european cement research academy

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NEWSLETTER

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- Production of Blended Cements and their Performance in Concrete
  13–14 October 2009
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Chances and limits of cements with low clinker content

Performance of concrete with cements containing limestone, blastfurnace slag and fly ash

As an industry which uses a high volume of energy and raw materials, the cement industry is affected by the global issue of climate protection as well as the availability of suitable constituents. Against this background, the question arises as to the performance of cement types which have, in the past, only been produced and used in small quantities and/or are today not yet included in the European cement standard EN 197-1. The evaluation of such cements with well known and tried constituents but new compositions is in fact one of the current topics being discussed on a European level.

The aim of a recent research project was to extend the data basis for the application of such cements with new compositions by reviewing the performance characteristics of corresponding concretes. The results obtained within the scope of the project can certainly not be generalised. They can, however, be used as a basis for further development work, and complement the current research regarding ternary cements being undertaken by the Belgian Center for Scientifical and Technical Researches for the Cement Industry (CRIC-OCCN).

Manufacture and optimisation

The focus of the research project was the laboratory and factory manufacture of test cements with compositions within and outside the scope of EN 197-1. Thus cements with up to 35 mass % of other main constituents besides clinker (e. g. limestone) as well as cements with limestone contents between 10 and 20 mass % in combination with 20 to 40 mass % blastfurnace slag and with 20 and 30 mass % siliceous fly ash respectively were used for the investigations of mortars and concretes. The main cement constituents were varied in their proportions as well as in their origin (according to availability). Limestone from various regions, for example, was used as well as blastfurnace slag and fly ash of different chemico-mineralogical composition. The type and proportion of the sulphate agents and the granulometric parameters of the main cement constituents were specifically varied in the manufacture in order to achieve a setting behaviour conforming to standards and an adequate strength development of the cements.

Work programme

The focus of the work programme was placed on the durability investigations of the concretes made from these cements. Furthermore, test specimens of selected concretes were stored in an outdoor exposure site under practical conditions to determine their freeze-thaw resistance with and without de-icing salts over a longer test period. On the basis of the research results regarding the durability, so-called probabilistic calculations of service life were carried out. Finally, calculations on the basis of Life Cycle Assessments showed the consequences of the use of the cements manufactured within the framework of the project for energy saving and reduction in CO_2 emissions.

Results

Figures 1 and 2 show selected results of the resistance to freeze-thaw and chloride penetration of concretes which were made from a Portland-limestone cement with 30 mass % limestone (LL) as well as from two Portland-composite cements with 25 mass % limestone (LL) in combination with 10 mass % blastfurnace slag (S) and fly ash (V) respectively. Moreover, results are shown which were achieved by using cements containing 10 mass % limestone (LL) in combination with 40 mass % blastfurnace slag (S) as well as 20 mass % limestone (LL) in combination with 20 mass % blastfurnace slag and fly ash (V) respectively.

The CDF test was used to test the freeze-thaw resistance of the concretes with de-icing salts. The scaling of the air-entrained concretes tested here was between 0.35 and 1.25 kg/m² after 28 freeze-thaw cycles. The concretes met the assessment criterion of

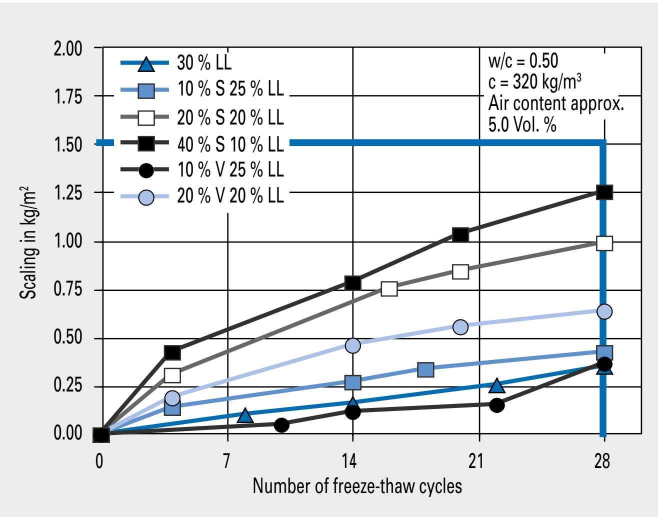


Fig. 1: Scaling of air-entrained concretes in the CDF test with different test cements in relation to the number of freeze-thaw cycles.

