



**ecra**

european cement research academy



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# NEWSLETTER

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## Next ECRA event:

- Hydration of Blended Cements  
7-8 November 2012

# A closer look at the hydration of fly ashes used as a cement constituent

Correlations between the chemical composition of siliceous fly ashes and their reactivity

Since 2000 the proportion of CEM I cements in the total domestic delivery in CEMBUREAU countries has dropped from nearly 35% to around 25%. In 2010 more than 70% of cements produced in Europe were cements with several main constituents, such as lime-stone, granulated blast furnace slag and fly ash. The use of siliceous fly ash in particular is becoming increasingly more interesting as a cement main constituent because it saves primary raw materials and fuels.

For the production of efficient binder systems containing supplementary cementitious materials a fundamental understanding of their hydration reactions is essential. Topics like the corrosion mechanisms of fly ashes in alkaline media and the influence of their reaction products on the compressive strength development of cements have therefore been in the focus of several research projects during recent years.

Fly ashes react pozzolanically to calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H). Both reactions are influenced by the reactivity and the interaction of different elements such as Si, Al, the alkalis and others. If fly ash re-

acts in a Portland cement matrix, the differentiation of the reaction products can be extremely complicated. An extended knowledge of the composition of these products is essential for a better understanding of fly ash reactivity.

## Suspension tests

By means of suspension tests on fly ashes in different media the dissolution of the fly ash glass and the incorporation of different ions into the reaction products could be observed. Fig. 1 shows the sodium and potassium contents of eluates derived from suspension tests on fly ash/calcium hydroxide mixtures consisting of 73 mass % fly ash and 27 mass % calcium hydroxide in an artificial pore solution ( $c(\text{KOH}) = 0.54 \text{ mol/L}$  and  $c(\text{NaOH}) = 0.11 \text{ mol/L}$ ) with a water/solid ratio of 2. The proportion of fly ash to calcium hydroxide is equivalent to their amounts in a completely reacted CEM II cement with 35 mass % fly ash. The dotted lines mark the amount of the alkalis in the artificial pore solutions at the initial state. It is noticeable that more potassium than sodium is incorporated into the fly ash reaction products.

The formation of ettringite during the pozzolanic reaction of siliceous fly

ashes and calcium hydroxide is governed by different factors. The soluble sulphate content of the fly ashes plays an important role in this. Fig. 2 shows the amounts of different ions in eluates after 7 days' suspension of different fly ash/calcium hydroxide mixtures consisting of 86 mass % fly ash and 14 mass % calcium hydroxide in an artificial pore solution. The proportion of fly ash to calcium hydroxide is equivalent to their amounts in a completely reacted CEM IV-B cement with 50 mass % fly ash. With an increasing amount of sulphate in the eluates the amount of aluminium decreases. Dissolved aluminium reacts to ettringite if sufficient soluble sulphate is present in the fly ash. Therefore, eluates from ashes which can form ettringite contain only low amounts of aluminium.

## Hydration products

X-Ray diffraction analyses and dynamic scanning calorimetry on hydrated mixtures of fly ashes and calcium hydroxide confirm the selective formation of ettringite as a function of the sulphate content of the fly ashes. Besides ettringite, the fly ashes form mono- and hemical-boaluminate as crystalline hydration products as well as strätlingite to some extent. With a rising water/solid ratio the conversion of the pozzolanic reaction of the fly ashes and their consumption of calcium hydroxide increase.

In fly ash-containing cements the formation of different carboaluminates depending on the chemical composition of the fly ash could be shown by means of X-Ray diffraction.

