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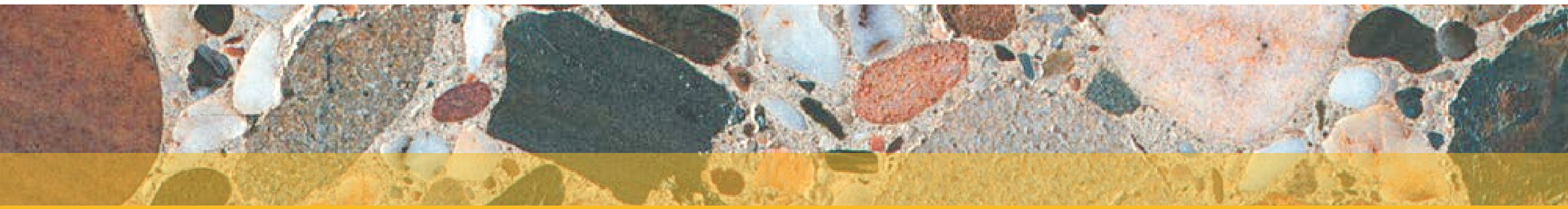
european cement research academy



3 / 2014

NEWSLETTER

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The use of natural calcined clays as a main constituent in cement

Correlations between types of clay and their suitability as a cement constituent

The use of pozzolanic and/or latent hydraulic cement constituents instead of Portland cement clinker represents a key leverage factor for the environmentally important reduction of CO_2 emissions within the cement industry. In view of the predicted significant increase in demand for cement and the necessity of further reducing the clinker factor, calcined clays are becoming more important for the cement industry as a pozzolanic main constituent in cement.

The use of calcined clays as a main constituent in cement in accordance with EN 197-1 is possible if the content of reactive silicon dioxide is at least 25 mass %. Although suitable raw material resources exist in Europe and some cement manufacturers have access to these, calcined clays have rarely been used in cement manufacture up to now, mainly due to a lack of research work in this field. In particular, the influence of the chemical and mineralogical composition of the clays on their suitability as a main constituent in cement has not yet been sufficiently investigated.

Calcination of clays

15 different mined clays from clay deposits, which could be assigned to the four groups “kaolinitic clays”, “bentonitic clays”, “kaolinitic-illitic clays” and “chloritic clays” were investigated concerning their suitability as a cement main constituent.

The determination of the optimum burning conditions is an important step to generate a sufficient pozzolanic reactivity of the clays. Therefore, between 2 and 9 calcination steps were carried out per clay, varying in burning temperature (500 – 1300 °C) and duration (5 or 30 minutes). After fixing suitable burning conditions for each clay, larger amounts of calcined clays were produced accordingly. **Fig. 1** shows exemplarily the X-ray diffractograms of the calcined samples of a kaolinitic-illitic clay in comparison to the starting sample. It is recognisable that after calcination at 1000 °C all clay minerals (illite/muscovite, kaolinite and montmorillonite) were converted to amorphous reactive phases. New, less reactive high temperature phases were sillimanite and/or mullite, and hematite from as low as 900 °C.

Fig. 2 shows the link between the content of reactive silicon dioxide according to EN 197-1 and the insoluble residue in KOH/HCl according to EN 196-2 for all calcined clay samples. Regardless of the relevant burning conditions, the EN 197-1 requirement of having at least 25 mass % of reactive silicon dioxide was met whenever the clay had insoluble residue of under 50 mass %. The insoluble residue in KOH/HCl is therefore a significant parameter for estimating the quality of clay calcination. Due to selecting suitable burning conditions the requirement of the standard regarding the content of reactive silicon dioxide could be met in each of the 15 clays investigated.

Investigation of clay-containing cements

CEM II/A-Q with 20 mass % and CEM IV/B (Q) with 40 mass % of the respective clay components were produced by intensively mixing the calcined clays with a CEM I 42,5 R. Additionally, cements with an industrial metakaolin as reference were manufactured the same way.

