaw attacks revealed that a decline in the dynamic modulus of elasticity (= internal damage) can be measured in the case of some concretes although the samples appear to be undamaged from the outside and exhibit only slight surface scaling. The significance that the decline in the dynamic modulus of elasticity of laboratory samples has with regard to the concrete properties to be expected following a freeze-thaw attack has not yet been determined in terms of the durability of the concretes in practical use.

Freeze-thaw resistance of high-strength concretes

The research project on the “Freeze-thaw resistance of dense, high-strength concretes” was completed at the Research Institute. The concretes investigated contained 500 kg/m^3 cement or cement and silica fume, respectively. The content of silica fume totalled 8 wt.% relative to the cement content. The equivalent water/cement ratio $(w/c)_{eq}$ varied between 0.25 and 0.45. Even after 100 freeze-thaw cycles, the relative dynamic elasticity modulus of all the concretes without silica fume as well as the concretes with silica fume and a $(w/c)_{eq} < 0.35$ did not decline. These concretes have a high freeze-thaw resistance. By contrast, the concretes containing silica fume and having a $(w/c)_{eq} \geq 0.35$ exhibited a significant drop in the relative dynamic modulus of elasticity, which in some cases occurred after only a few freeze-thaw cycles (**Fig. V-20**).

As described above, damage to the internal microstructure is caused by stresses generated when pore solution freezes as a result of a freeze-thaw attack. The ratio of the pore solution present and the expansion space is defined as the degree of pore filling. According to theory, a concrete will be damaged during one single or at least during few freeze-thaw cycles, if the degree of pore filling reaches a value of about 91%, i.e. the “critical saturation” defined by Fagerlund. Work therefore concentrated on the microstructure and the moisture content of the high-strength concretes. The investigations regarding the significance of the relative dynamic modulus of elasticity as a characteristic variable of damage to the internal microstructure were continued additionally.

Pore size distribution of the concretes

The Hg porosity of the mortar matrix of the high-strength concretes as a function of the pore radii was determined by means of mercury intrusion porosimetry. In the investigation, at the age of 28 days the porosity declined in line with a decrease in $(w/c)_{eq}$ as a consequence of the denser microstructure (**Fig. V-21**). The total Hg porosity and the capillary pore fraction included were lower with the mortars of the concretes containing silica fume than with the comparable mortars of the concretes made without silica fume.

The threshold radius was a further characteristic variable of the concrete microstructure that was derived from the results of pore size distribution (Fig. V-21). The threshold radius describes the pore size starting from which larger quantities of mercury begin to penetrate the micro-

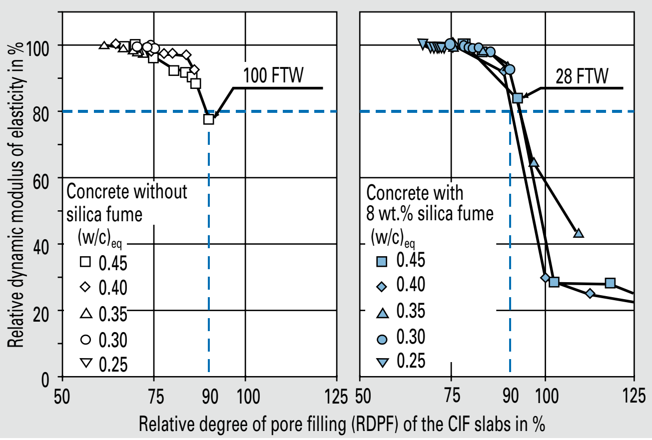


Fig. V-22: Relative dynamic modulus of elasticity as a function of the relative degree of pore filling of the concretes; left-hand side without silica fume, right-hand side with 8 wt.% silica fume (results of the CIF test comprising 0 to a maximum of 100 freeze-thaw cycles [FTW])

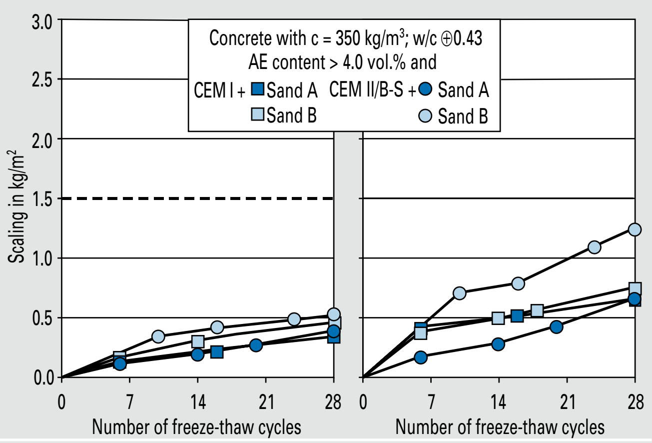


Fig. V-23: Scaling as a function of the freeze-thaw cycles of the concretes, determined according to the CDF method; curing according to the standard is shown on the left-hand side and shortened curing on the right-hand side

structure. At this point the continuity of the pore structure is disturbed. The transport of liquids through certain pore portions is impaired at that point (“pore blocking effect”). When applied to high-strength concretes, this may mean that the pore solution cannot reach the reserve space required to discharge stresses caused by freeze-thaw attack, or can reach them only in part. As the $(w/c)_{eq}$ decreases, the limiting radii are generally shifted towards finer pore radii.

The evaluation of the Hg porosity, the gel and capillary pore proportions, respectively, and the limiting radius did not yield any significant discrepancies between the concretes with and without silica fume which would have adequately explained the different behaviour observed when high-strength concretes containing silica fume were exposed to freeze-thaw attack.

Microstructure properties and freeze-thaw resistance

The overall porosity of the concretes was determined as water absorption at 15 MPa at the age of 28 days. As expected, it decreased as the equivalent water/cement ratio was lowered. When the $(w/c)_{eq}$ was identical, the overall porosity of concretes containing silica fume was about 7 to 9% higher than that of concretes without silica fume. At the same time, the natural moisture content of the concretes was determined by drying at 105 °C until constancy of mass was reached. It was generally higher with the concretes containing silica fume than with the concretes without silica fume. For the concretes with $(w/c)_{eq} > 0.35$ the difference totalled about 30%, whereas it amounted to about 20% for the concretes with $(w/c)_{eq} < 0.30$. The higher natural moisture content of the concretes containing silica fume is presumably attributable to a change in the morphology of the CSH phases caused by the pozzolanic silica fume reaction, which results in more water being combined physically.

In the wake of freeze-thaw testing based on the CIF method, the relative degree of pore filling (RDPF) was calculated as the quotient of the respective total moisture content – i.e. the moisture content after 28 days plus the water absorption during freeze-thaw testing – and total porosity at each testing time. In **Fig. V-22** the RDPF is put in relation to the change in the dynamic modulus of elasticity determined at the same time. When the RDPF reached a value of about 90%, a marked decrease in the dynamic modulus of elasticity was observed regardless of the concrete composition. Thus, the damage to the microstructure observed was caused by the “critical saturation” according to Fagerlund being exceeded locally at least.

Resistance to freeze-thaw with de-icing salt of road paving concrete with CEM II/B-S

A new research project on the “Resistance to freeze-thaw with de-icing salt of road paving concrete with CEM II/B-S” was commenced at the Research Institute. This project was prompted by damage that had occurred in concrete road paving made from CEM II/B-S 32,5 R as a result of freeze-thaw attack. With the exception of a short section in which different sand had been used, the road pavement was found to have suffered large-surface scaling of the surface mortar and occasional pop-outs after a service life of about one year (one winter period). To determine the cause of the damage, the Research Institute investigated the concrete microstructure of drill cores that had been extracted from the damaged sections of federal highway A4. The results obtained did not explain the scaling observed. For that reason, a research programme aimed at establishing the potential impact that the constituents (cement, aggregate, curing agents) have on the freeze-thaw resistance of road paving concretes is being carried out.

Laboratory investigations

The investigations covered concrete compositions typical of road pavings, i.e. with a cement content of 350 kg/m³, a water/cement ratio of 0.43 ± 0.02, and an air void content in the fresh concrete of about 4.5 vol.%. Concrete consistency was adjusted to be nearly identical in all concretes by varying the water content. In addition to ordinary Portland and Portland-slag cement from one manufacturer, two Portland-slag cements with fine and coarse ground granulated blastfurnace slag (GGBS), respectively, were utilised. The aggregates used were Rhenish gravel, high-grade diabase and orthophyre chippings as well as two sands with low (sand A) and high (sand B) water absorption, respectively. The concretes that had suffered damage in practical application had been made using sand B (high water absorption).

The freeze-thaw resistance was examined as scaling using the CDF method according to E DIN EN 12390-9. In addition to the surface concreted onto a teflon disk in accordance with the standard, a realistic concrete surface textured by a broom stroke was investigated as well. In conformity with the standard, the specimens were cured in the mould for 1 day, under water for 6 days and in a climatic chamber at 20 °C and 65% r.h. for 21 days. In addition to that, shortened curing (mould for 1 day, at 20 °C and 100% r.h. for 1 day, and in the climatic chamber at 20 °C and 65% r.h. for 26 days) and a curing agent that was sprayed onto the concrete surface textured by a broom stroke in accordance with the manufacturer's instructions were employed.

Fig. V-24: Concrete specimen (w/c = 0.60) on the basis of Portland cement (CEM I 32,5 R) and quartz gravel after 45-month storage in 0.44% sodium sulphate solution at 8 °C

Resistance to freeze-thaw with de-icing salt

It was possible to clearly differentiate the sands in terms of their water suction capacity. The water quantities absorbed within 24 hours totalled about 1.5 wt.% for sand A and about 3.5 wt.% for sand B. In compliance with requirements, all the concretes possessed an air void system with a microvoid content > 1.8 vol.% and a spacing factor that ranged significantly below 0.20 mm. The scaling observed in all the concretes cured in accordance with the standard was very slight, irrespective of whether the test surface had been concreted onto a teflon surface or textured by a broom stroke (**Fig. V-23**, left-hand side). The cement type or the sand quality were not found to have any impact on the resistance to freeze-thaw with de-icing salt. Scaling of the concretes was slight (Fig. V-23, right-hand side) even when curing had been insufficient (shortened curing). Only the combination of ordinary Portland-slag cement and sand B seemed to be somewhat more sensitive to curing. Even in that case, however, scaling was below the acceptance criterion of 1.5 kg/m^2 discussed for the CDF method according to E DIN EN 12390-9.

Road paving cements have to comply with requirements beyond those specified in DIN EN 197-1. As a consequence, Portland-slag cements with coarser ground granulated blastfurnace slag (GGBS) are frequently applied. Similar to coarsely ground Portland cements, these cements may, under certain circumstances, show a tendency towards higher water secretion and possibly towards heightened curing sensitivity. In practical use, high water secretion is counteracted by higher fineness of certain main cement constituents. Investigations on the resistance to freeze-thaw with de-icing salt of road paving concrete manufactured from laboratory-made Portland-slag cements containing GGBS of different fineness are to reveal to what extent the fineness of GGBS influences the curing sensitivity of such concretes, and thus their resistance to freeze-thaw with de-icing salt. To that purpose, concretes of the above-mentioned composition containing sand B (high water absorption) are produced and tested following the CDF method according to E DIN EN 12390-9. Moreover, the Research Institute is currently preparing a project on the influence and the optimisation of the curing of road paving concrete containing different cements. The project will be executed in cooperation with the Bauhaus university in Weimar.

Sulphate resistance

The question of whether damage to concrete structures caused by thaumasite, which was detected in about 50 concrete structures in England over the past 10 years, might occur in Germany as well was increasingly discussed by the interested parties over the past three years. This damage affected concretes that had been placed in soil containing pyrite. They did not possess adequate sulphate resistance as no sulphate attack had been expected to occur. The soil was aerated intensively when the structures were erected. As a consequence, sulphidic rock oxidised to form sulphate (pyrite oxidation). This resulted in an extraordinary sulphate attack, which in various cases even lowered the pH value of the ground water. The damage observed is thus attributable to a sulphate attack or a combined sulphate-acid attack, respectively, that had not been perceived at the time.

The Research Institute of the Cement Industry gathered the experiences and findings on the topic of "Damage potential due to thaumasite formation", most of which derive from other countries, and incorporated them into the status report on "Sulphate attack on concrete", which was issued by the German Committee for Reinforced Concrete (DAfStb) in 2004. To review whether the findings made in England can be transferred to the conditions prevailing in Germany, the DAfStb further compared the soil containing pyrite in Germany and in England. The results are described in the status report as well. Soil containing pyrite that is comparable to that in England does actually exist in Germany (e.g. Poseidon slate). For that reason, the possibility of a sulphate attack caused by pyrite oxidation has to be taken into account in the regions concerned. Since, however, no damage has been reported to date, the concretes in Germany can be assumed to possess adequate resistance in accordance with the specifications of the concrete standard DIN 1045-2. Basically, DIN 4030-1 already deals with hazards to concrete structural elements posed by pyrite in the soil, stipulating separate assessment by an expert, if the sulphide content exceeds 0.01 wt.%. Since almost any soil contains pyrite in this order of magnitude, a working group set up by the DAfStb has called for more precise specifications in DIN 4030-1. The competent standards committee will make the necessary amendments shortly.

Following the occurrences of damage caused by thaumasite, the regulations governing concrete construction in the case of sulphate attack were modified in England three years ago. For example, the utilisation of carbonaceous aggregates and cements was restricted. Against this backdrop, the use of carbonaceous constituents in concrete was discussed in Germany as well. However, there have been only few systematic investigations on the use of carbonaceous aggregates (limestone, dolomite) and carbonaceous cements and cement/fly ash mixes in the case of sulphate attack to date. The laboratory investigations conducted at the Research Institute revealed that thaumasite formation macerating the microstructure may occur at low temperatures, when the concrete contains carbonaceous constituents and was not manufactured in conformity with the standard.

Fig. V-25: Concrete specimen (w/c = 0.60) on the basis of Portland cement (CEM I 32,5 R) and limestone chippings after 45-month storage in 0.44% sodium sulphate solution at 8 °C

Fig. V-26: Concrete specimen (w/c = 0.60) on the basis of slag cement (CEM III/B-HS) and limestone chippings after 45-month storage in 0.44% sodium sulphate solution at 8 °C

This is illustrated in **Figs. V-24** and **V-25**. Specimens based on Portland cement only displayed marked thaumasite-induced damage when limestone was used to replace quartz as an aggregate. With the specimens based on highly sulphate resisting cements in conformity with the standard, by contrast, no sulphate-induced damage at all – neither in the form of expansive phases, nor in the form of thaumasite formation – was used even when limestone had been used (**Fig. V-26**).

The sulphate resistance behaviour of Portland-limestone cement/fly ash mixes was investigated at the Research Institute as well (see also Chapter III). The results confirm the DAfStb assumption that the thaumasite formation occasionally observed in laboratory trials ensues from inadequate compaction of the microstructure, i.e. from insufficient physical sulphate resistance. This is due to the high initial porosity, which is caused by a water/cement ratio of 0.60, and the reactivity of fly ash, which is diminished at low ambient temperatures (< 10 °C).

To allow better alignment of the laboratory investigations and the experience gained in practical application, concrete specimens are to undergo tests under practical conditions and laboratory trials more closely geared to practice over the next three years. The Research Institute will perform this work in cooperation with the university of Weimar and the technical university of Munich on behalf of the DAfStb.

Fair-faced concrete

Fair-faced concrete has been enjoying newfound popularity in the architectural design of structures. The artificial "rock" concrete, which can be shaped in the mould at will, is extraordinarily suited to simultaneously perform constructive and creative functions. Renowned architects, such as Ieoh Ming Pei, Tadao Ando and Zaha Hadid have taken advantage of the virtually inexhaustible creative potential inherent in the construction material concrete to make their architectural visions come true (**Fig. V-27**). In this context, the implementation in building practice of the optical appearance of the concrete surface visualised is of paramount importance for the creative objectives of the designing architect or engineer being achieved. In their view, it is no longer the heavily textured concrete surface, but the shape of the structure that is to characterise its appearance. There has been increasing demand for slim, heavily reinforced structural elements of complicated

Fig. V-27: Fire station of the company Vitra in Weil am Rhein, designed by Zaha Hadid

shapes that display totally even, poreless surfaces of uniform colour and sharp edges without any discernible construction joints. Given the current state of knowledge in the domains of concrete technology, moulding technique and execution technique, it is, however, not always possible to unerringly meet these demands.

Need for research

During the concreting process, it is not possible to either check or control whether the concrete surface quality specified has been obtained. The quality of the exposed concrete achieved cannot be evaluated until the concrete has been demoulded and the concrete surface has dried. Discrepancies in coloration, which cannot be safely avoided in spite of expert planning and execution, have repeatedly given cause for complaint. These include local discoloration and pore formation, but also large-surface “cloud formation” and “marbling” caused by the action of release agents, excessive compaction, discoloration of the mould and concrete bleeding at leakages of the mould, which cannot be prevented completely. The personal empirical experience of the people in charge of building execution and the experts assigned the task of concrete design or supervision, respectively, presently plays a larger role in accomplishing a fair-faced concrete surface that meets expectations than corroborated findings. Some fundamental rules for avoiding deficiencies in exposed concrete have been derived from experience so far. They have been included in the new code of practice on fair-faced concrete issued by the German Concrete and Construction Engineering Association (DBV) and the Federal German Association of the Cement Industry (BDZ), which does, however, not comprise a scientifically founded description of the causes and relationships underlying the phenomena resulting in complaints.

Joint research on fair-faced concrete

An investigation programme called “Joint research on fair-faced concrete”, which is sponsored by the Federation of Industrial Cooperative Research Associations (AiF), is conducted under the joint overall responsibility of the German Cement Works Association (VDZ) and the German Concrete and Construction Engineering Association (DBV). This programme comprises a total of 4 research proposals processed by 6 research centres. **Tab. V-2** gives an overview of the research centres involved and their subjects. The relationships resulting in complaints about fair-faced concrete surfaces are to be identified in close cooperation. Mechanisms and influencing variables as well as effective control measures apt to avoid colour phenomena will be derived from the results obtained.