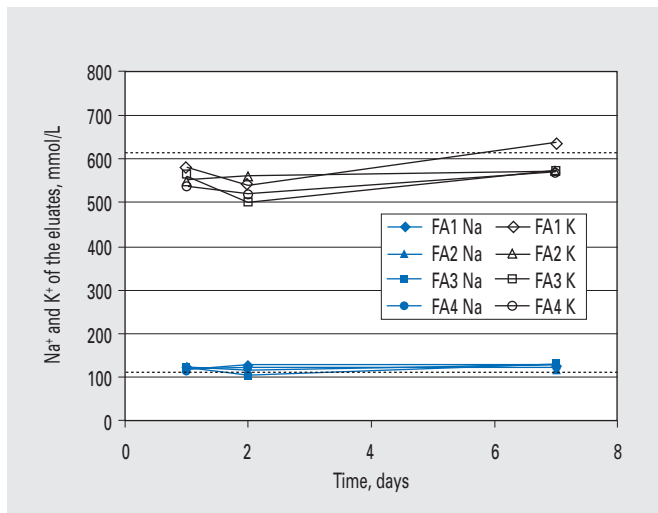


Figure 1:  $\text{Na}^+$  and  $\text{K}^+$  content of eluates derived from suspension tests of fly ash/calcium hydroxide mixtures (FA/CH = 73/27).

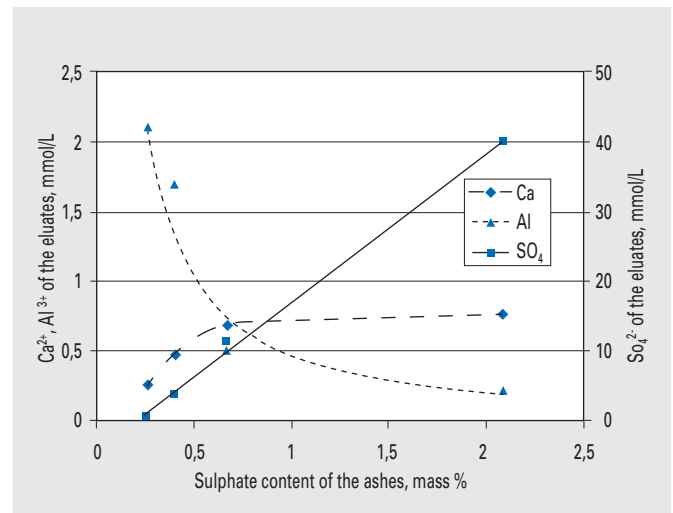
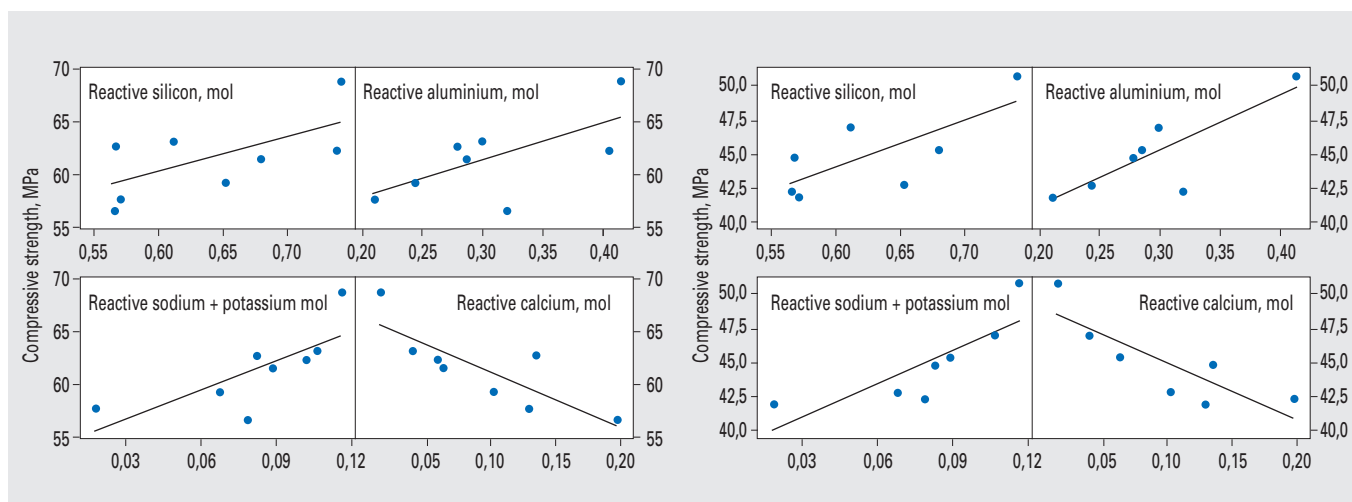


Figure 2:  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  content of eluates derived from suspension tests (after 7 days) of fly ash/calcium hydroxide mixtures (FA/CH = 86/14) vs.  $\text{SO}_3$  of the ashes.