The water demand closely following EN 196-3 of the CEM II/A-Q was between 28.0 and 34.5 mass %; the water demand of the CEM IV/B (Q) was between 28.5 and 38.5 mass %. As expected, the water demand increased as the proportion of clay in the cement increased.

The compressive strength tests on the CEM II/A-Q were carried out with a water/cement ratio of 0.5, and on the CEM IV/B (Q) with a water/cement ratio of 0.6 for process-related reasons. The strengths of the CEM II/A-Q were between approx. 21 and approx. 29 MPa at the age of 2 days and between approx. 48 and approx. 66 MPa at the age of 28 days. The strengths of the CEM IV/B (Q) were between approx. 9 and approx. 13 MPa at the age of 2 days and between approx. 24 and approx. 49 MPa at the age of 28 days. The highest levels of compressive strength were reached with the kaolinitic clays.

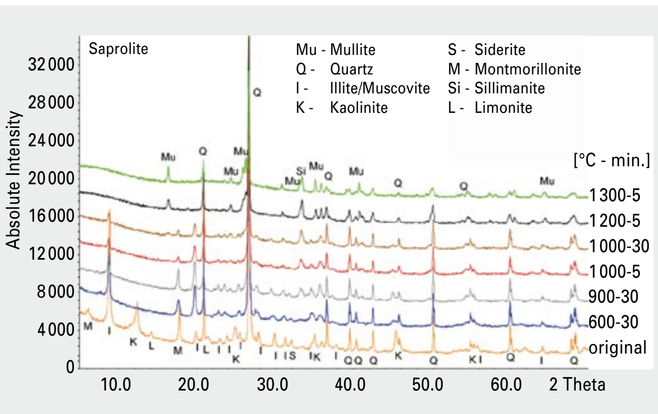

Figure 1: X-Ray diffraction pattern of an kaolinitic-illitic clay, burning parameters see on the right

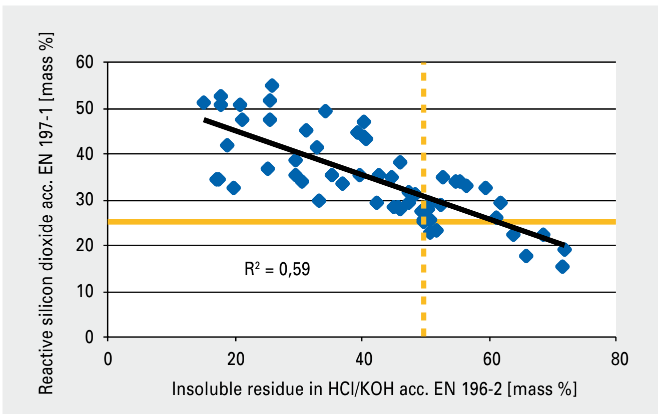

Figure 2: Reactive silicon dioxide acc. EN 197-1 of the calcined clays depending on their insoluble residue in HCl/KOH acc. EN 196-2