Tab. V-2: Overview of the research centres involved in the “Joint research on fair-faced concrete” and their key resarch subjects

Research centre(s)		Subject
1.1	Research Institute of the Cement Industry, Düsseldorf	Influences on the rheological properties and the sedimentation behaviour of fines paste and concrete, with special consideration of compaction by vibration in comparison to self-compaction
1.2	Institute for building material science and material testing at the technical university of Munich	Transport mechanisms in hardening concrete – transport and crystallisation processes in view of coloration phenomena
2	Faculty for building material science and building material testing at the technical university of Berlin	Fair-faced concrete: investigation of the chemico-mineralogical interaction of fresh concrete, formwork shell and separating agent as a basis for new methods of testing in construction practice
3	Institute for building materials at the university of Hanover	Robust fair-faced concrete compositions and their testing
4.1	Institute for building and construction at the technical university of Darmstadt	Interaction of formwork shell, release agent and concrete surface
4.2	Laboratory for building materials and materials testing at the technical college of Cologne	

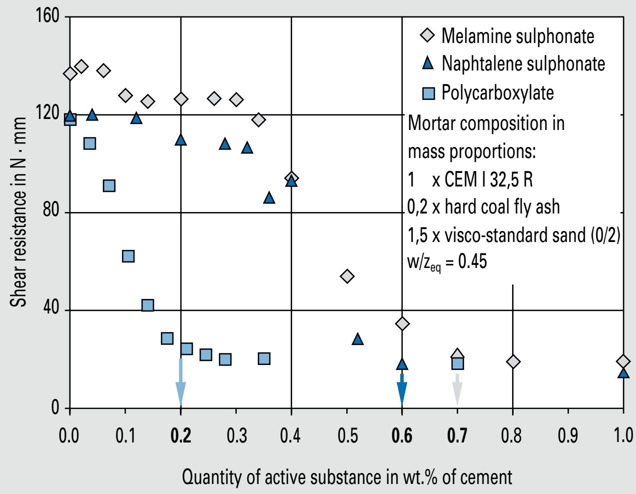


Fig. V-28: Influence of the quantity of active substance in the admixture on the shear resistance of mortar; arrows denote the respective saturation points

The main focus of research activities will be placed on investigating the influences on the sedimentation behaviour of cement paste and concrete containing super-plasticiser during compaction by vibration. The first step consisted of determining the saturation point of mortars made from different cement/addition/admixture combinations, the composition of which was derived from mix formulations for exposed concrete. This point characterises the maximum plasticising effect of the super-plasticiser not accompanied by sedimentation of the mortar. The saturation points of the mortars made using super-plasticisers are shown in **Fig. V-28**. The three super-plasticisers applied were based on one active ingredient each (melamine sulphonate, naphthalene sulphonate, polycarboxylate ether). The diagramme illustrates the well-known fact that the super-plasticiser based on polycarboxylate ether (PCE) is most effective. An active substance quantity of about 0.2 wt.% relative to the cement suffices to reach the saturation point. With the super-plasticisers based on naphthalene and melamine sulphonate, the maximum plasticising effect was not reached until 0.6 and 0.7 wt.% active substance, respectively, had been added. This is due to the different working mechanisms of the super-plasticisers. In the case of the naphthalene and melamine sulphonate, respectively, which act electrostatically, large quantities of active ingredient are required for the complete charge reversal of the parti-

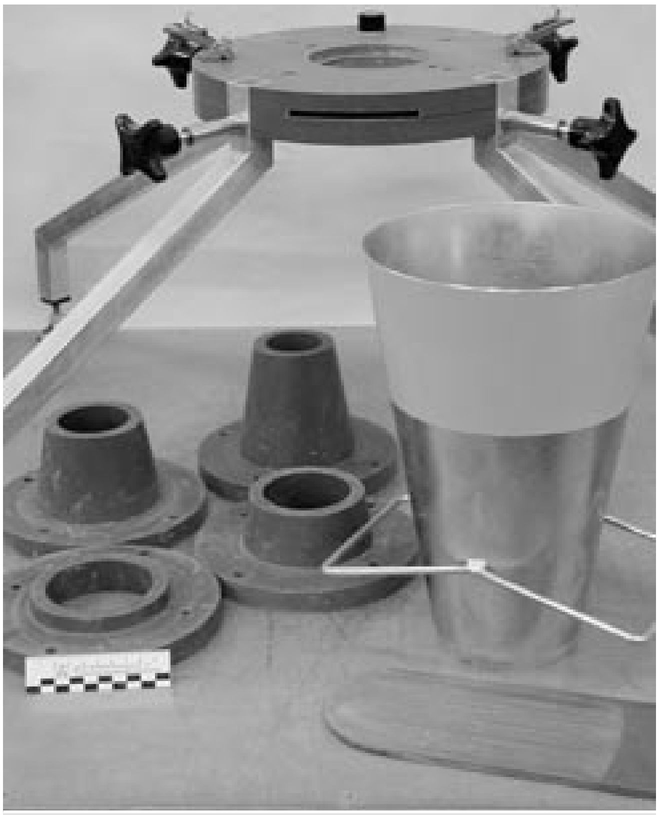


Fig. V-29: Constituents of the flow cone: slump funnel cone, supporting stand for the slump cone, discharge nozzles, and slide

Fig. V-30: Determination of the flow time and the slump flow measure with the flow cone

cle surface. Given the sterical effect, i.e. the sterical repulsion of the side chains, of the polycarboxylate, by contrast, a fairly small quantity of active ingredient suffices for the saturation point to be reached. Utmost diligence must be exercised in metering to obtain adequate sedimentation stability of the mortar, especially when super-plasticisers based on PCE are used.

Proceeding from these findings, sedimentation trials on mortars will be conducted. "Stable" mortars will be employed to investigate the influence of the compaction energy on the sedimentation behaviour. Concrete trials will be performed to check whether the results obtained from the mortars are transferable.

Self-compacting concrete ■

Self-compacting concrete (SCC) is a high-performance concrete the distinctive performance feature of which consists of the fresh-concrete property of "self-compaction". It possesses vast potential for streamlining both the production of precast concrete elements and the course of construction at building sites. To benefit from these advantages, utmost diligence in the manufacture and quality assurance is indispensable.

The "window solution" for SCC laid down in the DAfStb guidelines allows manufacturers of self-compacting concrete to determine the workability properties of their SCC in fresh and hardened concrete investigations, and to verify them in initial testing. The manufacturer guarantees the "self-compaction" feature and specifies the target values and permissible deviations for the slump flow measure and the V-funnel flow time. The limits of the range must be continually checked by factory production control in regular production since they may change as a result of fluctuations in constituents. If at least one value is not within the range, e.g. when the concrete is handed over before being poured, the concrete is rejected, or appropriate corrective measures have to be initiated (e.g. subsequent metering of super-plasticiser) in order to bring the SCC back into the workability range, i.e. into the limits of the SCC range for which conformity has been verified. To reduce the cost and effort involved in testing when the self-compacting concrete is handed over in the form of ready-mixed concrete at the building site, the flow time may be applied as an alternative to the V-funnel flow time according to Section 5.4.1 of the SCC guidelines, when a definite correlation with the V-funnel flow time was verified in initial testing.

In addition to determining the influences on the properties of fresh and hardened self-compacting concrete, the possibility of modifying a slump cone in such a way as to allow reproducible and adequately accurate flow times to be measured with it was investigated under the terms of a joint research project of the Research Association for Ready-Mixed Concrete (FTB) in Kamp-Lintfort and the Research Institute of the Cement Industry (FIZ). The flow times were varied by extending the length of the slump cone to different outlet cross sections while maintaining the slope of the cone and the concrete volume to be tested. To that effect, an ordinary slump cone was mounted on a supporting stand. A slide provided in the supporting stand allowed the cone to be closed at the bottom end. Different outlet nozzles having diameters of 50, 60, 70 and 80 mm can be arranged at the bottom end of the supporting stand. The stand was adjusted so as to arrange the slump cone 300 mm above the base plate. **Fig. V-29** shows the slump cone, the supporting stand for the slump cone, 4 different flow sections and the slide. The mounted flow cone is depicted in **Fig. V-30**.

Six self-compacting concretes of different composition were tested to determine the flow times using the flow cone. The combination of constituents and their mutual ratios allowed to cover almost the entire rheological range, from low-viscosity up to high-viscosity self-compacting concrete. After the slump cone had been filled and the slide had been pulled, the time the SCC needs to flow from the cone was measured in analogy to the funnel method according to the DAfStb guidelines. Only the concretes that did not display any relevant decrease in workability during the test cycle were used in evaluation. Thus, the differences in flow times between the various flow cones and the flow time from the funnel are exclusively attributable to the different cross sections.

In **Fig. V-31**, the flow times from the cones having flow diameters of 80, 70 and 60 mm are plotted against the V-funnel flow time of the concretes investigated. A linear relation between the respective cone flow times and the V-funnel flow time was obtained in all cases, the correlation coefficient exceeding 90%. While the flow times from the flow cones having a diameter of 80 and 70 mm were underproportional to the V-funnel flow time, the flow cone with a 60 mm diameter exhibited a slightly overproportional flow performance. Although the flow cone having a 50 mm diameter also showed a linear relation to the V-funnel flow time of the concretes investigated, it produced very high flow times, which can be regarded as unfavourable in building practice. For that reason, the 50 mm flow diameter was excluded from the further examinations. In addition to that, it has to be taken into account that, with a diameter of 50 mm, the grading curve and the obstruction tendency of the SCC may have an impact on the flow time from the cone.

On the basis of the research results a cone flow section having a diameter of 63.5 mm was calculated, which resulted in a nearly direct correlation with the V-funnel flow time. The flow cone thus constitutes an alternative method for determining the viscosity of self-compacting concretes the application of which is advantageous in acceptance testing at the building site in particular.

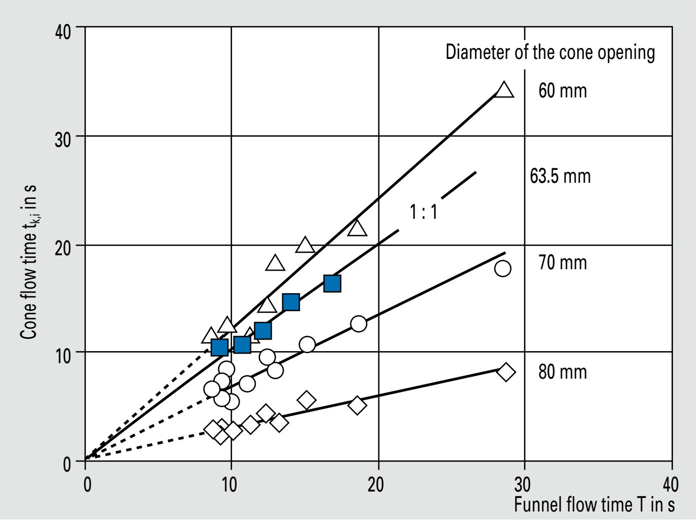


Fig. V-31: Correlation between flow time from funnel and from cone

Fig. V-32: Instant formwork removal from a large concrete pipe made from earth-dry concrete

Earth-dry concrete

Earth-dry concrete is applied in road construction products, such as paving blocks, slabs, curbstones or concrete pipes. In stationary production facilities of the concrete plants the dry concrete mixes are compacted so thoroughly by intensive vibratory/compressive compaction in rigid steel moulds that the products can be demoulded immediately, retaining their shape due to what is known as green stability (**Fig. V-32**). If the concrete composition is appropriate, the concretes compacted in this way achieve the working properties required, such as high strength and density as well as adequate durability, for example with regard to stressing caused by freeze-thaw with de-icing salt or chemical attack.

Concrete technology advancement

Experience has shown that fluctuations in the water content and in the properties of the concrete constituents can have the effect that earth-dry concretes cannot be optimally compacted during processing and are therefore not stable in shape or green stable, respectively. In that case, they do not attain the working properties intended. The material composition concretes should have in order to attain the properties required in spite of major mix fluctuations was investigated in a research project sponsored by the Federation of Industrial Cooperative Research Associations “Otto von Guericke” e.V. (AiF) and carried out by the department for materials in the building trade at Kassel university in cooperation with the Research Institute of the Cement Industry.

The investigations show that the density and strength of earth-dry concretes can be improved by choosing particle compositions with a lower sand portion and by adding fines of medium and high fineness. The inter-particulate attraction, which increases continually as a consequence of fineness, requires the use of high-performance superplasticisers or plasticisers, respectively. In this way it becomes possible to achieve

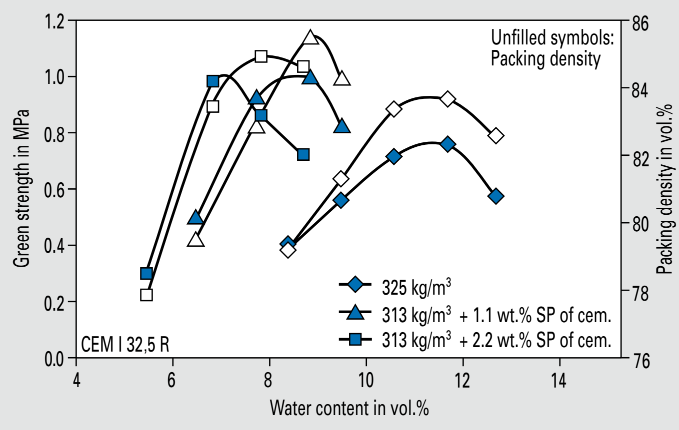


Fig. V-33: Influence of the content of water and super-plasticiser on the green strength and the packing density of earth-dry concrete

and even enhance optimum packing density and adequate green stability at a low water content (**Fig. V-33**). In practical use, mixes have to be optimised for each single works since machine-induced processing conditions have to be taken into account. It is indispensable to include durability criteria into the evaluation of optimisation measures, e.g. the substitution of inert fines for cement portions. Too high w/c or $(w/c)_{eq}$ ratios, respectively, and certain fines may impair durability characteristics even though high degrees of strength are attained.

In the wake of the investigations, a testing instrument with dynamic compaction allowing the realistic production of earth-dry concrete specimens was developed, which can be applied in production control as it enables to test green strength in parallel to production.

Brown discoloration

Through the cooperation of representatives from the cement industry and from precast concrete product manufacturers, further progress was made in solving the problem of brown discoloration, which chiefly occurred in road construction products made from earth-dry concrete, in the period under review. The findings made on the complex chemico-mineralogical and physical influences helped to analyse and frequently eliminate the occurrence of discoloration. Solving the problem presupposes an extensive and objective case analysis. The "Brown discoloration" panel in which bilateral industrial talks were held developed a questionnaire and a checklist, respectively, to compile the relevant material and production-induced parameters for each individual case and jointly initiate measures to reduce or eliminate risks, respectively. Awareness of the problem and the willingness to engage in dialogue to find solutions obviously led to the result that brown discoloration was reported only occasionally any more in 2004. Cooperation in the discussion circle will be continued.

Water-permeable block paving surfaces

Demands to pave fairly large surfaces, such as parking lots, in such a way as to allow rain water to seep away have become more and more frequent for environmental reasons. At the same time, pollutants are to be retained to prevent them from entering the subsoil and the groundwater, respectively, together with the rain water seeping away. An expert committee of the German Institute for Building Technology (DIBt) prepared the approval of corresponding water-permeable and pollutant-retaining concrete paving blocks in cooperation with the Research Institute. In this context, the topic of the environmental compatibility of cement-bound products in terms of soil and ground water protection was broached as well. A corresponding connection was established with the DIBt code of practice on evaluating the effects of construction products on soil and groundwater.

Traffic route engineering

Given its central position in Europe and the progressing enlargement of the European Union to the east, the traffic volume, and the volume in goods traffic in particular, will increase heavily in Germany over the next few years. Although the railway network has been expanded, the main share of the goods traffic will have to be absorbed by the road network. In view of the high traffic load and the introduction of Public-Private Partnership Agreements, which transfer responsibility for the construction and maintenance of a road to a contracting company, the question regarding the service life and the maintenance costs of a road design has taken centre-stage. Durable, low-maintenance and thus economically efficient construction methods accompanied by high environmental compatibility are advantageous.

Road construction

The high durability in spite of exposure to most heavy lorry traffic and the low maintenance costs during service life constitute important arguments in favour of building concrete road pavements. The service life of concrete paving usually tops 30 years. A few occurrences of damage have given rise to uncertainty among the interested parties. The investigations carried out by Research Institute showed that a harmful alkali-silica reaction (ASR) could not be ruled out in some cases (see section on alkali-silica reaction). To ensure a high degree of security against a harmful ASR in concrete road pavements prophylactically, VDZ recommended the following measures:

1. Reduction of the effective alkali content of cements for road paving (**Tab. V-3**),
2. No use of reactive aggregates included in the alkali guidelines,
3. Use of quartz porphyry, greywacke, chippings from the Upper Rhine valley and all imported aggregates only if an expertise is available.

The associations of the aggregate industry and the Quality Community for Traffic Pavements have adopted these recommendations. The Federal Minister issued these regulations in a circular in early 2005. The list of aggregates that may only be used upon presentation of an expertise was extended to include recycled aggregates.

The Research Association for Roads and Traffic (FGSV) set up a new working group to investigate and discuss the occurrences of damage mentioned as well as further durability aspects of concrete paving. Durability does not only imply the prevention of a harmful ASR, but also the diligent production and curing of concrete. The working group also discussed the use of CEM II cements in road construction. These cements are approved for road construction, but have been applied only very rarely so far. An ad-hoc group of VDZ's Transport engineering working group is currently compiling a summary of the experience gained with CEM II and CEM III cements in road construction which will also incorporate the Research Institute's investigations on the resistance to freeze-thaw with de-icing salt of road paving concretes made from different Portland-slag cements (see section on durability). According to the recommendations, cements containing blastfurnace slag should be characterised by higher grinding fineness than the CEM II/B-S 32,5 R cements applied previously, and should be utilised as CEM II/B-S cements of strength class 42,5 N in the future. The higher grinding fineness and the faster strength development diminish the water segregation tendency and reduce any potential curing sensitivity.