**Figure 3: Compressive strength acc. EN 196-1 of CEM II/B-V with 30 m.% fly ash (left) and CEM IV/B with 50 m.% fly ash (right) after 91 days' hydration depending on the chemical composition of the fly ash glass.**

### Compressive Strength

The compressive strength of CEM II/B-V and CEM IV/B cements was determined acc. EN 196-1 in order to work out the impacts of the fly ash glass composition on the compressive strength contribution of fly ashes in the cements.

The pozzolanic reaction contributes to the compressive strength after

7 days. Up until 28 days of hydration the fly ashes built up the most strength contributing reaction products in the analysed cements.

**Fig. 3** illustrates the compressive strength of CEM II/B-V cements with 30 mass % fly ash (left) and CEM IV/B cements with 50 mass % fly ash (right) after 91 days' hydration depending on the chemical composition of the respective fly ash glasses.

In comparison to particle size effects a prevailing influence of the chemical composition of the fly ash glass can be observed for both types of cement. The strength contribution of the fly ashes rises with increasing contents of silicon, aluminium and alkalis in the glassy phase and decreases with increasing calcium content.

## ECRA's CCS project moves into phase IV with a focus on oxyfuel

Research programme extended to include other pre-competitive issues

**ECRA regards itself as a platform for the European cement industry for the dissemination of technical knowledge via seminars and workshops and for the implementation of joint research projects on a pre-competitive level. The themes of its research work are contemporary issues which will affect the future of the cement industry as a whole. ECRA's CCS project is a long-term research project which started in 2007. After the successful completion of phase III, ECRA's Technical Advisory Board has decided to continue the project and commence work on phase IV with a focus on oxyfuel technology.**

From the beginning ECRA's CCS project was conceived as a long-term activity consisting of at least five phases. Up to phase III, the scope of the

project was relatively broad, covering both post-combustion and oxyfuel technology as the two most promising carbon capture processes for the clinker burning process.

### Oxyfuel in focus

Until recently the prevailing opinion was that only post-combustion technologies (as end-of-the-pipe measures) could be applied to existing kilns. However, during phase III of the project it became evident that oxyfuel technologies could also be applied to existing installations, requiring only a moderate redesign of plant components (cooler, burner, etc.). Furthermore, trials in an electrically heated laboratory oven showed that clinker burning under oxyfuel conditions did not cause deterioration in the quality of the clinker or the subsequently manufactured cements. In a similar

way, investigations with refractory materials were also carried out. It emerged that at least basic materials could withstand the oxyfuel conditions and did not suffer significant wear. Due to these facts, the application of oxyfuel combustion exhibits several advantages over post-combustion plants, especially for economic and energy reasons. The ECRA Technical Advisory Board therefore decided to focus the forthcoming research work on oxyfuel technologies (**Fig. 1**).

Besides its focus on oxyfuel technology ECRA will continue to pursue the planned post-combustion pilot project at Norcem's Brevik cement plant in Norway. It is planned to build a test facility where amine-scrubbing and eventually also other post-combustion technologies could be inves-