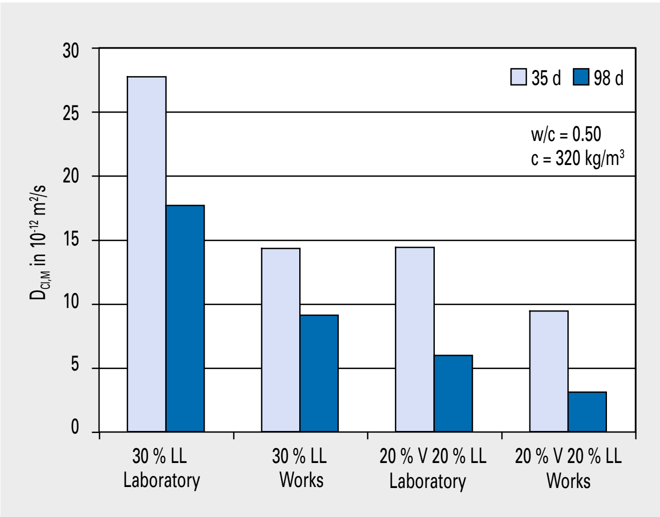
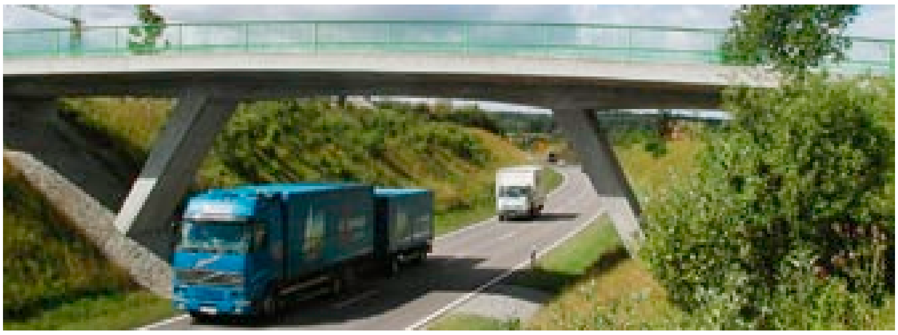


Fig. 2: Chloride migration coefficients of concretes containing laboratory and works test cements at a test age of 35 and 98 days.

1.5 kg/m² after 28 freeze-thaw cycles, which is one criterion applied for this method.

Laboratory-made and factory-made cements

Some of the cements initially produced in the laboratory were also produced in factories. A requirement for the cement production in factories was to adapt the manufacturing process to suit constituents that were available locally. The factory-made optimisation of the sulphate agents in combination with the respective grinding technology used showed a corresponding effect, also with regard to the properties relevant for durability. Thus, for example, the concretes produced from factory-made cements exhibited a higher resistance to chloride penetration than the concretes produced from laboratory-made cements, both at a test age of 35 days and 98 days. The results were in the same range as concretes made with Portland cements and blastfurnace cements respectively. Similar results were achieved with regard to the resistance to carbonation. Carbonation depths of the concrete with use of the cements shown in **Fig. 1** were in the range of the results for Portland cement and blastfurnace cements CEM III/A. The investigations form the basis for further development work. Some of the cements outside the scope of EN 197-1 turned out to be technically suitable in principle. The results cannot be generalised.



An example of the successful use of CEM II/A-LL 32,5 R: The Merklingen Bridge (Germany), built in 1998.

Determination of biogenic CO_2 emissions from cement kilns

Measurements at the stack as an option for future applications

The proportion of biogenic carbon is an important parameter in the characterisation of alternative fuels. The carbon contained in plants or living organisms is referred to as "biogenic". Under the terms of emissions trading, an emission factor of zero is applied to CO_2 derived from biogenic carbon. Biomass fuels are thus considered CO_2 neutral. These biomass fuels include for example scrap wood, sewage sludge or meat and bone meal. Depending on their origin and composition, paper residuals, textiles or processed commercial and industrial waste may also contain considerable portions of biogenic carbon.