Tab. V-3: VDZ recommendations for the alkali content given as Na_2O equivalent (characteristic value) of cements used in the construction of concrete road pavements in the road engineering sector

Cement	Blastfurnace slag content in wt.%	Alkali content of the cement Na_2O equivalent in wt.%	Alkali content of the cement without blastfurnace slag or oilshale Na_2O equivalent in wt.%
CEM I CEM II/A		≤ 0.80	-
CEM II/B-T		-	≤ 0.90
CEM II/B-S	21 to 29	-	≤ 0.90
CEM II/B-S	30 to 35	-	≤ 1.00
CEM III/A	36 to 50	-	≤ 1.05

Fig. V-34: Test section for continuously reinforced concrete paving on Federal Highway A5

Regulations

The introduction of the European standards in particular has made it necessary to adapt the regulations applicable in road engineering. The laying of sub-base courses using hydraulic binders, which was previously regulated by the supplementary technical terms of contract and guidelines for sub-bases in road construction (ZTVT-StB), and the construction of road pavements, which was previously regulated by the supplementary technical terms of contract and guidelines for concrete in road construction (ZTV Beton StB), will now be subject to several European standards that have been published. These will have to be transposed into corresponding national regulations and introduced in building practice. In conjunction with the revision of the existing regulations, the regulations for all courses containing hydraulic binders are to be combined in a set of provisions that will cover hydraulically bound sub-base courses in addition to concrete pavements in the future. The future regulations, in the elaboration of which FIZ is involved, will be subdivided into three parts:

- Technical terms of delivery for concrete in road construction (TL Beton StB) to regulate the delivery of building materials and building material mixes
- Supplementary technical terms of contract and guidelines for concrete in road construction (ZTV Beton-StB) to regulate production and
- Technical terms of testing for concrete in road construction (TP Beton-StB) containing technical testing provisions for all tests conducted on building materials, building material mixes and on the finished work.

New construction methods

The "Silent traffic" research programme (sponsored by the Federal Ministry for Education and Research, coordinated by the Federal Highway Research Institute BASt), in which the Research Institute was involved, consisted of optimising novel, open-pore draining concretes in laboratory trials and testing them in a practical trial. A test section with a length of about 300 m was laid out on a national road in September 2002. The draining concrete layer, which was about 8 cm thick, was placed both on an asphalt and a concrete sub-base. The pavement has been exposed to traffic for three winters. Noise measurements carried out by BASt have demonstrated that it is acoustically equivalent to open-pore drainage asphalt. The "Silent traffic" programme was completed in 2004. Consultations on its continuation are currently being held.

The standard construction method previously applied in Germany has been an unreinforced concrete pavement with dowelled transversal dummy joints arranged at a 5-metre distance. In neighbouring countries, by contrast, the construction of continuously reinforced concrete pavements with unrestrained crack formation has gained increasing acceptance. The reinforcement results in the formation of numerous, finely distributed cracks in the concrete; as a consequence, the customary cutting of transversal joints can be dispensed with. The costs for the production and dowelling of the joints and the expenses for joint maintenance during service life no longer accrue. As damage chiefly occurred as a consequence of poorly maintained, permeable joints in some cases, experts expect the new construction method to entail improved durability. To gather experiences with the continuously reinforced concrete paving in Germany as well, a test section was laid out on Federal Highway A5 in late 2004 (**Fig. V-34**). VDZ's „Transport engineering" working group attends the developments and experiences.

Permanent way – ballastless track

The high demands made by Deutsche Bahn AG (German rail) on the positional stability of the rails requires the installation of a ballastless track. Various systems were applied in the new railway track from Cologne to Frankfurt taken into operation in 2002. The Rheda system consists of accurately levelling the sleepers into a prefabricated concrete trough and binding them monolithically in the trough with a joint filling concrete. With the "Züblin"

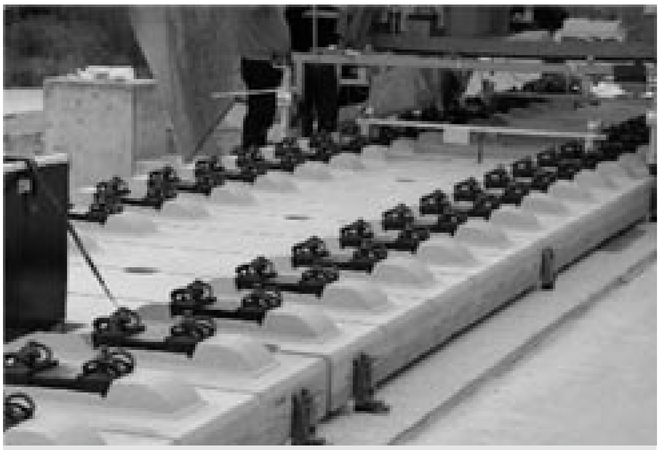


Fig. V-35: Bögl ballastless track system: accurate levelling of precast concrete slabs on the hydraulically bound sub-base

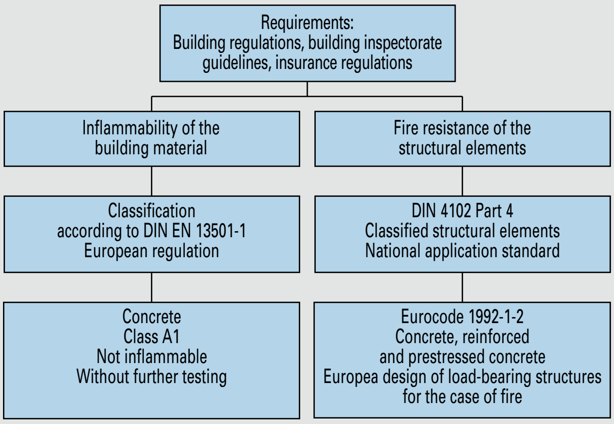


Fig. V-36: Concept for the rules on classification and design in terms of fire protection during transition to the European standards; current status

design, the concrete sleepers are vibrated into the fresh concrete. In the new section from Nuremberg to Ingolstadt, the Bögl design was executed on larger track sections (about 35 km) for the first time. The system consists of concrete slabs manufactured in precasting works, which are placed onto a hydraulically bound sub-base at the installation site (**Fig. V-35**). Each slab is provided with a total of 10 pairs of supporting points (sleepers) for rail fixation. After accurately levelling the slabs by means of screwable devices, the gap between the sub-base course and the slab is grouted with a mortar modified by bitumen. After underpouring, the precast slabs are connected to each other lengthwise by means of turnbuckles, and the transversal joints are grouted with concrete, thus generating a continuous pavement. The advantages inherent in this construction method are its high positional accuracy due to prefabrication and tight fitting of the slabs as well as the possibility of replacing individual slabs in case of damage. The varied development work is attended by VDZ's "Transport engineering" working group.

Fire protection ■

Residential buildings and buildings in which humans linger have to be constructed in such a way as to protect humans and their possessions as well as the buildings from the effects of fire. Concrete makes a major contribution to implementing the necessary protective functions. Concrete does not burn. As a consequence, no smoke is generated and no poisonous gases are released. Moreover, concrete structural elements withstand fire for a fairly long time.

These fire protection properties can be taken advantage of effectively to impede the spreading of the flames in case of fire and to maintain the load-bearing capacity of the design and thus preserve the building. This benefit serves the protection of people as it allows them to save themselves or be safely rescued by the fire brigade in the case of fire. It further serves property protection since the fire brigade gets the possibility of effectively fighting the fire inside the building, which experience has shown to reduce the impact of the fire. In the case of concrete components possessing high fire resistance, the individual elements get through the fire largely unscathed. Thus, the building can still be used afterwards.

Fire protection activities in the industrial sector

The "Fire resistance" joint working group under the direction of VDZ, which pools the activities of the concrete and precast concrete element industry, the German Concrete and Construction Engineering Association, the aerated concrete industry and the cement industry, listed the protective functions performed by concrete buildings in the case of fire that ensure

- the protection of people,
- the protection of property for the individual building and adjacent buildings, and
- environmental protection in the case of fire.

This catalogue is available to consultants, building owners and users for information.

The working group members further contributed to concrete being graded as a class A1 construction material, i.e. a material that is absolutely non-combustible without requiring verification, in the classification of construction materials in terms of their fire protection properties, which will be applicable throughout Europe in the future (**Fig. V-36**, left-hand side). The status applicable in Germany was thus laid down at European level as well.

To classify structural elements in terms of their fire protection properties, the existing design standard DIN 4102 Part 4 was adapted to the future European provisions of Eurocode 1992-1-2 (Fig. V-36, right-hand side). The concrete and cement industries were involved in this work. On the basis of the adapted regulations, dimensioning of structural elements with regard to fire resistance can be carried out according to the proven principle of DIN 4102-4. Design rules of general applicability have been added for structural elements made from high-strength concrete and for the domains of concrete masonry, porous lightweight concrete, and reinforced aerated concrete.

If the load-bearing capacity of concrete structures is to be measured on the basis of partial safety factors in application of the future European concept according to Eurocode 2, fire protection design can still be performed in accordance with DIN 4102-4 since a national application standard was established which ensures that the design for the normal state (cold-state design) applicable in Europe in the future and the familiar design for the case of fire (hot-state design) according to DIN 4102-4 can be combined in a manner geared to practical requirements in concrete construction.

Given this development in the field of fire protection standards, practical users will be able to refer to proven tabular provisions, for example regarding minimum density, minimum width and the arrangement of reinforcements in concrete structural elements, in the fire protection of concrete buildings for the next 8 to 10 years.

European activities

Under the direction of CEMBUREAU, task force 2.2 "Fire safety with concrete" has been working on fire protection issues of overriding importance for the European countries. The task force is a panel set up by the European associations of the precast concrete element (BIBM), ready-mixed concrete (ERMCO) and cement (CEMBUREAU) industries. It became apparent during the project, which has been underway for 4 years, that the topics of constructional fire protection relating to concrete engineering are nearly the same in the different European countries. On the one hand, technical marketing has to be applied to draw attention to the high importance concrete components have for comprehensive constructional fire protection, and on the other hand the position of concrete construction in the composition and implementation of the European fire protection provisions has to be argued appropriately and expertly.

As a result of cooperation and agreement within the task force, it was possible to downgrade the heat penetration coefficients for concrete exposed to fire, which had been set too high without justification. Fire resistance time is determined by the heating of concrete cross sections as a function of time. The faster heating takes place, the lower fire resistance is. Road tunnels are of major importance in several European countries. An argumentation paper that highlights the advantages of concrete road paving in the case of fires erupting in tunnels was compiled.

The work of the CEMBUREAU task force is to be finished in 2005 with the compilation of a leaflet on fire protection with concrete, which is to furnish fundamental information for practical use.

Modelling ■

The prediction of the properties of cement and of concrete in particular enables users to make a quick, target-oriented selection of raw materials, and especially of the cement to be used in the respective concretes. To that effect, a growing number of mathematical models that allow to assess the performance of cements on the basis of their chemical composition has been developed. The extension of these models to include the evaluation of concrete properties presupposes that the properties of the other constituents can be described with adequate precision as well.

Simulation of cement hydration

The prerequisite for simulating cement hydration by calculation is an adequately accurate hydration model. Assumptions and simplifications must be made to allow such a model to be converted to a mathematical simulation model. This implies examinations regarding the development with time and the spatial change of the microstructure. Preconditions for this are the correct choice of initial material parameters and an adequately discretised mathematical simulation of the chemico-mineralogical interactions. This includes the experimental determination of material parameters, such as reactivity and density.

Simple models for simulating cement hydration are not up to representing the complex chemico-mineralogical processes. Only due to advances in the field of software and hardware has it been possible for a couple of years to master correspondingly complex mathematical models for the construction material cement by means of calculation. Computer-aided models are used to simulate cement hydration and microstructure development, which in turn serve as the basis for predicting mortar and concrete properties.

Fundamental modelling work in the field of cement properties was performed at the National Institute of Standards and Technology (NIST) in the U.S. The German Cement Works Association is presently the only German partner involved in the current work performed by an international consortium, which consists of developing a so called Virtual Cement and Concrete Testing Laboratory (VCCTL).

Modelling of cement hydration

NIST has performed basic work on modelling cement hydration with the help of "cellular automata" since the early 90ies. The latter consist of a three-dimensional model to describe the development of the hydrate phases and the hardened cement paste microstructure in a cuboid having an edge length of 100 µm. To that end, the cuboid is subdivided into elemental cells having an edge length of 1 µm, which are referred to as "voxels". This cuboid is first filled with cement particles, the particle size distribution and phase distribution of which are taken into consideration, and with water. In addition to hydration reactions, the chemical reactions taking place in the model comprise the processes involved in the dissolution and nucleation of the solids. They result in a gradual change in the material composition of the solids and the pore solution as well as the microstructure, during which storage conditions can be taken into account as well. In each iterative step, cement particles (voxels) that are in contact with the water of the capillary pore space disengage and move through the pore space. If they meet suitable reaction partners, they can react to form new phases. The partially hydrated hardened cement paste thus essentially consists of 4 phases: cement that is not converted, capillary pore water, CSH gel and calcium hydroxide. The volume percent of the individual phases is analysed to allow the pore structure to be calculated. Evaluations of the progress of hydration relate to the physical properties of the microstructure (strength development, porosity, transport properties, cross-linking density of the reaction products), the spatial chemical composition, chemical shrinkage and temperature development.

This cellular model further allows to examine blastfurnace slag, limestone, fly ash and silica fume, for which reactivity parameters determined by their mineralogical and chemical composition are introduced. According to Powers, the compressive strength of the respective cements is derived from the degree of hydration calculated. Finite-element methods, which refer to the modulus of elasticity of the individual phases, will be employed to that purpose in the future.

Calculations using the NIST model are based on a network of hydration reactions of different scope and varying complexity. The model first requires a complete characterisation of the cement as an input parameter to perform the calculation. To calibrate and validate the model, mathematical simulation is accompanied by experimental investigations of the cements selected. They substantially relate to investigations of hydration and strength development. **Fig. V-37** shows schematically how a simulation calculation is carried out.

The modelling of cement hydration based on the NIST model offers the possibility to use calculation to contribute to solving questions of practical relevance about the

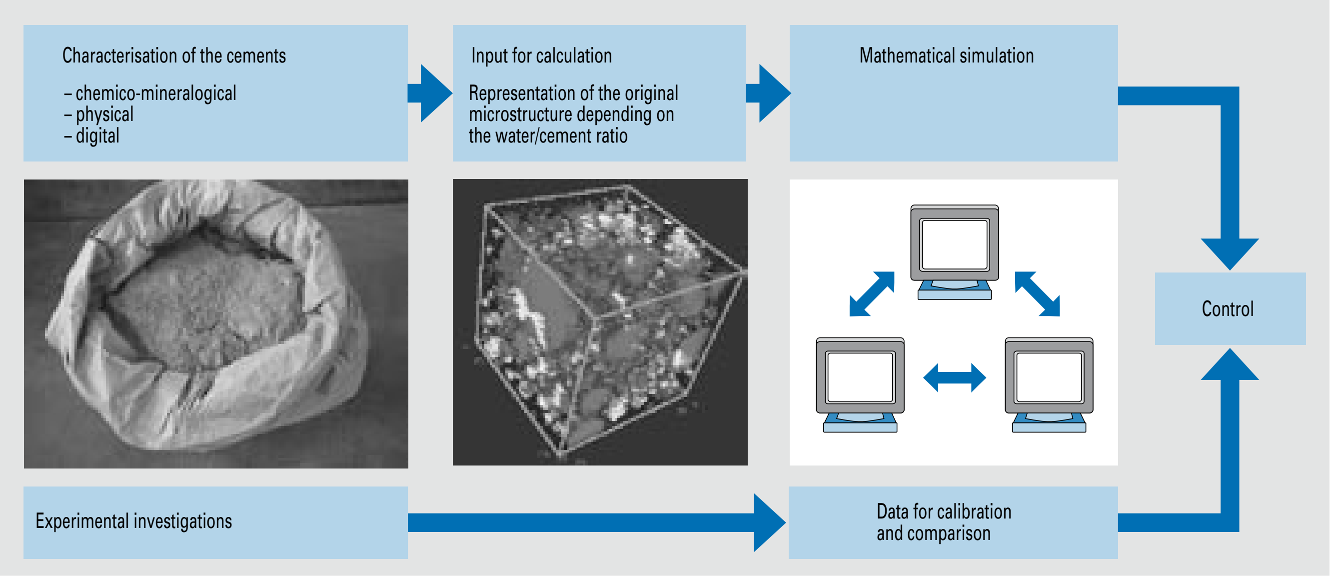


Fig. V-37: Schematic representation of a simulation calculation

Tab. V-4: Characterisation of the cement

Chemico-mineralogical charcterisation		
Clinker phases (C_2S, C_3S, C_3A, C_4AF)	Total in vol.%	Rietveld refinement, etc.
Alkalis (Na_2O, K_2O)	Total in wt.% Soluble in wt.%	X-ray fluorescence analysis ASTM C 114
Sulphates (total, hemihydrate, anhydrite)	Total in vol.%	Rietveld refinement Heat flux calorimetry (DSC)
Physical characterisation		
Grinding fineness	Specific surface area (Blaine value)	Specific surface area determined by air permeabilty method
Particle size distribution	Particle size fraction	Screening analysis and approximation by RRSB distribution
Digital characterisation		
Image analysis	Phase distribution	Digital image evaluation using SEM and electron microscope analysis by means of EDX
Stereometric parameters	Surface, perimeter	

performance of cement and concrete. The effects that changes in clinker composition caused by deviations, e.g. in the control of the rotary cement kiln or in the particle size distributions of the main cement constituents, have on the strength development of the cements can be predicted immediately.

The Research Institute of the Cement Industry is currently concerned with the modelling of cement hydration, pursuing the overarching target to predict the 28-day standard compressive strength of cements already after a short time. In the long run, mathematical modelling is to allow the cost-effective and realtime determination by calculation of the properties of cements as well as the mortars and concretes to be made from them.

It is perfectly conceivable that high-performance models of cement hydration will become firmly established in the standard testing of cements in the future, enabling fully automated online production of cement with integrated quality assurance. The results could be applied directly in production control and concrete manufacture. Moreover, virtual testing opens up the possibility of investigating a large number of parameters in order to develop new materials and optimise existing ones without expending too much effort.