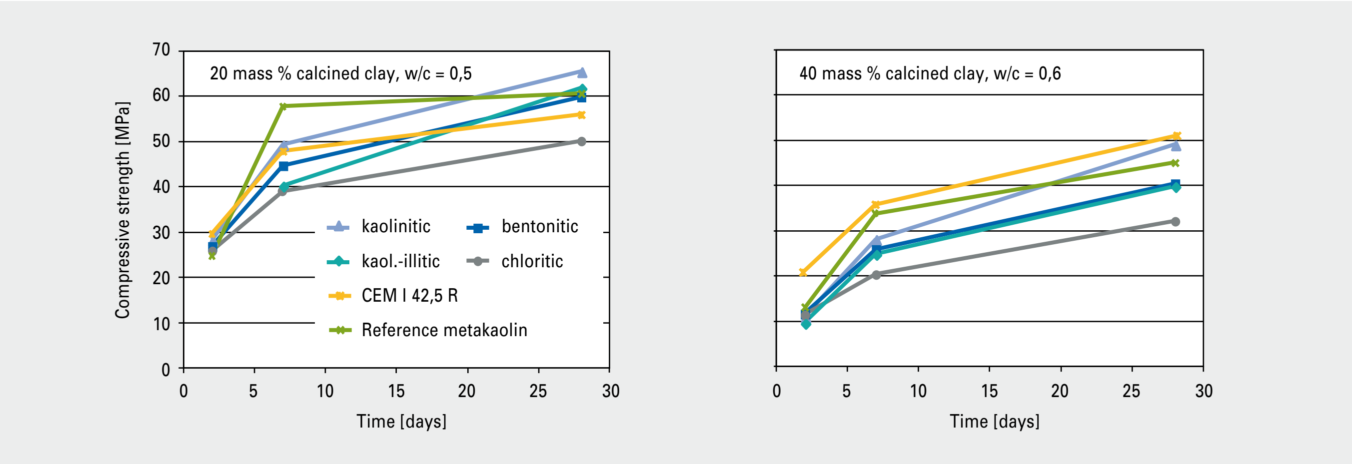

Figure 3: Compressive strength of CEM II/A-Q (left, w/c = 0,5) and CEM IV/B (Q) (right, w/c = 0,6) compared to the respective cements with metakaolin and to the CEM I as references

Fig. 3 shows the compressive strengths of the clay-containing cements that reached the highest levels of compressive strength at an age of 28 days in each of the four different clay groups. It is evident that the cements with the kaolinitic clay each displayed the highest levels of compressive strength. The levels of strength at the age of 2 days were affected by the dilution of the clinker by the calcined clay in both types of cement, and were therefore relatively close together. Overall, the cements with the chloritic clay showed the lowest compressive strengths. Of the tested CEM II/A-Q, only the latter cement did not achieve the level of compressive strength of the metakaolin-containing reference cement after 28 days of hydration, and also remained clearly below the level of strength of the CEM I 42,5 R reference. However, it was possible to produce CEM II/A-Q in strength class 42,5 R with all clays investigated, without either granulometric optimisation or additional sulphate adjustment. The influence of clay mineralogy on the contribution to the strength of the cement provided by the calcined clays was confirmed, with the ranking kaolinite, montmorillonite, muscovite/illite.

Aspects regarding the optimisation of strength development and the durability of cements with calcined clays are currently being investigated in several research institutes.

Training and development as a factor for sustainable success

ECRA's seminars, workshops and trainings: an excellent combination of theory and practice

The processes involved in modern cement works are complex and highly automated. Technical innovation, the use of alternative fuels, cutting-edge environmental technologies and growing productivity have, in recent years, greatly increased requirements in terms of qualifications and flexibility for employees in the cement industry, whose work is being influenced more and more by technical progress. Without such advances it would be virtually impossible to run the high-tech plants found in this sector. The training and development of highly qualified staff and the continual improvement of employee skills are therefore key factors for success for many companies in industrialised countries and emerging economies.

For emerging economies and growth markets the greatest challenges are undoubtedly the enormous increase in production, improvements in manufacturing processes and energy efficiency, and the switch to cutting-edge technology. Training programmes must be implemented to educate unskilled or semi-skilled workforces in order to operate production systems safely and efficiently. Engineers, control room operators and foremen need further training at an advanced level to handle challenges like energy efficiency, alternative fuels, environmental technology and leadership. The consolidation of specialist knowledge and the communication of experience can also speed up integration in a company and boost levels of productivity and versatility. In Germany, for example, targeted training and development programmes have decreased the proportion of unskilled and semi-skilled workers to less than 10 %, a trend which is set to continue to intensify and spread on a global level.