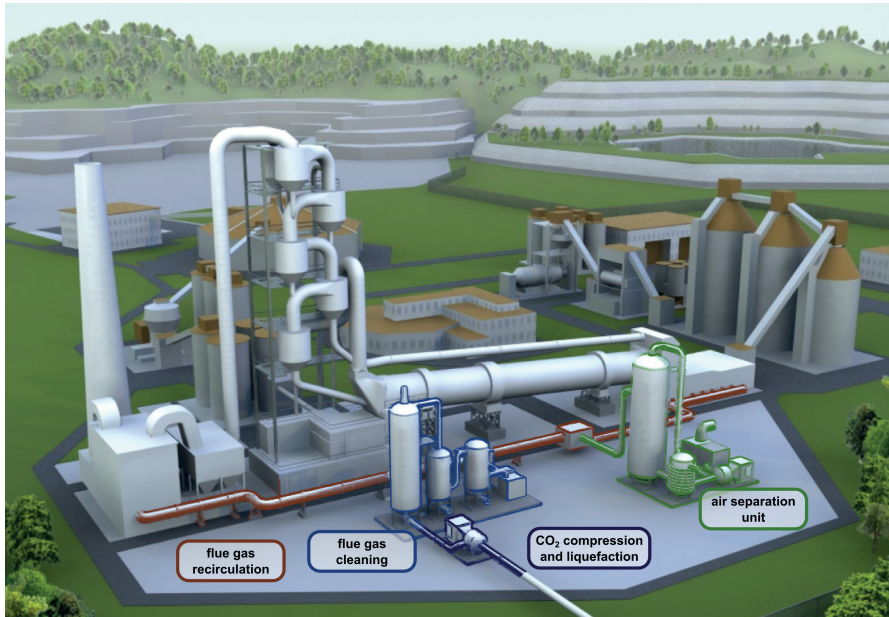


Figure 1: The principle of an oxyfuel cement plant.

tigated on a small-scale level. ECRA remains involved in the respective research consortium and will participate with in-kind contributions as and when required.

Against this background, the planning of phase IV of the project was initiated. As in phase III, several work packages have been defined to be assigned to different project partners. Appropriate candidates possessing the required expertise and technical background are currently being approached with open calls for tender. The new Steering Committee of phase IV, which was established in September 2012, will then carry out the selection of the most eligible project partners.

#### Phase IV restructured

The originally planned structure of phase IV has been modified and the work split into two phases, phase IV.A and phase IV.B. The objectives of phase IV.A are to develop a concept for a pilot kiln and to continue the investigations on the application of oxyfuel technologies at a virtual 3,000 t/d kiln. Phase IV.B would cover a pre-engineering study for an oxyfuel pilot kiln and an economic sensitivity analysis.

The forthcoming phase IV.A consists of eight individual work packages, which comprise amongst other things the continuation of the simulation studies, the development of an advanced cooler design, future oxygen supply and the experimental verification of sealing potentials. For the sealing studies a volunteer ce-

ment plant is required where the improved maintenance measures and the associated measurements can be carried out.

Work package B - the development of a concept for a pilot plant - is the most complex topic. It is subdivided into six work packages with more detailed research objectives. A potential project partner should have extensive experience as a technology provider or an engineering company.

Within work package D, a CO<sub>2</sub> overall balance for the oxyfuel process will be elaborated. As in the previous phases, the coordination of phase IV.A (WP E) will be carried out by the Research Institute of the German Cement Industry.

In accordance with the revised structure of phase IV, the remaining project phases have also been modified. The construction and operation of a pilot kiln is envisaged only in phase V of the long-term project, whereas a full-scale demonstration project would be carried out - if at all - in a new phase VI of the research project.

#### New research projects

In addition to its CCS research, ECRA's Technical Advisory Board has decided to extend the Academy's research programme to include other contemporary issues. The studies which have been chosen are on the themes of grinding technologies, methanol synthesis, the recycling and reuse of concrete, and ultra-fine particles.

The study on the state of grinding technologies is a particularly important issue for the cement industry. Representatives from technology providers, universities and cement companies will be approached and brought together in order to gather ideas about more efficient and future-oriented grinding processes. It is expected that this activity will require a dedicated steering group for the coordination of all activities.

The study on methanol synthesis may gain in importance due to the fact that there is still a lack of sufficient public acceptance with regard to the storage of captured CO<sub>2</sub>. The reutilisation of CO<sub>2</sub> is therefore being discussed, for example, for the production of methanol. The study will summarise the most important technical and chemical aspects of methanol production, also taking into account energy and sustainability aspects. ECRA has emphasised that all studies will be carried out on a pre-competitive level. ECRA members will be able to use the results of the studies to carry out their own research. Phase IV.A of the CCS project and most of the other research topics are scheduled to be completed by the end of 2013. Following this, a decision regarding phase IV.B of the CCS project will be taken.

An overall budget has been drawn up for the implementation of the research activities. The majority of the budget is earmarked for phase IV.A of the CCS project and the remaining proportion for the realisation of the other research studies. The required budget is provided by a research consortium which consists of cement companies, cement organisations and technology providers.



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