Characterisation of cements

The representation of particle distribution prior to the onset of hydration is a basic constituent of the NIST model. For the purpose of cement characterisation, this requires both data on the chemical and mineralogical composition and the physical properties of the cements, and digitalised microscopic images of the cement. A crucial parameter obtained by digital characterisation is the surface proportion of the cement constituents. It may deviate from the corresponding volume and mass percents, respectively, and therefore has substantial influence on the progress of hydration with time, since the constituents located on the surface of a cement particle get in contact with water more quickly than those in its core. **Tab. V-4** summarises the parameters required to characterise the cement as a basis for the mathematical simulation of cement hydration and possible experimental determination methods.

Fig. V-38 shows the steps by which the initial structure of the mathematical element is modelled. The further mathematical simulation of cement hydration proceeds from the basis of this element. The statistical evaluation of clinker phases and gypsum as well as the additional main constituents permits experimental data and numerical evaluation to be compared and controlled, respectively, before simulation calculation is begun.

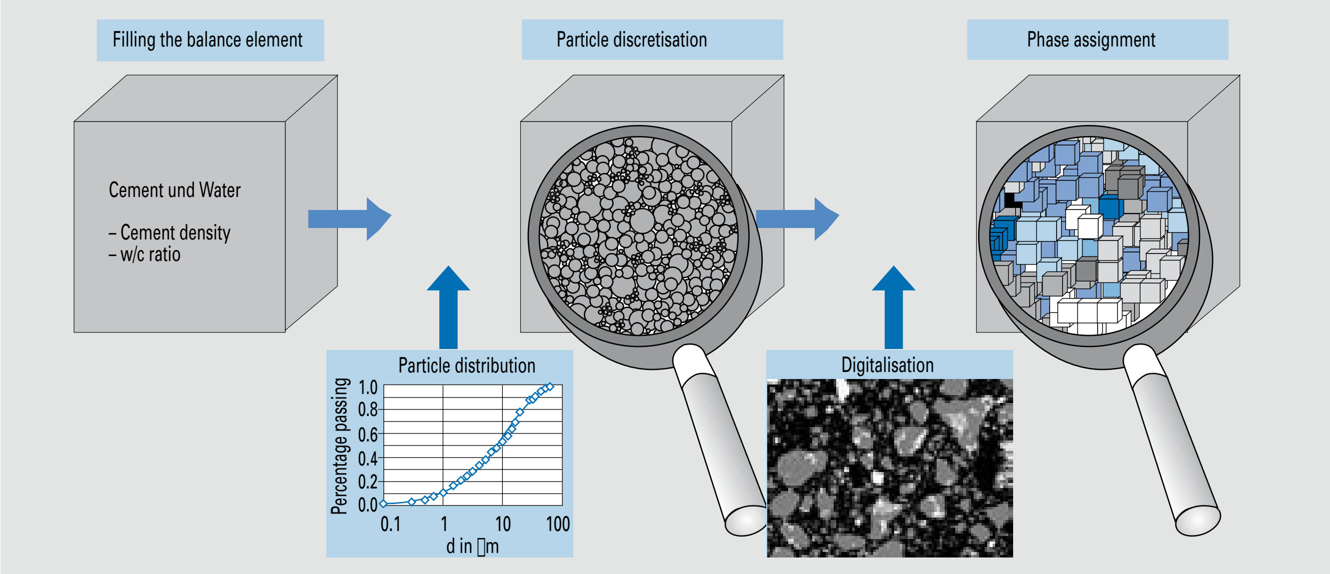


Fig. V-38: Filling the balance element that serves as the basis for simulation with the NIST model

Simulation results

By way of example, **Fig. V-39** shows the microstructure development of a hardened cement paste made from a Portland cement CEM I with a water/cement ratio of 0.50 at selected points of time. The particle size distribution of the cement is taken into account in the original situation (t = 0). The individual clinker phases were determined in terms of quantity and assigned to the individual grain size fractions upon evaluation of the clinker by image analysis. The hydration process clearly shows the dissolution of the cement particles and the increasing formation of a microstructure.

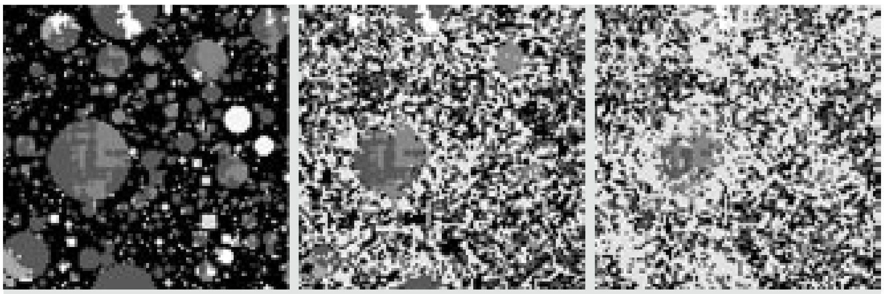

Cycles = 0 Cycles = 500 Cycles = 2 000

Fig. V-39: Microstructure development in the hardening cement paste due to of the hydration process

The results yielded by simulation calculation include the degree of hydration and the development of the volume percent of the hydrate products and the decomposition of the individual cement clinker phases, respectively. By way of example, **Fig. V-40** shows the development with time of the degree of hydration and the porosity as well as the volume percent of CSH, CH, gypsum and ettringite as a function of the number of calculation cycles. Empirical relationships which include the alkali content allow hydration in relation to time to be represented as a function of the calculation cycles. In addition to that, the mathematical simulation of cement hydration furnishes results on how the pH value of the pore solution and the heat of hydration develop with time.

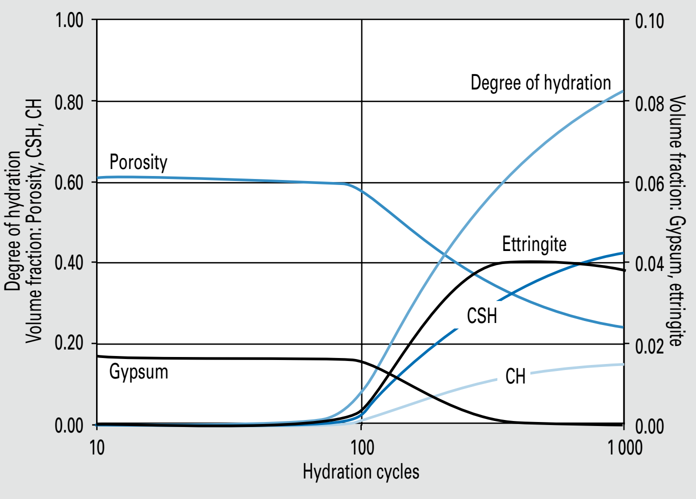


Fig. V-40: Results of a simulation calculation

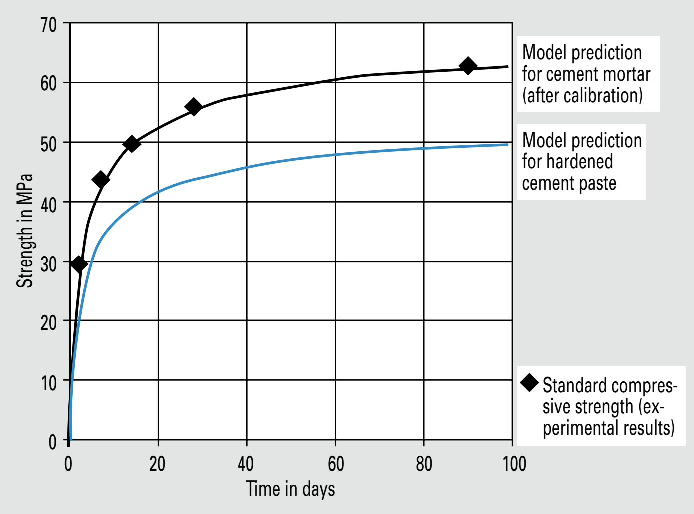


Fig. V-41: Compressive strength development determined experimentally and by calculation

Determination of compressive strength by calculation

The parameter that is of vital importance for the compressive strength of the hardened cement paste is chiefly the capillary porosity, which substantially depends on the degree of hydration and can be determined empirically by applying various models. To calculate strength, the equation according to Powers, which puts capillary porosity in relation to the volume of the hydration products, can be input in the NIST model first. It proceeds from the assumption of a basic strength, which is diminished by porosity and corresponds to the strength of a microstructure devoid of pores. It is thus irrelevant to the strength of the hardened cement paste whether capillary porosity is based on a higher portion of unhydrated cement, i.e. a decreased degree of hydration, or on a lower capillary porosity of the hydrated cement. It is thus not possible to transfer hardened cement paste strength to standard compressive strength without some restrictions. Influences of aggregates and reactivity as a function of the water/cement ratio, the particle shape and distribution of additives and fines have to be taken into account additionally.

The NIST model permits to consider the reaction potential for the formation of compact grained reaction products, surface reactions and the porosity of the matrix. The model allows to incorporate grading influences of the inert and reactive substances into the calculation. The influence of sand has not yet been implemented at present. Porosity changes in the contact zone as a function of the hydrate products generated can be implemented mathematically. The deformation properties of the hardened cement paste in relation to the stiffness of the hydrated and unhydrated portions are determined by means of finite element calculations. In this way it becomes possible to determine the modulus of elasticity of the hardened cement paste and to predict its dependence on other cement properties. A research project aims at finding out to what extent these results can be transferred to standard compressive strength. By way of example, **Fig. V-41** shows the mathematically determined compressive strength of a hardened cement paste as a function of age. The compressive strength for cement mortar determined experimentally is bound to deviate due to the proportions of aggregates. It is, however, possible to calibrate the curves, and thus also to make predictions about the standard compressive strength of cements.

Standardisation ■

The new concrete standards DIN EN 206-1 and DIN 1045 were adopted by the building supervisory authorities in August 2002. An A1 amendment to DIN 1045-2 was elaborated in order to bring the set of standards up to date in technical and formal respect by the time the transition period expired on December 31, 2004. This amendment of the standard became necessary to allow the following items to be taken into account:

- Inclusion of the allowance concept for fly ash in combination with CEM II-M cements
- Changes resulting from the new national or European product standards for cement, concrete admixtures and aggregates
- Incorporation of the corrigenda to DIN 1045-2

In addition to that, the new concrete standards were found not to cover the particular features of massive concrete components. These items are dealt with in guidelines by the German Committee for Reinforced Concrete (DAfStb), which were established in parallel with the A1 amendment in the course of 2004. Employees of the Research Institute were intensely involved in elaborating the amendment to the standard and the guidelines.

Application rules for cement

The A1 amendment regulates the application of the following cements:

- Low heat common cement according to DIN EN 197-1/A1 (LH cement)
- Low early strength blastfurnace cement according to DIN EN 197-4 (CEM III/L)
- Very low heat special cement according to DIN EN 14216 (VLH)
- Special common cement according to DIN 1164-10 (highly sulphate resisting (HS) and low-alkali (NA) cement)
- Cement with short setting time according to DIN 1164-11 (early-setting (FE) and fast-setting (SE) cement)
- Cement with a higher quantity of organic constituents according to DIN 1164-12 (HO)

The A1 amendment introduced the following regulations governing the application of cements according to these standards: VLH cements of CEM III/B composition may be applied like CEM III/C cements. CEM I and CEM II cements can be employed as SE cements (shotcrete cements). All the other cements of the above-mentioned standards are subject to the application rules laid down in DIN 1045-2.

Application rules for fly ash

The previous regulations governing the application of fly ash and silica fume as concrete additions laid down in the fly ash guidelines and the national technical approvals for silica fume were adopted in the new concrete standard DIN 1045-2. They are restricted to some of the cements already included in the former DIN 1164. These regulations had to be revised now in order to ensure equal treatment of the “new” cements according to DIN EN 197-1 which some cement works produce (see also section on “Portland-composite cements”). Fly ash can be set off against the water/cement ratio as a concrete addition with an assumed cement-equivalent effect of 40% (k = 0.40). The quantity to be set off must not exceed 33% of the cement content (f/c = 0.33). The above-mentioned regulation was adopted for some CEM II-M cements not containing pozzolana. With CEM II-M cements containing up to 20 wt.% pozzolana, the maximum quantity of an additional fly ash input must not exceed 25% of the cement content (f/c = 0.25). The use of the k-value concept is excluded for CEM II/A-V and CEM II/A-M (P-V) cements used in concrete of exposure class XF 3 (freeze-thaw attack with high water saturation). The previous regulation, according to which the k-value concept must not be used in case of freeze-thaw attack with de-icing salt (exposure classes XF2, XF4) continues to apply. **Tab. V-5** gives an overview of the new regulations and shows the cements for which the possibility of fly ash allowance was newly introduced. Corresponding provisions were adopted to ensure the alkalinity reserve of the pore solution when fly ash and silica fume are utilised. This is why addition of fly ash is limited to f/c < 0.15 for cements containing silica fume (e.g. CEM II/A-M (D-LL), CEM II/B-M (S-D)). With CEM II/A-M (S-T, S-LL, T-LL) cements, the maximum quantity of fly ash permissible is limited to f/c < (0.15 – s/c) · 3 when a combination of fly ash and silica fume is used. For all the other cements listed in Tab. V-5, the combined use of fly ash and silica fume is not permitted.

Tab. V-5: Extension of the application rules for fly ash and silica fume according to DIN 1045-2/A1

Portland-composite cement	Allowance			Maximum fly ash quantity that can be set off f/c	Maximum silica fume content s/c	No allowance for exposure classes
	f	s	f+s			
CEM II/A-M (S-T, S-LL, T-LL)	x	x	x1)	0.33	0.11	XF2, XF4
CEM II/B-M (S-T)						
CEM II/A-M (S-D, D-T, D-P, D-V, D-LL)	x	-	-	0.153)	-	
CEM II/B-M (S-D, D-T)						
CEM II/A-M (S-P, P-T, P-LL)	x	x	-	0.25	0.11	
CEM II/A-M (S-V, V-T, V-LL)						
CEM II/A-P	x	x2)	-			
CEM II/A-V, CEM II/A-M (P-V)	x	x2)	-			XF2, XF4 and XF3

Allowance of fly ash and silica fume calculated against the equivalent water/cement ratio:

$$(w/c)_{eq} = \frac{w}{c + k_f \cdot f_{allow.} + k_s \cdot s}$$

1) In case of combined use: $f/c \leq (0.15 - s/c) \times 3$

2) Already permissible for CEM II/A-P and CEM II/A-V according to DIN 1045-2

3) No fly ash addition beyond f/c = 0.15

CEM II-M cements for concretes with high sulphate resistance

Just like the application rules for fly ash, the “fly ash regulation” for concretes with high sulphate resistance had to be supplemented by “new” cements. In case of sulphate contents of SO_4^{2-} < 1 500 mg/l of the attacking water, it is possible now to use mixes of cement and 20% fly ash with fly ash cement CEM II/A-V, Portland-composite cement CEM II/A-M with the main constituents S, V, T, LL or CEM II/B-M (S-T) in the production of highly sulphate resisting concrete.

Aggregates

Since June 1, 2004, the properties of aggregates for normal weight concrete have been regulated by DIN EN 12620 (aggregates for concrete) in combination with the national application standard DIN V 20000-103. The properties of lightweight aggregates are laid down in DIN EN 13055-1. The associated application standard is DIN V 20000-104. For that reason, the corresponding standard references, which had previously been geared to the set of standards of DIN 4226, had to be adapted. Apart from that, no fundamental technical modifications were necessary. The requirement for the resistance of aggregates to wear was cancelled from DIN 1045-2 as compliance cannot be verified, and as it is primarily the hardened cement paste that is exposed to abrasive stress.

Concrete admixtures

In analogy to aggregates, a harmonised European product standard was completed also for concrete admixtures – DIN EN 934-2. To be applied in the domains of building inspectorate relevance, concrete admixtures previously required national technical approvals issued by the German Institute for Building Technology (DIBt). Since May 1, 2003 all admixtures within the scope of the harmonised European standard EN 934 have had to be labelled with the CE marking and had to comply with the requirement this implies. The specifications regarding certain applications which had previously been laid down in the guiding principles for approval and conformity evaluation issued by the DIBt, and the verification of harmlessness in terms of a corrosion-inducing effect on the embedded steel and the tendons, respectively, were included in the standards DIN V 18998 “Assessment of the corrosion behaviour of admixtures” and DIN V 20000-100. Admixtures for grouting mortar used with tendons are covered by DIN EN 934-4 in combination with DIN V 20000-101.

DAfStb guidelines

DAfStb guidelines are compiled in cases when, for example, the European standardisation process does not materialise, or when rapid implementation of research results in practical use is desired. Employees of the Research Institute were again intensely involved in the work on a large variety of DAfStb guidelines during this period under review.

Work on the following guidelines was completed in the period under review:

- Massive structural concrete elements
- Self-compacting concrete
- Concrete with recycled aggregates
- Water-impermeable concrete structures
- Concrete construction in the domain of water-polluting substances

Massive structural concrete elements

The guidelines apply to massive structural elements made of concrete, reinforced concrete and prestressed concrete in which the heat-up caused by hydration is higher due to their large dimensions. The regulations apply to structural elements the shortest component dimension of which totals at least 0.80 m and in which restraint and internal stress have to be taken into account to a particular extent. In footnote b to Table F. 2.1, DIN 1045-2 already comprised the possibility of lowering the minimum cement content by 20 kg/m^3, i.e. from 320

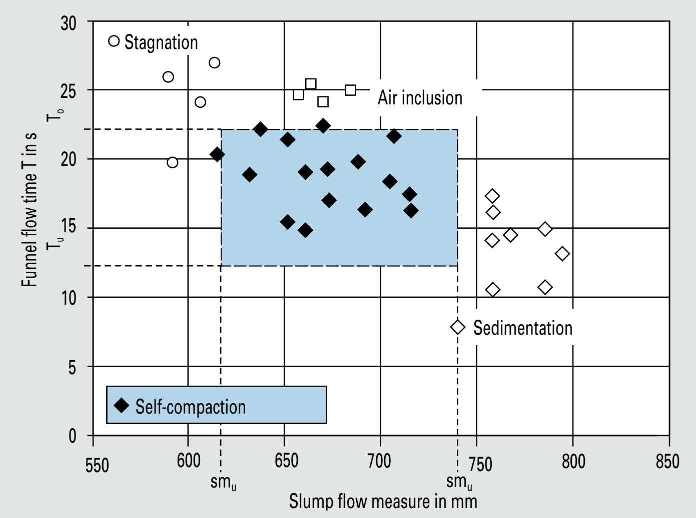


Fig. V-42: Example for the workability range of a self-compacting concrete

to 300 kg/m^3, for massive structural elements with minimum dimensions of 80 cm in exposure classes XD/S 2 and XD/S 3. A reduction in the cement content is aimed at lowering the heat of hydration and the associated restraint and internal stresses. The guidelines now permit the reduction of the minimum cement content from 320 to 300 kg/m^3 also for exposure classes XF2, XF3, XF4 and XA2. The reduction of the cement content in the different exposure classes in order to minimise heat of hydration was regarded as uncritical with massive structural elements under durability aspects, but it contributes sizeably to reducing a rise in temperature.