In May 2009 CEN/TC343 published the new draft standard prEN 15440: 2009. This draft specifies the following three normative methods for the determination of the biomass content in alternative fuels:
– manual sorting method
– selective dissolution
– ^{14}C-method.
The manual sorting method is based on the separation of different fractions by visual aspects. For the application in cement plants in particular, this method plays only a minor role, if any.

Selective dissolution is based on the reaction of biomass material with the mixture of sulphuric acid and hydrogen peroxide. The method as such offers the advantage that it can be applied by skilled chemical laboratories without any further specific equipment. But it has to be pointed out that the different analytical steps must be carried out thoroughly. Furthermore, the selective dissolution method fails when the sample contains non biomass constituents such as charcoal or lignite. Moreover, some biomass constituents do not dissolve. From this point of view, the selective dissolution method cannot be applied to every sample. Nevertheless, due to a lack of suitable alternatives, it is currently widespread in the characterisation of alternative fuels for the cement industry. If the method is applied properly it can deliver reliable results.

Based upon these experiences it is incomprehensible why the current draft standard prEN 15440 wants to prescribe the ^{14}C-method as mandatory if the measurements are carried out for CO_2 trading matters. The selective dissolution method has its weak points. But it if is carried out according to the standard, taking the well known restrictions into consideration, the results should be applicable for CO_2 trading matters also. The European cement industry is preparing an objection against these unreasonable constraints in the current draft standard.

The ^{14}C-method is based on the well established analytical procedures that are used for the determination of the range of carbon-containing objects. Contrary to selective dissolution, this method is suitable for samples of all types and fuels. But it has to be noted that the ^{14}C-analysis as such can only be carried out by a few laboratories so far. Moreover, the analytical costs are much more expensive for the ^{14}C-method than for selective dissolution. This is the reason why the ^{14}C-method has predominantly only been applied for those samples where selective dissolution fails (e. g. used tyres).

So far, all the above mentioned procedures only apply to (solid) fuels. This means that the representativeness of the actual sampling plays an important role in the quality of the results.

Output control

- Measurement at stack
- Impingers filled with liquid absorbent
- Parallel measurement of stack gas parameters (CO_2-concentration, O_2-concentration, temperature, humidity, gas velocity distribution etc.)

Fig. 1: Experimental setup at the stack

^{14}C-method at stacks

One way out of this dilemma could be the application of the ^{14}C-method to a sample which has been gained directly from a CO_2-sampling at the stack. The periodic sampling procedure as such is not a real challenge as the standardised procedures known from emissions monitoring can be applied.

ECRA has been working on this project over the last years. During this period, two huge comparative measurement campaigns have been carried out. During these campaigns CO_2 samples from the stack have been analysed. Simultaneously, all intake materials have been analysed as well. **Fig. 1** shows the experimental setup at the stack. **Fig. 2** shows the results from the analysis of the stack gases. These results agree pretty well with the figures gained from the analysis of the intake material. The overall biogenic content in the fuel was about 20 %.

Further ECRA research is now targeted at finding a method that allows a sampling at the stack over a longer period, e.g. one week, one month, etc. By doing so, more reliable and more representative results could be gained. Simultaneously, the method should be combined with an automated sampling at the stack. This could reduce effort and costs significantly in comparison to the periodic sampling of the intake materials. The current research activities are therefore focused on the testing of different optional absorption liquids with a high retention capacity for CO_2. At the same time, different techniques for automated sampling have to be considered.

A crucial point: analytical accuracy

Additionally, it should be pointed out that the results which have been gained until now from different laboratories applying the ^{14}C-method have shown significant differences in their accuracy. So far, the ^{14}C-method as such has not been validated sufficiently even for its application on solid fuels. Therefore, another major focal point will be the validation of the ^{14}C-method and the reliable determination of the respective uncertainty levels. This is an inevitable prerequisite for the further application of this specific method on samples which have been gained by measurements at the stack.

Currently, the ^{14}C-determination can be carried out in principle by the following methods:
- proportional scintillation counter method (PSM)
- beta ionization (BI)
- accelerator mass spectrometry (AMS).

In principle, the above mentioned constraints apply to all the three methods.

ECRA has been in touch with different laboratories in order to further determine and assess the relevant parameters. After a reliable validation process, the method as such should be applicable to exhaust gases from all combustion processes such as waste incinerators or power plants.

Fig. 2: Results from stack measurements

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