Against the background of the growing demand for cement, ECRA provides support for cement producers worldwide in order to help them build up, secure and update the knowledge and fundamental skills of their personnel. The pressures facing cement manufacturers in the coming years due to the growing demands on energy efficiency and environmental requirements will not decrease. Increasing importance will be placed on development programmes for all employees, whether they are unskilled workers, technicians, engineers or managers. In addition, the swift transfer of knowledge from research projects is set to play a greater role at a practical level in order to respond to the requirements

Table 1: Themes covered by ECRA seminars, workshops and trainings

Seminars, workshops and training courses			
Environment	Cement	Concrete	Chemistry
– NO_x Reduction – Trace Elements – CO_2 Monitoring and Reporting – Continuous Emission Monitoring – Behaviour of Organic Compounds – Legal requirements CO Management – Environmental Risk Management – Biomass and its Impact on CO_2 Emissions – Trends in Secondary Abatement Technologies – Alternative fuels: Quality and environmental control	– Sulphur and Choloride Cycles – Use of Alternative Fuels and Materials – Precalciner – Burner Technology – Modern Grinding Techniques – Pretreatment, Handling Storage and Feeding of Waste Fuels – Modern Clinker Cooler – Bypass Systems – Refractory Materials – Kiln Examinations – Electrical Energy Efficiency – Cement Grinding Technologies – Clinker and Cement Production – Thermal Energy Efficiency and Waste Heat Recovery – Fuels of the future – Safety – Corrosion	– Interactions between Cement and Concrete Admixtures – Alkali-Silica Reaction – Trends in Concrete Technology and their Influence on Concrete Constituents – Blended Cements – Production of Blended Cements and their Performance in Concrete – Cement and Admixtures – Alkali-Silica Reaction – Hydration of Blended Cements – New Cements and Innovative Binder Technologies – Environmental Requirements and Performance of Cement-based Building Materials	– Chromate Reduction – Chromate Analysis – Clinker Microscopy – X-Ray Diffraction – Rietveld Refinement – Clinker Reactivity – Quality control of cement

made on products and manufacturing processes.

Motivation and Efficiency

The sustained success of development seminars and trainings depends not only on the topics chosen and the motivation of the students, but also on clear explanations and competent, experienced instructors, who must be able to help translate the theoretical knowledge acquired into practical skills and also discuss and answer queries from participants about specific operational processes. This frequently offers students new insights into existing issues and topics, helping to boost efficiency, motivation and performance. The combination of classroom presentations and site visits provides a basis for successful learning.

The ECRA training course "Clinker and Cement Production" for young engineers or foremen combines both training methods. The theoretical training focuses on the core aspects of cement production, such as grinding and burning technologies. It also has a special emphasis on the use of alternative fuels and the latest environmental issues. During the course the participants are involved through discussions and exercises with the opportunity to ask questions ensuring that the training is interactive. The course ends with a site visit to a cement plant (**Fig. 1**). Feedback from the participants has shown that they obtain a better understanding of the process by the combination of theory and practice and the intensive exchange with the instructors.

Latest technology and research results

For experts and experienced engineers ECRA provides seminars and workshops focusing mainly on recent developments, the exchange of experiences and the latest research results. Here, the participants benefit from the wide range of research projects in the field of cement production and application in concrete in which ECRA and its members are involved. Presentations on the latest developments and the results from scientific research contribute to making the seminars and workshops a success. To date ECRA has held more than 70 seminars and workshops attended by more than 1500 participants, with the themes chosen covering all relevant aspects of cement and concrete technology (**Table 1**).

Figure 1: Plant visit during a training course

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European Cement Research Academy

Tannenstr. 2 · 40476 Duesseldorf
P.O. Box 30 03 32 · 40403 Duesseldorf
Germany

Phone: +49 (0)211 2 39 83 8-0
Fax: +49 (0)211 2 39 83 8-500

info@ecra-online.org
www.ecra-online.org