The same scenario prompted the reduction of the minimum cement content from 270 to 240 kg/m^3 in exposure class XA1 when additions are allowed for. Finally, an increase in the maximum permissible w/c ratio from 0.45 to 0.50 for XS3 and XD3 and the associated change in the minimum compressive strength class was considered necessary in order to ensure adequate workability of mass concrete without having to add disproportionate quantities of concrete admixtures. The increase in the capillary pore portion in the hardened cement paste and the lower chloride penetration resistance resulting from it, which ensued from the change in the maximum permissible w/c ratio, had to be compensated for, however. This is to be achieved by restricting this regulation to concretes made from CEM II/B-V, CEM III/A, CEM III/B or combinations of cement and fly ash as a concrete addition. Provided that curing is adequate, these cements and cement/addition combinations are assumed to contribute to enhancing the resistance to chloride penetration.

Self-compacting concrete

The DAfStb guidelines on "Self-compacting concrete (SCC)" published in the spring of 2002 was adapted to the new standards. The revised version of the guidelines on "Self-compacting concrete" consists of three parts and was issued in November 2003. The guidelines comprise amendments and supplements to the new standards that relate to dimensioning and design, concrete and building execution.

The previous experiences gained in the approval procedures left their mark on the revision of the guidelines. Furthermore, additional detailed quality assurance measures were incorporated. These include the "window solution" for SCC developed by the Research Institute in particular. It allows manufacturers of self-compacting concrete to determine the workability characteristics of their SCC by investigating the fresh and hardened concrete, and to verify them in initial testing. The manufacturers guarantee the "self-compaction" feature and specify target values and permissible deviations for the slump flow measure and the funnel flow time. The limits of the range must be continually checked in regular production by factory production control as they may change as a result of fluctuations in constituents.

By inclusion into the Building Regulations List, the guidelines published in the spring of 2004 were adopted by the building supervisory authorities.

Concrete with recycled aggregates

The DAfStb guidelines "Concrete containing recycled aggregates" are now available with comments included in the version issued in December 2004.

The present Part 1 of the guidelines limits the share of recycled aggregates in the overall aggregate volume of the concrete. This share depends on the composition of the recycled aggregates, i.e. the type delivered. Part 1 of the guidelines regulates the use of aggregate types 1 and 2 according to DIN 4226-100. Type 1 covers gravel and sand from pure crushed concrete. The recycled aggregates of Type 2 may contain up to 30 wt.% non-porous bricks and sand lime bricks in addition to crushed concrete and natural aggregates. Depending on the area of application, the proportions > 2 mm permissible in the concrete are limited to a maximum of 45 vol.% for Type 1 and 35 vol.% for Type 2. Recycled aggregates < 2 mm must not be used. Dimensioning is carried out analogous to the design of normal weight concrete according to DIN 1045-1.

The further work of the DAfStb subcommittee "Concrete with recycled aggregates" is now focused on the second part of the guidelines, in which the share of recycled aggregates > 2 mm may total up to 100%. The use of recycled aggregates < 2 mm is to be excluded in this case as well. A new design concept will be elaborated for the changed concrete properties.

Water-impermeable concrete structures

The use of water-impermeable concrete was regulated by new DAfStb guidelines, which closed a gap in the regulations on the water-proofing of buildings according to DIN 18195 that often turned out to be a competitive disadvantage for concrete construction. The "Water-impermeable concrete structures" guidelines regulate requirements for the fitness for purpose of those structures for which no provisions existed before. They are applicable to structural concrete elements that are fully or partly embedded in the soil and for which concrete assumes both load-bearing and sealing functions. As expensive and time-consuming external sealing measures can be dispensed with, building with water-impermeable concrete is a very cost-effective mode of construction when the groundwater table is high.

Consultants have the task to determine the corresponding exposure and utilisation classes. The exposure classes distinguish between the various ways in which a structure or structural element is exposed to moisture or water. Exposure class 1 applies to structural elements in contact with pressing and non-pressing water. Capillary water and non-accumulating seepage water are subject to exposure class 2. The properties of the subsoil and the design water level must be taken into consideration for specification.

The term of "utilisation class" was newly introduced. Classes need to be specified in relation to the function of a structure and the service requirements to be met by a structure. Transport of moisture in liquid form is not permissible for structures or structural elements of utilisation class A, i.e. moist spots on the surface of structural elements caused by water passage must be ruled out. Limited water passage is allowed in utilisation class B. Consultants have the task to correctly implement the building owner's specifications for the planned use of the rooms and to point out to the building owner any measures regarding the atmospheric environment that may possibly be necessary. Explanatory notes supplementing the WU guidelines will presumably be published in early 2005.

Concrete structures in contact with water-polluting substances

The DAfStb guidelines "Concrete structures in contact with water-polluting substances" have been effective for building structures since 1996 in order to protect the soil and the groundwater from water-polluting substances. The experience gathered during the erection and operation of plants corroborate the assumptions made in the guidelines. The guidelines have proven their worth since they first appeared in September 1996.

The guidelines, which comprise six parts, were adapted to the new generation of standards in the period under review. The practical experience gathered over the years found its way into the revision of the guidelines. Parts 1, 3 and 6 of the 1996 issue of the guidelines were revised and integrated in Part 1 of the new guidelines. In addition to the impermeability verification it comprised previously, Part 1 now also includes a simplified selection procedure specified as construction method 6 in the TRwS 132 (Technical Rules on Water-Polluting Substances). The safety parameters for this method, which is on the safe side, can be chosen depending on the inspection interval.

Parts 2 and 4 of the 1996 issue of the guidelines were revised under the direction of the Research Institute. Part 2 of the guidelines in particular, which deals with construction materials and exposure to water-polluting substances, was not only adapted to the new generation of standards, but also revised in terms of concept. For instance, the rules relating to the use of liquid-proof concrete after penetration test (FDE concrete) were simplified. The concretes with water/cement ratios $w/c < 0.45$ and strength classes > C50/60 previously classified as FDE concretes were assigned to the range of liquid-proof concrete (FD concrete) without penetration test. By reducing testing liquids from 4 to 2, the effort involved in testing was diminished. The regulation on the expansion of design penetration depths in case of low moisture contents was simplified and adapted to the concept of the exposure classes according to DIN EN 206-1. For exposure class XC1, "dry", a 50% increase in the design values of the penetration depths has to be taken into account. The old Part 4 of the guidelines, which covers the test methods, was incorporated in an Annex A.

VI

Environmental compatibility of cement and concrete

The significant rise in the environmental awareness of the general public has conferred ever greater importance on the environmental compatibility of construction materials over the past years. Decisions in favour of certain building materials and types of construction are influenced not only by technical and economic aspects, but increasingly also by ecological aspects these days. The aim behind this is to erect a structure tailored to the needs of its user which incurs as little cost as possible and causes only a slight overall environmental impact from its erection via its utilisation and up to its dismantling. The environmental compatibility of the construction materials used constitutes a crucial prerequisite for this.

Cement and concrete have proved their excellent suitability for structural elements that get in contact with soil, groundwater and drinking water for decades. Extensive investigations substantiate that the quantities of trace elements or critical organic substances present are extremely small and correspond to the input via raw and process materials. Given the high binding capacity for trace elements of the hardened cement paste and the encapsulation into the solid and dense microstructure of the hardened cement paste, the release of such trace substances during use of the structures is very low and ranges frequently around the detection limit of modern, highly sensitive analytical methods.

Reliable and durable concrete structural elements and structures, such as sewage and waste water treatment plants, contribute to environmental preservation. Direct environmental benefits are derived from the use of secondary raw materials and fuels in clinker manufacture and the utilisation of appropriate residuals in cement production. Utilisation is on principle restricted to secondary materials that do not have an adverse effect on emissions, the homogeneity and construction properties of the cement, and its environmental compatibility.

The growing importance of environmental legislation for construction is also reflected in regulations and standards. In addition to national regulations, which for example lay down the hygienic and environmentally relevant specifications for cement-bound construction materials that get in contact with soil, groundwater and drinking water, corresponding European provisions are currently being elaborated. By cooperating in the corresponding bodies, the Research Institute pursues the aims of ensuring that existing favourable experiences with the environmental compatibility of cement-bound building materials are enshrined in the regulations, and of limiting the scope of testing to the actually necessary degree.

Wahnbach dam near Siegburg

Environmental criteria for cement-bound construction materials ■

The clinker burning process is characterised by the strong alkaline reaction of the kiln feed, high kiln feed temperatures, and intensive contact between the solids and the kiln gas, which reaches temperatures of up to 2000 °C. The rotary kilns of the cement industry thus afford excellent conditions for the reliable and environmentally harmless utilisation of a large variety of residuals.

Through its use of suitable residuals, the German cement industry makes a vital contribution to reducing environmental pollution. This helps save primary energy sources, ease the waste-disposal burden of industry and municipalities, and preserve natural raw material resources. Utilisation is on principle restricted to materials that do not have an adverse effect on emissions, the homogeneity and construction properties of the cement, and its environmental compatibility.

Secondary materials and fuels

In the year 2003, 38% of the primary fuels in clinker production were substituted for by secondary fuels in Germany. Reprocessed fractions of industrial and commercial waste, used tyres, waste oil, meat and bone meal as well as animal fat, and scrap wood are most important in this context. The recovery in clinker manufacture of the thermal content of residuals containing energy contributes to CO_2 abatement without any additional product-specific residues being generated. Given the very high temperatures prevailing in the rotary kiln firing unit, organic substances are almost completely converted to carbon dioxide and water. For that reason, the emission concentrations of dioxins and furans in particular are very low. This is true irrespective of the fuels utilised.

In addition to secondary fuels, suitable secondary by-products, such as industrial lime, used foundry sand, roasted pyrite, fly ash and residuals from the iron and steel industries, can be used as raw material constituents or corrective materials for the raw mix, respectively, in an environmentally compatible manner depending on the raw material situation of a cement works.

Trace element contents in the cement

Like all building materials made from natural raw materials, cement contains small quantities of trace elements that enter the production process via the raw materials and the fuels. Depending on their volatility and the process conditions, these are bound in the clinker to varying degrees. For that reason, the trace element content of secondary raw materials and fuels is an important criterion for evaluating their environmentally compatible utilisation. It has to be taken into consideration, however, that these secondary materials merely substitute for a corresponding proportion of primary feed materials which contain trace elements as well.

All investigations carried out to date substantiate that the utilisation of secondary materials common in the German cement industry today does not entail any sizeable change in the trace element contents in the product. Overall, the trace element contents of German cements range in the same order of magnitude as the contents in natural rock, soil and clay, regardless of whether or not secondary materials are used in cement manufacture.

Release of trace elements

Just like cement, also aggregates and concrete additions contain small quantities of trace elements. It is, however, not the content of trace elements contained in a building material that counts in assessing its environmental compatibility, but merely the proportion that can verge into the environmental media water, soil and air during production and use. The factor decisive for release is the proportion of trace elements dissolved in the pore water. Numerous investigations confirm that most trace elements, such as antimony, arsenic, lead, cadmium, vanadium, zinc, etc., are present in almost insoluble form in fresh mortar and concrete and are released in tiny quantities only. In contrast to the trace elements enumerated before, the alkali and chromium compounds contained in the cements can be more readily soluble in the pore water. For that reason, the quantities of these substances that can be released from mortar and concrete had to be determined. Intense research activities at the Institute for Construction Research (ibac) confirmed the Research Institute's investigations on the release of alkali and chromium compounds from fresh concrete. Accordingly, chromium is the only trace element investigated that may be released from fresh concrete on a scale of environmental relevance. The investigations further showed, however, that elevated chromium contents exclusively occur in the immediate contact zone and for a short time only. The fact that release is reduced appreciably by the dense, solid hardened cement paste matrix formed as hydration progresses is applicable to all substances. With chromium, this effect is intensified by the dissolved proportion being combined chemically in the chromate ettringite, thus verging into a virtually water-insoluble compound after a time lag.

All investigations boil down to the result that elevated element concentrations in the groundwater solely occur in the immediate vicinity of the structural element and only for brief periods of time when the concrete is placed in the saturated soil zone. Given the very low quantities, they do not durably or significantly affect the groundwater and are thus irrelevant under environmental protection aspects.

In order to gain more profound understanding of the release of trace elements from cement-bound building materials and derive criteria for assessing the environmental compatibility of mortar and concrete, a European consortium tackled the “Environmental Criteria For Cement Based Products” (ECRICEM) research project several years ago. The partners involved in this project are the Energy Research Centre for the Netherlands (ECN), Holcim Group Support Ltd., Ciments d’Obourg, Norcem A.S. and the German Cement Works Association. The main focus of research work was initially placed on characterising the leaching behaviour of cement-bound building materials, which had been made from worldwide purchased Portland cements with the highest possible trace element contents. Furthermore, two laboratory-made cements having an artificially increased trace element content were used. In this process, the leaching methods most frequently applied in Europe at present were employed. All investigations revealed that the release of trace elements from cement-bound building materials did not have any adverse effects on the environment under usual application conditions even when the trace element portion in the cement had been increased significantly by purposeful doping.

The first part of the ECRICEM project, which chiefly concentrated on trials using Portland cements, was completed at the end of 2001. In the period under review, cements with several main constituents were thoroughly investigated as part of phase two (ECRICEM II). The results of the leaching tests conducted confirmed the favourable environmental behaviour of cement-bound materials. They further showed that mortars made from cements with several main constituents generally have the same characteristics regarding trace element release as mortars made from Portland cements.

For example, **Fig. VI-6** illustrates the bandwidth of the zinc quantity leached from crushed mortar as a function of the pH value of the leaching medium. Mortars (particle size < 2 mm) made from more than 40 different cements (CEM I to CEM V) were used in these investigations. It becomes apparent from the Figure that a comparative relation of zinc leaching to the pH value exists in spite of the considerable bandwidth. It has to be taken into account in evaluating the zinc quantities released that these leaching tests were carried out using crushed mortar and covered a wide range of pH values. Under usual application conditions, the leaching behaviour of cement-bound building materials is determined by the natural alkalinity and the density of the hardened cement paste. Zinc release is therefore not environmentally relevant. The element chromium was found to be an exception with regard to general release characteristics. Mortars made from cements containing blastfurnace slag turned out to release only very small quantities of chromium which were even appreciably lower than the values of chromate-reduced Portland cements. The results suggest that the low release is attributable to the reducing constituents contained in blastfurnace slag.

In addition to the leaching tests, the modelling of chemical reactions in cement-bound building materials formed a key subject in the period under review. Understanding of these reactions, which determine the solubility of the corresponding substances in the pore water and thus diffusion-controlled leaching, too, forms the basis for describing the long-term behaviour of cement-bound materials in contact with drinking water, groundwater and soil. This modelling can further serve to better describe criteria for the environmentally compatible utilisation of secondary materials in the cement industry.

The work performed further covered potential release scenarios and modelling of the leaching and spreading of substances in soil and groundwater. Laboratory results can only be assessed appropriately on the basis of a given soil and groundwater quality at a certain distance from the structure, in combination with suitable standardised release scenarios. The results of the ECRICEM project will leave their mark on the scheduled European standardisation work.

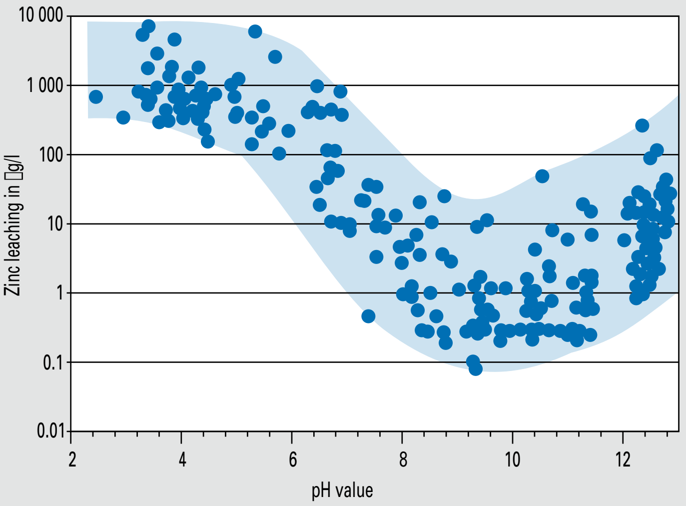


Fig. VI-1: Bandwidth of the zinc quantities leached from crushed mortar in relation to the pH value of the leaching medium

They can contribute to affording a scientifically secured basis for the discussions on enshrining the essential requirements for hygiene, health and the environment in the harmonised European product standards.

European Construction Products Directive ■

The European Construction Products Directive was adopted in the year 1989. It stipulates that the construction products traded in the European domestic market be such that the structures made from them comply with all major requirements, e.g. for stability, fire resistance, fitness for use, and durability. In addition to these requirements traditionally enshrined in building legislation, the European Construction Products Directive purposefully refers to the protection of hygiene, health and the environment.

Standards harmonised for the purposes of the European Construction Products Directive are required to comprise the provisions necessary to ensure the protection of the immediate vicinity of a structure. The elaboration of such provisions presupposes, however, that the corresponding building regulations in the EU member countries include qualitative and, if necessary, also quantitative specifications. An analysis of the specifications existing in the member countries revealed that quantitative specifications for construction products obviously exist in only two member countries – Germany and the Netherlands – at present. These pursue the goal of limiting the release of hazardous substances from construction products to the environmental media water, soil and air during the use of structures.

As a result of this low number of corresponding national regulations, the harmonised European product standards adopted to date, which include the European cement standard EN 197-1, exclusively comprise general references to existing national specifications so far. A concept for attestation of conformity and pertinent conformity attestation instruments, such as methods of testing and analysis, are to be worked out for the future compilation and revision of harmonised technical specifications now. To that end, the EU Commission drafted a mandate entitled “Development of horizontal standardized assessment methods for harmonized approaches relating to dangerous substances under the construction products directive”. The “Standing Committee on Construction (SCC)” agreed to the mandate at the end of 2004.

Conformity attestation concept

With the involvement of the interested parties, a multistage concept for attestation of conformity could be asserted with the EU. Acting as representatives of the European building materials industry, employees of the Research Institute took an active part in the corresponding consultations. The multistage concept is to ensure that conformity attestation is only required when it is actually necessary upon assessment of the potential hazards which the respective building material may cause to the environmental media water, soil and air. In detail, the three following options for conformity attestation have been provided for:

- Attestation of conformity without testing, so-called "WT products"
- Attestation of conformity without further testing, so-called "WFT products"
- Attestation of conformity with further testing, so-called "FT products".

To assess potential environmental hazards by building products, the release of hazardous substances to the interior air of structures (liberation of gases) and the release of hazardous substances to the soil and the groundwater (leaching) are examined. The liberation of hazardous substances in the form of gases should be irrelevant for purely inorganic cement-bound building materials.

Conformity attestation instruments

In order to be able to assign the construction products to the types of conformity attestation described above, the required instruments are to be harmonised throughout Europe by establishing corresponding European standards. Prior to their application, it must be ensured that practical experiences gathered from the application of the respective construction products are incorporated appropriately. This is particularly important when conformity attestation does not imply testing (WT product).

When tests are required to classify a construction product as WFT product, characterisation tests have been provided for. These tests serve to assess both the content and the release of hazardous substances. In the case of products to be tested to evaluate conformity, these are called initial and routine tests. To that purpose, standardised methods of testing which are largely horizontal, i.e. basically independent of the individual products, have to be worked out.

According to the ideas of the EU Commission, the decision on the attestation of conformity required for a construction product is to be made by the member states, which are represented by the "Standing Committee on Construction". This applies to the exemption from testing for WT products in particular. The EU Commission will set up the "Dangerous Substances" expert group to prepare these decisions. If possible, the expert group is to refer only to drafts that have been drawn up by the European standardisation and approval institutions CEN and EOTA, respectively, i.e. by the competent product committees. FIZ representatives are involved in the crucial product committees and will introduce their positions into the competent expert group via the Association of European Building Material Manufacturers (CEPMC).

Effects on cement-bound building materials

Cement-bound building materials have proved themselves in structural elements that get in contact with soil and groundwater for decades. Extensive laboratory investigations substantiate that trace elements or critical organic compounds are present only in trace amounts that correspond to the input via raw and process materials. Under the use conditions of the structures, the release of such trace substances is very low, often ranging around the analytical detection limit. This statement can be corroborated by extensive investigations that also covered cements made using secondary raw materials and fuels (see section on "Environmental criteria for cement-bound building materials").

From the cement industry's perspective, the present investigation results afford the basis for the use of cements according to EN 197-1 in the manufacture of construction products and structural elements in contact with soil and ground water without testing (WT product). More specifically, this classification will have to be argued in member countries where construction products have to meet requirements regarding the protection of the soil and the groundwater. This currently applies to the Netherlands and Germany.

DIBt Guideline „Assessment of the effects of construction products on soil and ground water"■

The corresponding approval tests for those construction products which require building inspectorate approval also have to take into account potential hazards to soil and ground water. The Guideline „Assessments of the effects of construction products on soil and ground water" issued by the German Institute for Building Technology (DIBt) summarises the corresponding scientific, technical and legal fundamental principles. This general evaluation concept, which is effective for all construction products in contact with soil and ground water, was published in the version of November 2000 and is currently being revised.

In order to take the material-specific properties of the different building materials into account in an appropriate manner, the general evaluation principles are specified for different construction products in Part II. To that end, the DIBt set up the task forces

- concrete and cement-bound building materials,
- soil injection agents and
- agents for sewer renovation.

During the period under review, the "Concrete and cement-bound building materials" task force completed the evaluation concept for "Concrete and concrete constituents". Although this evaluation concept has not been published yet, the DIBt is already applying it in approval testing.

The evaluation concept applies to cement, concrete additions, concrete admixtures and aggregates as well as to construction mortars and concretes which require general building inspectorate approval. The DIBt experts specify the tests to be carried out, making reference to the information on the construction product provided by the manufacturer. Different leaching methods are available to determine the release of substances.

For the rare cases of water-permeable concrete construction, the competent expert committee specifies the testing methods on a case-by-case basis. Water-impermeable construction above ground water level is generally regarded as uncritical, which is why leaching tests have been provided for in exceptional cases only. These have to be conducted in accordance with the trough method developed by the Research Association for Roads and Traffic (FGSV). Accordingly, the ingredients in the eluates are required to comply with the no effect levels laid down in the DIBt code of practice or the limit values of the drinking water ordinance or comparable values straight away.

Water-impermeable construction in the ground water is evaluated by referring to the contact ground water to assess the release from real structural elements. Model calculations serve to determine leaching from the building material by means of a diffusion model, and the dispersion of the substance in the soil / ground water by means of a geological flow and transport model. The combination of the two models allows to predict substance concentrations in the ground water in relation to time for defined framework conditions (**Fig. VI-2**).

The calculation of release by means of the diffusion model can be performed based on the results of long-term tank leaching tests.

A working group of the German Committee for Reinforced Concrete (DAfStb) prepared the standardisation of a corresponding test for hardened concrete in cooperation with the Research Institute. It includes leaching tests of concrete cubes (10 x 10 x 10 cm³) and the extraction of six eluates obtained after different testing times. The total test duration is 56 days.

The framework conditions for model calculation specified in Part II of the DIBT Guideline "Concrete and concrete constituents" are a structural element surface of 400 m², a permeability factor of the soil of 10^{-4} m/s, an effective porosity of 0.1, and a hydraulic gradient of 10^{-3}. The layer of the contact ground water (X_R) applied for small-scale averaging is 0 to 0.3 m thick. The period of time for which the average is determined is 6 months. A soil temperature of 10 °C is assumed. Retardation, chemical or biological decomposition must not be taken into account in the calculation. These tight framework conditions were set deliberately in order to ensure that a large variety of application areas are covered by conventional conformity attestation.

On the basis of these model parameters, the maximum permissible release quantities to be complied with during the 56-day tank leaching test can be calculated by means of the release model with reference to the respective no effect levels specified for the various substances. **Tab. VI-1** summarises the trace elements to be investigated in cement-bound building materials at present, and the permissible release quantities.

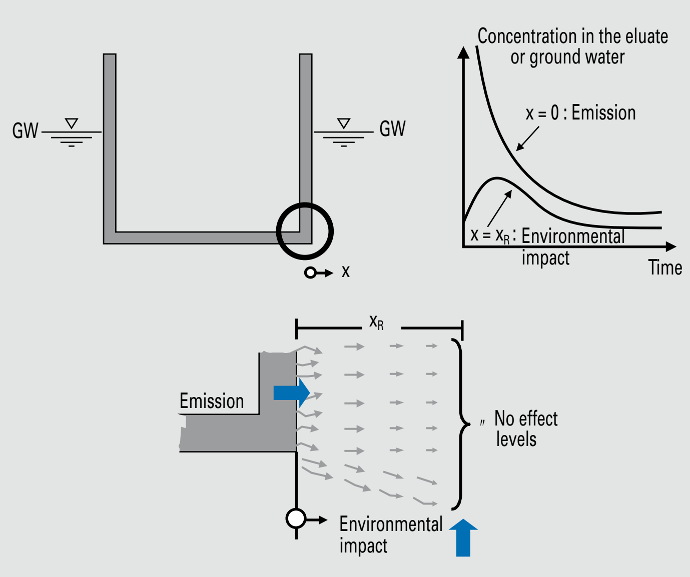


Fig.: VI-2: Scheme for evaluating the leaching from building materials using mathematical models

Tab. VI-1: Maximum permissible release from cement-bound building materials in the long-term tank leaching test after 56 days according to the DIBt Guideline Part II

Element	Maximum permissible release in the long-term tank leaching test after 56 days in mg/m²
Arsenic (As)	5
Lead (Pb)	12
Cadmium (Cd)	2,4
Chromium (total Cr)	24
Chromium (Cr(VI))	4
Cobalt (Co)	24
Copper (Cu)	24
Nickel (Ni)	24
Zinc (Zn)	150

A subcommittee of the Federal State Water Consortium (LAWA) has been concerned for quite some time with revising the existing no effect levels and deriving new values for further parameters. These include barium and vanadium, for example. The Conference of the Ministers for the Environment gave the go-ahead for publishing the revised and supplemented no effect levles at the end of 2004. DIBt can be assumed to incorporate the new values and parameters in the code of practice. Which of the new parameters will be relevant to the specific Part II "Concrete and concrete constituents" is still open to discussion. **Tab. VI-2** lists the new no effect levels laid down by LAWA opposite the DIBt values currently in effect. It becomes obvious from the Table that the values were lowered drastically in some cases. This applies to cadmium and zinc, for example. The new value for vanadium was set very low, too. Application of the no effect level for vanadium has been suspended until December 31, 2007, however, in order to enable industry to complete the incomplete data base on toxicity to humans and ecology and to furnish proof that a higher value is justified under scientific aspects.

The new no effect levels and parameters and the associated considerable reduction of the permissible rates of release are emphatically questioned by the parties in building practice concerned. Moreover, it appears to be unusual and astonishing that industry has to furnish the proof required for appropriate classification.

To gather more profound experiences with the DIBt evaluation concept for cement-bound building materials, the Research Institute produced 13 concretes in accordance with the concept and tested them in long-term tank leaching tests in the period under review. In order to get a bandwidth of trace elements in standard cements manufactured in Germany that is as large as possible, cements having the highest content possible of one or several trace elements were deliberately employed in concrete production. **Tab. VI-3** lists the maximum values of the 13 cements investigated opposite the average values of German standard cements (VDZ: Trace elements in German standard cements 2001).

Tab. VI-2: Comparison of the DIBt values currently in effect and the new LAWA no effect levels for inorganic parameters for evaluating locally restricted ground water pollution

Inorganic parameter	No effect level in µg/l	
	DIBt code of practice	LAWA value
Antimony (Sb)	10	5
Arsenic (As)	10	10
Barium (Ba)	-	340
Lead (Pb)	25	7
Boron (B)	-	740
Cadmium (Cd)	5	0.5
Chromium, total (Cr)	50	-
Chromate (Cr)	8	7
Cobalt (Co)	50	8
Copper (Cu)	50	14
Molybdenum (Mo)	50	35
Nickel (Ni)	50	14
Mercury (Hg)	1	0.2
Selenium (Se)	10	7
Thallium (Tl)	-	0.8
Vanadium (V)	-	4*
Zinc (Zn)	500	58
Tin (Sn)	40	-
Chloride (Cl$^-$)	-	250 000
Cyanide, total (CN$^-$)	50	50
Cyanide, easily releasable (CN$^-$)	10	5
Fluoride (F$^-$)	750	750
Sulphate (SO$_4^{2-}$)	-	240 000

*Application of the no effect level for vanadium has been suspended until December 31, 2007.

Tab. VI-3: Comparison of the maximum trace element contents in the cements used for concrete production and the mean values of German standard cements (VDZ: Trace elements in German standard cements 2001)

Element	Maximum value of the cements in mg/kg	Mean value of German cements in mg/kg
Antimony (Sb)	23.1	2.9
Arsenic (As)	37.5	7.0
Barium (Ba)	14 990	No information
Lead (Pb)	34.4	17
Cadmium (Cd)	1.0	0.4
Chromium (Cr)	118	41
Cobalt (Co)	13.1	8.7
Copper (Cu)	108	31
Manganese (Mn)	4 503	759
Molybdenum (Mo)	14.2	No information
Nickel (Ni)	44.3	23
Mercury (Hg)	0.08	0.06
Thallium (Tl)	1.8	0.4
Vanadium (V)	190	50
Zinc (Zn)	303	192
Tin (Sn)	5.4	3.6

The results of the long-term tank leaching tests show that the majority of eluate values for the various trace elements were below the determination limit of the highly sensitive detection methods applied. The tests did not yield measurable values for the elements arsenic, lead, cadmium, thallium and tin. All the elements investigated fell short of the DIBt values currently in effect (Tab. VI-1). With regard to the new no effect levels and parameters laid down by LAWA, the situation was slightly different. When the permissible rates of release in long-term tank leaching tests were calculated on the basis of the existing model and the framework conditions presently specified, the leaching of barium, chromate, nickel and vanadium turned out to exceed the limits in some cases.

The considerable lowering of the no effect levels is not acceptable to building practice. From the industry's point of view, LAWA did not furnish the required proof that precaution on such an extensive scale is necessary. With the exception of vanadium, however, LAWA is not willing to drop these values. They indicated, however, that the framework conditions applied in model calculation might possibly be adapted. For example, an increase from the current 0 to 0.3 m to a range from 0 to 1.0 m or 2.0 m (i.e. still the immediate vicinity of a structure) in the thickness of the layer (XR) for small-scale averaging would somewhat alleviate the impact of the tightened requirements. It is to be hoped that a solution satisfactory for both sides will be found in the scheduled discussions.

DVGW worksheet W 347

Due to the great importance of drinking water being supplied in perfect condition, all materials, which get into direct contact with the drinking water during its production or storage or during its transport from the producer to the consumer, are subject to strict hygiene specifications. Cement-bound materials haven proved themselves in all domains of drinking water supply for decades. The Worksheet W 347 "Hygiene requirements applying to cement-bound materials in the drinking water sector – testing and evaluation" (issue of October 1999) by the German Gas and Water Engineering Association (DVGW) is the first regulation ever established to take into account the specific properties of cement-bound materials in contact with drinking water in an appropriate manner. The Worksheet is currently being revised at the instigation of the DVGW. This measure was prompted by the introduction of the European standards for cement, aggregates, concrete admixtures etc. and the work of AHG 6 "Influence of cement-bound products on water intended for human consumption" of CEN/TC 164 "Drinking water supply".

In the current draft of the Worksheet, the pretreatment of the specimens and the composition of the testing water were adapted to the draft of the European test standard entitled "Influence of factory-made cement-bound products on organoleptic parameters". According to the research results available to date, however, this will have hardly any influence on the evaluation of cement-bound materials with regard to drinking water hygiene. Given the favourable experiences gained with the existing Worksheet, a number of tests were dispensed with in the new draft. For example, testing of TOC release is no longer required for structures located in drinking water protection zones, and testing of taste was cancelled from the organoleptic parameters.

An essential conceptual modification of Worksheet W 347 was prompted by the harmonised European cement standard EN 197. German drinking water hygiene specialists were not willing to accept the range of European cement types, which was extended considerably in comparison to the range included in DIN 1164, without additional specifications for the drinking water sector. They first stipulated to limit the total content of certain trace elements in the cement. The result achieved in intense discussions was that the trace element contents in the cement are not specified as absolute "limit values". Instead of that, the permissible contents listed in **Tab. VI-4** were laid down for some elements. If these values are complied with, no separate leaching tests are required. If these contents are exceeded, leaching tests must be carried out to verify that the maximum permissible release quantities of the corresponding elements, which are given in the Table as well, are observed. Lithium release only needs to be tested when lithium compounds are utilised as concrete admixtures.

Tab. VI-4: Total trace element contents in the cement the transgression of which requires a leaching test, and the corresponding permissible release quantities

Element	Total content in cement in wt.%	Release quantity in mg m^{-2} d^{-1}
Arsenic (As)	0.01	0.05
Lead (Pb)	0.05	0.1
Cadmium (Cd)	0.001	0.05
Chromium (Cr)	0.05	0.3
Nickel (Ni)	0.05	0.2
Lithium (Li)	No requirement	0.3

The cements manufactured in Germany meet the total contents and the permissible release quantities given in Tab. VI-4. The new issue of Worksheet W 347 is expected to be completed and adopted in the year 2005.

European Acceptance Scheme for construction products in contact with drinking water

Drinking water hygiene specialists authorised by the EU member states have been working on a "European Acceptance Scheme (EAS)" for construction products in contact with drinking water in the "Regulators Group for Construction Products in Contact with Drinking Water (RG-CPDW)" since 1999. The EAS is to apply to all construction products that get in contact with drinking water, such as plastics, metals, cement-bound materials, etc. Based on an EU mandate referring to the European Drinking Water Directive and the Construction Products Directive, attestation of conformity and the specific material requirements are to be harmonised. The European acceptance scheme to be worked out is to be based on the following principles:

- Preservation of the respective national consumer protection levels in place
- Guarantee of possible application for all common materials
- Compilation of a comprehensive acceptance system
- Guarantee of transparency and confidentiality

Regulators group "Cement"

While the work on plastics and metals in the drinking water sector was commenced in the immediate aftermath of the establishment of the regulators group, cement-bound materials were dealt with only marginally for a long time. At the end of 2003, a RG-CPDW subgroup "Cement" was set up, which is to work out proposals for positive lists, proven constituents and acceptance criteria. The subgroup is made up of regulators and experts, respectively, from Belgium, France, Germany, the Netherlands, Spain and the United Kingdom as well as a delegation of CEN/TC 104 "Concrete and associated products", which is in charge of concrete standardisation. The Federal Ministry for Health and Social Security appointed an employee of the Research Institute as the expert who is to represent Germany.

Discussion of the concept of an Approved Constituent List (ACL), i.e. a list that comprises the constituents that may be used in in-situ concrete with subsequent drinking water contact without testing, which was proposed by the CEN/TC 104, will represent a major aspect of the work to be performed. The ACL currently is a list of constituents, such as cements, concrete additions, concrete admixtures, etc., that have a tradition of use in the drinking water domain and are approved for that purpose in at least one member state. Furthermore, the starting materials for concrete admixtures have to be included in a positive list to be drawn up, which serves as an attestation of the substances' toxicological suitability for application in the drinking water sector. The data and information, respectively, which will be required for this initial list to be accepted for the purposes of the EAS in the future is not foreseeable yet. Moreover, the committee or expert group, respectively, that will have the say over the ACL has not been determined yet.

It is the objective of the ACL to reduce the scope of testing for products in contact with drinking water to the extent that is actually necessary. It is helpful for the classification of substances in the ACL when the requirements of the drinking water domain are already included in the pertinent product standards. Drinking water hygiene specialists take a very critical stance towards organic additives (in cement), for example. For that reason, a reduction in the maximum permissible input quantity of such substances from the current 0.5% to 0.2%, for example, is being discussed as part of the scheduled revision of the harmonised cement standard EN 197-1. If this value is exceeded, it has to be declared.

The Research Institute is intensely involved in the work regarding the drinking water sector, since the regulations laid down for this particularly sensitive domain might possibly become relevant for other areas of application for cement-bound materials as well. The ACL might, for example, serve as a model for establishing criteria governing the classification as a so-called WT product (attestation of conformity without testing) for the purposes of the Construction Products Directive.

Sustainable building

Sustainable building is defined as the erection of a structure tailored to the needs of its users which causes low overall costs and environmental impacts from its erection via its useful life, and up to its dismantling. The environmental compatibility of the building material, i.e. its completely harmless use in direct contact with water, soil and (interior) air, constitutes a fundamental prerequisite for this goal. In addition to that, the environmental impacts associated with the erection, such as the consumption of energy resources or air-borne emissions, are included in the integrated assessment of the structure, as is the cost of production. However, assessment invariably has to cover the costs accrued and environmental impacts caused throughout the service life. For that reason, the decisive contribution a building material makes to sustainability is inherent in its potential to be used in erecting a structure that simultaneously serves its purpose and saves costs as well as the environment.

Round table on sustainable building

The Federal Ministry for Transport, Building and Housing (BMVBW) set up a "Round table on sustainable building" in which the interested parties, i.e. building material manufacturers, the construction industry, architects and public-sector clients are represented. The objective of the round table is to find a consensus on the fundamental principles of sustainable building and their practical implementation. These are to be applied in building projects commissioned by the federal government in particular at first. In this way, the BMVBW continues the development of sustainable building, which was begun by the issuance of the guidance paper "Sustainable building" in March 2001.

The question about the distinctive features of sustainable building is a central topic of discussion at the round table. In the meantime, the round table specified indicators that are to be tested under practical conditions in construction projects commissioned by the federal government for a trial phase once some detail questions still open at present have been clarified. The list of indicators for example comprises parameters of life-cycle analysis. These include the greenhouse potential as well as construction costs and the costs incurred for use of the structure. Thermal comfort was proposed as an indicator for cosiness and may serve as an example for a parameter from the social dimension area. A consensus on an appropriate parameter for the description of some special facts, such as the utilisation of non-calorific raw materials, has not been reached yet. Furthermore, capturing special aspects by a characteristic value will prove difficult in some cases. This is true for cosiness, for example. Purely verbal description could be more appropriate in these cases. Moreover, the extent to which computer models may be applied in the integrated assessment of the sustainability of structures in the future will have to be examined. The decisive criterion for such software will be that it supports the consensus on the course of action reached at the round table, instead of the implementation being adapted to existing programmes.

The useful life of a structure has vital influence on its sustainability rating. In this context, the BMVBW has tried to replace the tabular summary of the service life of structural elements, which is considered too general on the whole, by a more differentiated approach. To that purpose, it must be possible to take into account the increases in durability achieved in the respective building tasks as a result of planning and execution. It will have to be checked whether this way of proceeding will do justice to the individual types of construction, such as concrete construction, for example.

The further activities of the BMVBW relate to the development of a guidance paper on sustainable construction for existing buildings, and to giving prominence to exemplary structures. VDZ attends this work in collaboration with the Federal German Cement Industry Association and the German Building Materials Association (BBS) through participation in the round table and its working groups.

Environmental labelling

Environmental declarations serve to document the environmental impacts ensuing from the manufacture of a product, thus creating the preconditions for the ecological assessment of its life cycle. In contrast to ordinary environmental labels, these environmental declarations do not comprise product evaluation. Much rather, they document the environmental impacts associated with the manufacture and – as far as known – with the use of a product.

Environmental impacts are determined by life cycle assessment; they are essentially based on the consumption of raw materials and energy as well as the emissions and the waste generated by production. In this context, the environmental impacts caused by the previous history, e.g. in the generation of the fuels required in the production process or of the electrical power consumed, are taken into consideration as well. In the field of construction, this information on construction products contributes to an integrated assessment of the life cycle of structures, provided that it is available for all major construction products. Proper evaluation, however, invariably has to include the environmental impact caused by the use of the structure, too, which is often significantly higher than that ensuing from the manufacture of the construction product.

Even the "Integrated assessment of building materials and structures (GaBi)" project, in which the cement industry was involved, already developed a building material profile that pre-empted the crucial elements of such a declaration (see Activity Report 1996 – 1999). The information contained in an environmental declaration for cement that is listed in **Tab. VI-5** largely corresponds to the data categories established in the GaBi project and has come to be generally regarded as a major constituent of a declaration in the European cement industry. The declaration can specifically refer to the cement manufactured at a certain plant. It may as well reflect the environmental impact for a generic cement, such as an assumed national or European average cement. In practical application, generic data will usually suffice as information for assessing a structure in order to incorporate the environmental impact associated with a construction product in the planning process.

The environmental declarations that the Consortium for Environmentally Compatible Construction Products (AUB) established for other construction products in Germany contain comparable information. If applicable, these environmental declarations additionally indicate the immediate environmental impacts on the media water, soil and, most particularly, interior air. Since these approaches are comparable, it may be possible to establish environmental declarations for cement which correspond to the declarations for other building materials issued in Germany, and which are largely understood and accepted in Europe at the same time.

Standardisation

The international standards organisation ISO has been working on a set of standards on sustainable building for several years already. The basic idea behind this broadly based set was to assess all structures throughout their life cycle. In this process, the construction products required for erection and the vicinity of a structure are taken into account (see **Fig. VI-3**). The potential parameters of sustainable building will be summarised in a draft standard that shows the ecological, economic and social aspects to be considered in general and illustrates them by parameters used as examples. The environmental evaluation of structures as part of sustainability assessment will be further specified in a separate draft standard, which will assess both parameters of life cycle assessment and indoors factors, such as noise, emissions to interior space, or light quality. Most progress has been made on the draft standard covering the environmental declaration of construction products, which goes beyond provisions regarding the content of the declaration. This draft standard for example also deals with aspects such as verification of the declaration, or the way of proceeding in deriving data inquiry rules specific to construction products. In many aspects, it follows standard ISO 14025, which is being revised at the same time and gives a general description also of the environmental declaration of products that do not belong to the construction sector. According to what is known, the building trade is thus the first sector in which the vision of sustainability has found explicit expression in standardisation projects.

Tab. VI-5: Data categories in a potential environmental declaration for cement

Raw material consumption	• Primary raw materials • Secondary raw materials
Water consumption	
Energy consumption (including electrical power)	• Primary energy sources • Secondary energy sources (each subdivided into renewable and nonrenewable sources of energy)
Potential environmental impact due to gaseous emissions	• Greenhouse potential • Acidification potential • Ozone depletion potential • Photo-oxidant potential (summer smog) • Nutrification potential
Waste for landfilling	• Non-hazardous waste • Hazardous waste

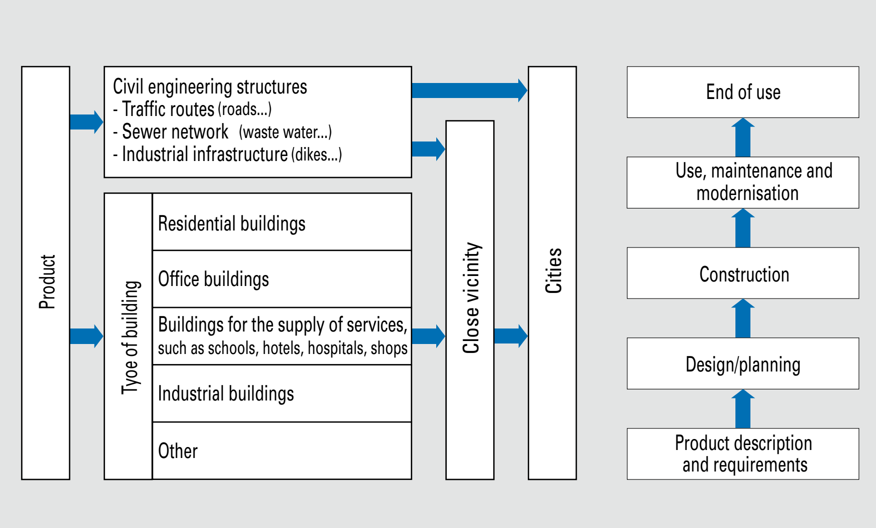


Fig. VI-3: Products (left-hand side) and processes (right-hand side) examined in sustainable building (pursuant to: draft standard ISO/CD 15392)

In spite of that, the approach pursued by the ISO does not go far enough in the European Commission's opinion. It fears that the diverging national trends regarding the construction product declarations in particular may result in trade barriers that cannot be countered adequately by ISO standardisation. As a consequence, CEN was given the mandate to develop more specific standards both for evaluating the environmental performance of structures and for the environmental declaration of construction products. This European set of standards is to comprise a standard on the life cycle assessment of construction products and a standard on summarising life cycle analysis data at structural level as well. As these standards will not be subject to the Construction Products Directive, they will remain voluntary. It is foreseeable all the same that these standards will have great influence on the environmental declaration of construction products in Europe.

Sustainable concrete construction

Implementation of sustainable building in practice presupposes the existence of specific aids for the individual types of construction. The German Committee for Reinforced Concrete (DAfStb) set itself the goal to compile a paper on the general principles of sustainable building with concrete in the medium run that is to close this gap. In order to achieve this aim, DAfStb prepared a research project the first phase of which is to be started in the year 2005, provided that the Federal Ministry for Education and Research grants sponsorship. Among other topics, the project is to examine the question of how sustainability evaluation can be adapted specifically to concrete construction. In addition to that, it will address central issues of building material technology, design and life cycle management. VDZ is involved in the planning of this project via the Research Institute. In case of the project being approved, it will contribute to the research activities by compiling a study on the potential of secondary material utilisation in concrete construction.

VII

Responsibility for employees

Promoting safety at work in the factories is one of VDZ's constitutional functions. The "Environment and process engineering" committee of VDZ is in charge of developing and introducing measures to improve safety at work, and is supported in its work principally by the VDZ "Safety at work" working group and the Research Institute. Accident statistics for German VDZ member plants have been recorded and statistically analysed since 1965. The Research Institute has run a safety at work competition on the basis of these figures every year since 1974, with awards for the plants with the best safety record. To improve industrial safety in the factories, the "Safety at work" working group discussed topical safety problems during factory visits and drew up corresponding safety codes of practice and checklists. In addition to that, the working group compiled a model document on explosion protection pursuant to the works safety ordinance for a coal grinding plant, and a code of practice on securing cargo consisting of bagged cement.

As part of the development programme for cement works employees, VDZ offers training courses and seminars. The 21st "lime/cement" industrial foremen's training course with 13 participants was successfully concluded in cooperation with the Düsseldorf Chamber of Industry and Commerce during the period under review. At the beginning of 2005, VDZ can thus look back on 47 years of successful training of industrial foremen. A total of 808 persons have been successfully trained on 29 courses during this period.

The development programme for production controllers has been continued in the proven fashion. Two courses with a total of 38 delegates were carried out during the period under review. Since 1998, VDZ's development programme has been expanded to include a series of one-day and extended seminars in addition to the courses for industrial foremen and production controllers and the safety at work seminars that were already running. These cover chemical analysis, ambient pollution control and environmental technology, the process technology of cement manufacture, the surveillance of cement quality, as well as the fundamentals of concrete technology and concrete processing. Nine and eight seminars, respectively, were held in the years 2003 and 2004. Eight more seminars are planned for 2005.

Cargo securing of bagged cement in accordance with regulations

Safety at work

Results of safety activities

Improving safety at work in the factories of the cement industry is one of VDZ's constitutional functions. Efforts at plant level and at the Research Institute are therefore a priority area for the association. VDZ's "Environment and process engineering" committee is in charge of developing and introducing measures to improve safety at work, and is effectively supported in its work principally by VDZ's "Safety at work" working group. The common goal of all this effort is to motivate employees at cement works to be safety conscious, to inform them regularly about ways of improving safety at work, and to encourage them to constantly review safety at the workplace.

The efforts of VDZ and its Research Institute have contributed notably to reducing the accident rate in German cement works to one third of the original figure over the past 30 years. As early as in 1984, the accident rate for all employees was at the very low level of about 20 accidents per 1 million working hours. The rate is in line with that of the chemical industry. In the year 2003, the average accident rate for the German cement industry was some 72% below the accident rate of all member companies of the Quarry Employers' Liability Insurance Association (StBG), and around 35% below the average accident rate for trade and industry as a whole. The comparison of accident figures for all member companies of the StBG was based on the number of full-time workers in the organisation; for example a full-time worker worked about 1578 hours per year in 2004.

The economic significance of safety at work is best illustrated by the percentage of lost time attributable to accidents at work. Whereas 30 years ago a mean relative lost time of approximately 0.81% was attributable to reportable accidents at work, this figure was down to 0.37% in 2003.

Tab. VII-1: Accident statistics for the workforce employed at the VDZ member works in the years 1969, 2003 and 2004

Year	1969	2003	2004
Number of works covered	98	51	50
Cement production in millions of tons	34.3	32.7	32.0
Plant headcount			
Number of employees	15 190	5 921	5 406
Hours worked	31 339 177	9 731 058	9 083 004
Production-related working hours in h/t	0.91	0.30	0.28
Reportable industrial accidents	1 376	127	138
Accident rate (accidents per 1 million hours worked)	43.90	13.05	15.19
Calendar days lost as a result of reportable industrial accidents	31 935	3 834	4 279
Working days lost per employee	2.10	0.65	0.79
Calendar days lost per industrial accident	23.20	30.19	31.01
"100-men-rate" (accidents per 100 employees)	9.10	2.14	2.55
Reportable transport accidents	180	24	20
Calendar days lost as a result of reportable transport accidents	5 822	711	599
Accident rate of the entire workforce	37.70	11.50	13.09

VDZ accident statistics

Figures for reportable industrial and transport accidents for German member plants have been recorded and statistically analysed by the Research Institute every year since 1965. The main results and key accident statistics for the years 2003 and 2004 are summarised in **Tab. VII-1**. For purposes of comparing and characterising the accident rate trend, the first column of the Table also shows the corresponding figures for the year 1969, the first year in which accident statistics were analysed in the cement industry. From 1993 onwards, the calculation is based on the whole workforce of the plant rather than on industrial workers, to take account of the changing personnel structure in the plants. Plant headcount declined by 15.5% in the year 2003, and by 8.7% in the year 2004 in a year-on-year comparison each. The drop in the number of working hours completed was slightly less pronounced; they fell by 12.0% in 2003 and by 6.7% in 2004. For that reason, the number of hours worked annually per employee increased from about 1578 in 2002 to 1643 in 2003 and to 1680 in 2004. It can be seen from the Table that output declined from 32.7 million t in 2003 to 32.0 million t in 2004 during the period under review. This results in production-related working hours of 0.30 h/t in the year 2003 and 0.28 h/t in the year 2004. The number of reportable industrial accidents rose from 127 in 2003 to 138 in 2004, which corresponds to an 8.7% climb. The average accident rate (number of reportable industrial accidents per 1 million hours worked) of 13.05 recorded for all plants in 2003 was gratifyingly close to the lowest level of 12.81, which was reached in 2001. In the year 2004, a slight increase to 15.19 was recorded. A 0.0 accident rate was achieved by eight clinker-producing plants both in 2003 and in 2004 (**Tab. VII-2**). The accident figures for the years 2003 and 2004 for industrial workers and all employees combined were 11.50 and 13.09, respectively.

The average number of calendar working days lost due to reportable accidents at work rose by around 2.7% from 30.19 in 2003 to 31.01 in 2004. The economic significance of accidents at work can also be assessed using the number of working days lost per year. This figure gives the number of calendar working days lost as a result of reportable industrial accidents related to the number of workers employed. The mean number of working days lost grew slightly from 0.65 in 2003 to 0.79 in 2004. At 2.14 in 2003 and 2.55 in 2004, the pattern of the "100 men rate" (the number of industrial accidents per 100 employees) remained at a low level. By contrast the "100 men rate" for the companies insured with the StBG was as high as 5.09 in 2003, corresponding to an accident frequency rate of 33.27. The number of reportable transport accidents during the period under review declined slightly from 24 in 2003 to 20 in 2004.

Promoting safety at work

Five safety codes of practice (Nos. 95 to 99) describing typical and especially significant industrial accidents and one safety code of practice dealing with securing cargo consisting of bagged cement were published in the last two years, as were six safety checklists (Nos. 75 to 79) for checking equipment and measures for improving safety at work in various areas.

For 28 years now awards have been granted to those clinker-producing member works with the lowest accident rates (Table VII-2 and **Fig. VII-1**). The award consists of a plaque and the VDZ safety symbol - a hexagon with the inscription "Safe working – VDZ". The plaque constitutes recognition of the efforts by plant management and workforce to ensure safety at work. The award is also intended to motivate employees and to raise safety awareness in the factories.

Since the hazard potential in clinker-producing works is quite different from that for employees in works without clinker production, there is a limit to how far a standard measure can be applied to assess safety standards at all works. In order to provide motivation to improve safety at work in grinding and blending plants, a special safety competition has been introduced for this group of plants from 1995. A special certificate is awarded to the grinding and blending plants with the lowest accident rates.

Tab. VII-2: Winners of the VDZ industrial safety competition for clinker-producing works in the years 2003 and 2004

	2003	2004
1st place	Dyckerhoff AG Mainz-Amöneburg works Accident rate 0.0	Dyckerhoff AG Geseke works Accident rate 0.0
	Dyckerhoff AG Göllheim works Accident rate 0.0	Dyckerhoff AG Lengerich works Accident rate 0.0
	Dyckerhoff AG Neubeckum works Accident rate 0.0	Dyckerhoff AG Neubeckum works Accident rate 0.0
	HeidelbergCement AG Burglengenfeld works Accident rate 0.0	HeidelbergCement AG Schelklingen works Accident rate 0.0
	HeidelbergCement Produktionsgesellschaft mbH & Co KG Wetzlar works Accident rate 0.0	HeidelbergCement AG Mainz-Weisenau works Accident rate 0.0
	Karsdorfer Zement GmbH Sötenich works Accident rate 0.0	Holcim (Deutschland) AG Höver works Accident rate 0.0
	Readymix Westzement GmbH Beckum Kollenbach works Accident rate 0.0	Lafarge Zement Karsdorf GmbH Sötenich works Accident rate 0.0
	Readymix Westzement GmbH Beckum Mersmann works Accident rate 0.0	Rüdersdorfer Zement GmbH Rüdersdorf works Accident rate 0.0
2nd place	Rüdersdorfer Zement GmbH Rüdersdorf works Accident rate 1.88	Lafarge Zement Karsdorf GmbH Karsdorf works Accident rate 3.48
3rd place	Dyckerhoff AG Lengerich works Accident rate 2.18	Schwenk Zement KG Allmendingen works Accident rate 5.22

Fig. VII-1: Presentation of the awards to the winners of the 2003 VDZ industrial safety competition

Safety seminars

The pattern of accident statistics for recent years clearly shows that the substantial efforts made at plant level with the support of the working group and the Research Institute have achieved a distinct improvement in safety at work. However, to improve safety at work still further there must be no slackening in the efforts made by all employees, and 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 works management – works managers, plant managers and especially foremen and chargehands. The industrial foreman is in constant contact with his team, and as a role model has the greatest influence on improving safety at work. In the light of this, the VDZ has offered intensive training courses for practising foremen and supervisors 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, and 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 the VDZ "Safety at work" working group and the StBG, last approximately two days and are organised and run off-site in groups of 15 to 20 participants by StBG seminar leaders. The seminars have been run since 1993 on a regular basis with 6 seminars per year. The speakers are qualified StBG staff. The course content is periodically reviewed, and is compiled and prepared principally by the VDZ "Safety at work" working group.

Model document on explosion protection

The works safety ordinance has been in force since 2002 and has to be implemented now. According to Article 6 of the works safety ordinance, employers have to ensure that a document on explosion protection is drawn up and kept up to date. In particular, this document has to indicate that

- explosion hazards have been identified and evaluated,
- appropriate precautions have been taken to guarantee explosion protection,
- the sectors have been subdivided into zones, and
- the minimum specifications are complied with in the sectors.

The following sectors in cement works may be exposed to potential explosions: gas regulator station, gas tanks, petrol tanks, pulverised coal silos, fuel silos, coal grinding plant, and parts of secondary fuel plants. With new plants, a document on explosion protection has to be compiled before the plant is commissioned. For existing plants, this document has to be drawn up by December 31, 2005. The Safety at work working group worked out a model document on explosion protection based on the example of a coal grinding plant that can be used to copy from. Depending on the frequency and duration of dangerous, potentially explosive atmospheres occurring, the sectors exposed to explosion hazard have to be subdivided into zones. The working group recommends having the division into zones reviewed by an expert. Furthermore, the document has to include a short description of the process engineering and the constructive conditions, information on explosion parameters of the materials utilised, and a list of the technical and organisational precaution measures.

Securing cargo consisting of bagged cement

Lacking or inadequate cargo securing is one of the most frequent causes of accidents in lorry transport, resulting in considerable injury to persons and damage to property. The police have increasingly controlled cargo securing, imposing fines and entries in the Central German Register for Traffic Offences in Flensburg on haulage contractors and chargers if the cargo is not secured adequately. Basically, all the persons involved in transport – i.e. haulage contractors, drivers and chargers – are responsible for cargo securing during cement dispatch. The haulage contractor has to provide a suitable vehicle and securing equipment. The driver is obliged to apply the lashing straps and contrivances correctly. The charger is responsible for stowing the cargo in accordance with traffic requirements. It is recommendable to try to solve this problem by means of close cooperation between the charger and the haulage contractor.

The Safety at work working group studied the questions relating to cargo securing and compiled a code of practice on this subject. Different securing measures are necessary depending on the type of vehicle. When vehicles with a dry bulk container are used, it is not necessary to tie down the pallets if form-fit cargo arrangement both in and opposite to the direction of traffic and to the sides is ensured. If form-fit loading to the sides is not possible, the cargo has to be secured by an antiskid pad or by tying down the pallets in these vehicles as well. However, the strength of the hydraulic platform wall has to be verified. With vehicles in which the cargo hold has no lateral boundaries (e.g. side curtain) or with vehicles in which the strength of the hydraulic platform has not been attested to be sufficient, a distinction has to be made between pallets not wrapped in foil, bags pasted together, and pallets wrapped in foil. In all these cases, the arrangement of the cargo in and opposite to the direction of traffic should be form-fit, and the height of the hydraulic platform must exceed cargo height. Pallets wrapped in foil or containing bags pasted up, respectively, have to be secured by one lashing strap having a prestressing force of 400 daN per row of pallets. Pallets not wrapped in foil have to be secured by 2 lashing straps of corresponding prestressing force per row of pallets. Wood ledges and edge protection should be lashed as well in order to prevent the straps from cutting into the bags. If form-fitness in forward direction cannot be ensured or the hydraulic platform strength of 4 500 daN and 7 500 daN required for HLVs and semitrailers, respectively, has not been attested, antiskid pads and diagonal lashing in and opposite to the direction of traffic have to be provided.

VDZ training and development ■

Training courses for industrial foremen

VDZ runs training courses and seminars as development programmes for employees in cement works. It has been conducting foremen's training courses in cooperation with the Dusseldorf 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 which VDZ has been running jointly with the Federal German Association of the Lime Industry since 1965 is unique in German-speaking countries. 534 delegates had successfully completed 21 "lime/cement" industrial foremen's training courses by March 2005 (**Fig. VII-2** and **Tab. VII-3**). In summary, VDZ can look back on 47 years of successful industrial foremen's training. A survey was conducted in early 2005 to establish the degree of interest by the works in a 22nd industrial training course for foremen, starting in autumn of 2005 and ending in March 2007. The training courses are residential, located at the training school in Dusseldorf-Hassels.

Production controllers' course

In response to an increased level of qualifications necessary for control room operators, VDZ decided in 1990 to organise production controllers' training courses. These development programmes are designed to provide control room operators with state of the art knowledge of process engineering and environmental technology in cement manufacturing and measurement, control and regulation 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 innovation, which will ensure reliable and effective operation of the cement plant. The programme includes a theoretical part offered by VDZ and a practical part that is carried out at the cement works. By 2004, a total of 11 training courses had been run, training 248 people as "cement" production controllers. The next training course is being held from April to September 2005 at the Dusseldorf-Hassels training school. The training course includes an introductory seminar and 240 hours of lessons that are spread over three residential periods.

Training notes

Training notes to be used in the development of industrial workers at the factories and in on-the-job-training of process mechanics have been compiled over the past years. After the first ten training notes had met with a very favourable response, another 21 training notes have been completed by now. They are available both in digital format on CD and in printed form as a paper and transparency set, and can be obtained via VDZ's Internet homepage.

Fig. VII-2: "Lime/cement" industrial foremen after completion of the final examination in March 2005

Tab. VII-3: Number of graduates from the industrial foremen's 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
Total			204	40	244
Grand total			658	150	808

The training documents referred to as "training notes", which are elaborated by VDZ's "Training notes" working group, each comprise two parts, one consisting of text, the other consisting of pictures and charts (transparencies). They are to serve qualified staff members (instructors) as a training aid. The topics these training notes deal with cover the entire process of cement manufacture, starting from raw material extraction and up to cement loading. The main focus is placed on those areas which relate to production processes at the works and are closely connected to the tasks performed by industrial workers. **Tab. VII-4** gives an overview of the subjects dealt with and lists the training notes already completed (CDs 1 to 3) as well as the training documents still being prepared. Examples of individual training notes can further be accessed via VDZ's intranet pages. The training notes currently being prepared will presumably be completed in the third quarter of 2005 (CD 4).

Table VII-4: List of training note contents by subjects

Subject of training notes		CD 1	CD 2	CD 3	CD 4*
1	Raw material extraction				
1.1	Detaching, loading, transportation	X			
1.2	Water raising systems				X
1.3	HLV wash mobiles		X		
2	Raw material processing				
2.1	Preliminary comminution				X
2.2	Mixing bed and feed materials			X	
2.3	Combined drying and grinding plants for raw materials	X			
2.4	Raw meal homogenisation plant				X
3	Clinker production				
3.1	Rotary kiln	X			
3.2	Firing units	X			
3.3	Preheater			X	
3.4	Calciner				X
3.5	Bypass				X
3.6	Clinker cooler			X	
3.7	Fuels	X			
3.8	Fire and explosion protection				X
4	Cement manufacture				
4.1	Cement grinding plant	X			
4.2	Tube mills			X	
4.3	Roller mills			X	
4.4	High-pressure grinding rolls			X	
4.5	Classifiers			X	
4.6	Cement cooling				X
4.7	Cement mixing system				X
4.8	Cement constituents, product range, cement application	X			
5	Bagging and dispatch				
5.1	Bagging machine		X		
5.2	Palletiser		X		
5.3	Cement storage		X		
5.4	Loading device		X		
6	General operating equipment				
6.1	Mechanical continuous conveyors	X			
6.2	Pneumatic conveyors			X	
6.3	Process measuring instruments			X	
6.4	Metering units		X		
6.5	Drive technology				X
6.6	Supply of pressurised air			X	
6.7	Supply of cooling water				X
6.8	Power supply, low voltage		X		
6.9	Power supply, high and medium voltage		X		
7	Environmental protection				
7.1	Laws and ordinances				X
7.2	Reduction in dust emissions	X			
7.3	Reduction in gas emissions				X
7.4	Noise protection		X		
7.5	Waste disposal				X
7.6	Sewage disposal				X
7.7	Re-cultivation, re-naturing		X		
7.8	Environment monitoring technology				X
8	Quality management / quality assurance				
8.1	Quality management / quality assurance	X			
8.2	Sampling devices			X	

* in preparation (scheduled completion CD 4: 3rd quarter of 2005)

Professional training seminars

VDZ offered a series of one-day and extended seminars for the first time in 1998 as part of its further education programme, in addition to the existing industrial foremen's and production controllers' training courses, as well as the safety at work seminars. This new series of seminars relates to chemical analysis, the protection from ambient pollution and environmental technology, process engineering in cement manufacture, the monitoring of cement quality, as well as the fundamental principles of concrete technology and concrete processing. 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. It was announced to the member works in the form of a brochure and also via the Internet.

According to the requirements of the 5th Federal Ambient Pollution Protection Regulation (5. BImSchV), pollution control representatives must attend advanced training courses at least every two years. Whereas basic training courses for pollution control representatives deal with all areas of environmental protection, advanced courses concentrate on selected key topics. VDZ has already delivered six such seminars especially tailored to the needs of the cement industry. The main emphasis was on current developments in German and European environmental legislation, emissions of organic compounds and trace elements, and reducing CO_2 emissions in the clinker burning process. These seminars, which are recognised as a further education programme for the purposes of the 5th BImSchV by the Ministry for the Environment and Nature Conservation, Agriculture and Consumer Protection of the federal state of North Rhine Westphalia, are offered every two years and deal with current topics.

The seminar "Introduction to Environmental Technology" is also held every two years, alternating with the advanced training seminar for pollution control representatives. The seminar, which was cancelled due to lack of demand in 2003, will be offered again in 2005. It introduces all aspects of environmental protection and environmental technology. Therefore, the topics discussed are environmental law, emission measurement techniques, reducing gas, dust and heavy metal emissions, as well as noise and vibrations, ecological recovery of waste and environmental protection as an integral element of production. The lectures are supplemented by practical exercises on emission and pollution measurement techniques. This seminar is recognised by the government as a basic training course for prospective pollution control representatives.

The four-day "Young plant engineers" seminar aims to give the widest possible overview of all areas of cement manufacture through to the use of cement in concrete. Accordingly, the seminar deals in depth with process engineering subjects, chemical/mineralogical questions, environmental law, environmentally compatible cement manufacture, environmental measuring technology, quality assurance and concrete engineering. The seminar, which was previously held every year, will be offered every two years from 2004. The next seminar is scheduled for 2006.

The modern methods of extraction technology, preparation technology and combustion technology, as well as their influences on the clinker and cement properties and emissions were discussed in the two-day seminar "Work of industrial foremen under practical conditions" held in 2004. Additionally, the contents of this seminar included important and new aspects from the fields of health and safety legislation, industrial and social law, employee management, as well as the fundamental principles for cost-conscious behaviour.

The seminar "From practical application – for practical application", which was offered for the first time in 2005, is to extend the range of practice-oriented development programmes. The seminar is primarily tailored to practising industrial foremen and production controllers. Participants acquire profound knowledge of the latest trends in process engineering and cement manufacture. Proceeding from this basis, the delegates are taught how to use the training notes in staging training courses geared to operational practice for industrial workers.

Four seminars on the subject of "Cement quality monitoring" are held every year. The target group of these seminars are laboratory managers and senior laboratory staff at the works. In the one-day seminar "X-ray fluorescence (XFA)", in-depth knowledge on XF analysis techniques is conveyed to the participants. The two-day seminar "Technical mineralogy" gives a presentation of how the chemical and mineralogical properties of cement raw materials, clinker, cement and concrete are determined using microscopy and X-ray diffractometry investigation methods, and of how the results are to be evaluated. Apart from explanations of the fundamental technical principles of the analysis systems, the main emphasis is on carrying out practical exercises. The two-day seminar "Testing according to DIN EN 196" introduces the physical and chemical tests of cement and cement-type binders as well as raw materials and constituents, respectively, that are specified in the standard. Particular importance is attached to compliance with the work processes stipulated in the standard and the detection and avoidance of sources or error. The main focus of a further one-day seminar is the determination of the blastfurnace slag content in cements by a combination of microscopic and chemical methods. This seminar will be complemented by a new one-day seminar entitled "Determination of the blastfurnace slag content – overview of methods" in 2005. Delegates will gain an insight into the methods that can be applied to determine the blastfurnace slag content in cement.

In the field of "Cement application", the two-day seminars on "Fundamental principles of concrete engineering" and "Durability of reinforced concrete elements" were held alternately every two years. Starting from 2004, the two seminars were combined to one two-day seminar, which will be offered every year now. In the first part of the seminar, the fundamental principles of concrete technology and concrete engineering are outlined to the delegates. The effects of the new standards DIN 1045 and DIN EN 206-1 are given particular attention. Practical presentations in the concrete laboratory serve to illustrate the theoretical explanations. In addition to that, questions arising in practical application, such as the processing of concrete both on the site and in the concrete plants, transport, conveyance, spreading and compaction of concrete, are addressed. The topic of the second part of the seminar is the durability of concrete and reinforced concrete elements. One of the aims of this part is to assess deformation, transport and damage mechanisms under consideration of exposure and resistance. Proceeding from the explanations given regarding elastic and plastic deformation of concrete, load-free deformation of the concrete caused by shrinkage and heat of hydration development is discussed, as are the possibilities for reducing the crack formation in structural elements. As part of the topic of "concrete corrosion", the resistance to freeze-thaw with de-icing salt, the resistance to acid and sulphate attack, as well as to harmful alkali-silica reaction are discussed. The concept of exposure classes (e.g. freeze-thaw XF1 to XF4) specified in the new sets of 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 a total of 9 seminars in 2003 and 8 seminars in 2004. 8 more seminars are planned for 2005.

Publications

Schriftenreihe der Zementindustrie (Publication series of the cement industry)

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Rickert, Jörg	*Zum Einfluss von Langzeitverzögerern auf der Basis von Phosphonsäure auf die Hydratation einzelner Klinkerphasen, Portlandzementklinker und Portlandzemente* Düsseldorf: Verl. Bau+Technik, 2004. - (Schriftenreihe der Zementindustrie; 65); ISBN 3-7640-0466-5

Merkblätter (Codes of practice)

Ausschuss Unwelt und Verfahrenstechnik (Environment and plant technology committee)

Arbeitskreis „Betriebsverhalten von Vorcalcinieranlagen“ (Working group „Operational performance of precalciners“)
Arbeitskreis „SO_2-Minderung / Stoffkreisläufe“ (Working group „SO_2 reduction/recirculating systems“)

Sicherheits-Merkblätter (Safety codes of practice)

No. 94	Augenverletzung bei Reinigungsarbeiten im Wärmetauscher
No. 95	Arbeitsunfall im Bereich der Packerei
No. 96	Beinaheunfall bei Feuerfest-Reparaturen im Wärmetauscher
No. 97	Sturzunfall von einer Treppe
No. 98	Unfall an einer Schlagschere
No. 99	Tödlicher Unfall bei Becherwerksreparatur

Sicherheits-Prüflisten (Safety checklists)

No. 74	Augenschutz
No. 75	Verkehrswege
No. 76	Feuerfest-Reparaturen im Wärmetauscher
No. 77	Treppen
No. 78	Schlagscheren
No. 79	Arbeiten an Becherwerken

VDZ-Mitteilungen (VDZ Newsletter)

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Process Technology of Cement Manufacturing: VDZ Congress 2002
Verein Deutscher Zementwerke (VDZ) (Hrsg.). - Düsseldorf: Verl. Bau+Technik, 2003; ISBN 3-7640-450-0

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vdz.
Deutsche Zementindustrie

Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie
Postfach 30 10 63
D-40410 Düsseldorf
Tannenstraße 2
D-40476 Düsseldorf