



ecra

european cement research academy



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NEWSLETTER

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Four years of ecra – future projects

ecra broadens its scope from communicating research results to arranging research projects

ecra's main focus since its foundation in 2003 was to arrange seminars and workshops which has been done with increasing success. But this is not the only objective of the Academy – dedicated research projects for which the ecra provides the research environment are its second goal. Several projects are planned or have already begun to take shape.

It is well known that the problems of CO₂ in regard to the global warming and the climate change are being thoroughly discussed at the moment. By taking the relevance of the subject into account the two projects which are of importance for the future of the cement industry deal with the ¹⁴C determination of CO₂ from biomass and on the questions of CO₂ Capture and Storage. The latter has already been one of the topics in the first ecra conference in Amsterdam 2003 and last year in an ecra workshop which took place in Düsseldorf on November 30.

Project: ¹⁴C determination of CO₂ from biomass

The subject of this project is the determination of the proportion of biomass in waste fuels by the ¹⁴C method. The project has to be seen in the framework of CO₂ emissions regulations. Under the European

emissions trading scheme for example, CO₂ from biomass is considered as neutral. As a consequence the monitoring of those emissions is important for those cement plants which substitute fuels or raw materials by secondary materials. Usually CO₂ from biomass is determined in solid recovered fuels by means of selective dissolution. However, there is a strong interference of the determined concentrations from different substances. Also systematic errors can occur for dedicated fuels. For the time being, additionally the procedures for taking samples and carrying out the analysis seem to be not very efficient in an economic sense.

Technically the first trial test of the ¹⁴C determination in the stack of a cement kiln was very successful. The correlation between the biomass CO₂ measurement at the stack and the input measurements of all fuels was excellent in the case of one laboratory, while another laboratory did not succeed in achieving a sufficiently low detection limit. It is clear, however, that the method still can be improved by better enriching the CO₂ in the samples taken at the stack. It was emphasized that the method would be very helpful for the correct and cost efficient determination of CO₂ from biomass in clinker production. ecra should proceed in improving the method and develop

it into a standard method able to be verified for CO₂ monitoring e.g. under the ETS trading scheme. It should be checked if the method might be subject to any failure due to traces of ¹⁴C from other sources.

Project: CO₂ Capture and Storage (CCS)

A second dedicated ecra project deals with the capture and storage of CO₂, a subject which has been of interest to the Academy throughout its existence. One of the topics of ecra's first conference in Amsterdam 2003 was CCS and after that it was the subject of an ecra workshop held in Düsseldorf in November 2006.

For more than ten years the energy sector has been very active in carrying out CCS research projects. Vattenfall seems to be the leading company in Europe in planning pilot and demonstration plants. The most important and most advanced project is based on Oxyfuel technology and CO₂ on-shore storage near Berlin. While the GeoForschungszentrum (Geological Research Centre) in Potsdam has got the permit to store some 6,000 t of CO₂ per year from the pilot plant, it is expected that it will be much more difficult to get the permit for long-term storage of the CO₂ from the demonstration plant. Storage as such seems to be possible in a safe way, provided that the foreseen demo-projects support the theoretical views of the geologists. Nevertheless, storage seems only to be an intermediate solution, since there will obviously not be sufficient safe storage capacity for an unlimited treatment of CO₂. The timeframe in which storage might be a solution is estimated to be 50 years. Today's



cost expectations vary from 20 Euro/t CO₂ captured, transported and stored up to 20 Euro/t CO₂ only captured. It became clear that even these high cost figures are still best estimates subject to great uncertainty.

Basically four options about CO₂ capture are discussed these days: pre-combustion, post-combustion, Oxyfuel technology and carbonate looping. From the cement industry's point of view each option has its pros and cons. Clearly all options are

not directly available for the cement industry today, however, if any of the technologies discussed ever become technically applicable the estimated costs would be extremely high in comparison e.g. to the cost of cement production.

In order to get a detailed overview about the current situation on CCS the Technical Advisory Board has assigned a comparative analysis (scoping study) on that subject to be worked out by ecra. The study will be

finalized in summer 2007, its findings of this study will be the basis for potential detailed research in the future.

2nd International ecra conference

The next conference of ecra is scheduled for May 16, 2008. It will take place in Prague/Czech Republic. Information about the conference will be made available on the ecra website in due course.

EC Directive on the incineration of waste – 2000/76/EC

Important aspects for the cement industry

The provisions of the European Waste Incineration Directive (WID) had to be applied as from end of December 2005 at the latest. The Directive sets strict emission limits for co-incineration plants. Nevertheless the EU legislation takes into consideration some specific characteristics of the clinker burning process.

The ecra seminar which took place in Greece from 25 to 26 April 2007 dealt with the cement specific requirements of the European WID. The seminar itself started with an interesting visit of Titan's Kamari plant close to Athens. On the second day the 29 participants vividly discussed the different aspects of the WID as they were presented by the lecturers. The following article gives a comprehensive overview on the main contents of the seminar.

Raw material related organic emissions

Concerning organic emissions an emission limit value of 10 mg/m³ as daily average value is stated for TOC. TOC comprises all gaseous and vaporous organic substances in the exhaust gas. Exemptions may be authorised by the competent authority in cases where TOC does not result from the incineration of waste.

In ordinary firing systems the emissions of organic compounds and carbon monoxide can be taken as criteria for proper burning conditions. Such a direct correlation between the exhaust gas level of organics and the quality of combustion is not applicable to cement kilns. Almost the entire organic compounds are introduced into the clinker burning process via the raw materials. The kiln feed passes counter-current to the combustion and kiln exhaust gases and intensive intermixing takes place. The temperature pattern and gas residence time in rotary kilns therefore offer particularly favourable conditions for complete destruction of organic compounds which are introduced via the fuels or are produced from them.

As a matter of fact the release of these organics from the kiln feed cannot be controlled via the operating conditions of the kiln system. During the preliminary heating process the organic constituents of the raw materials are liberated by the effect of temperature and emitted as organic compounds with the exhaust gas flow or are oxidized to carbon monoxide and carbon dioxide.

Even under optimized combustion conditions the exhaust gas from rotary kiln systems in the cement industry can contain carbon monoxide and TOC which exceed the

emission limit in the European Directive 2000/76/EC. On the other hand if an emission limit for CO has to be stated, the influence of the raw materials has to be taken into consideration.

SO₂ emissions caused by the raw materials

More or less the same applies for the emissions of SO₂. In the European Directive 2000/76/EC an emission limit value of 50 mg/m³ is stated for cement kilns. This strict value cannot be met by the majority of cement plants. The occurrence of fairly high sulphur dioxide emissions in the exhaust gas of rotary kilns can be attributed almost exclusively to volatile sulphur compounds in the raw materials. Highly volatile ferrous disulphides (FeS₂) in form of pyrite and marcasite already oxidise at temperatures between 370 to 420 °C in the upper cyclone stages. A portion of the SO₂ which was formed by the sulphide in the upper cyclone stages is again bound directly by the kiln meal. The remaining SO₂ leaves the preheater without any secondary reduction measures.

A first assessment of the reaction behaviour of sulphur compounds in the clinker burning process can be executed by examinations in a laboratory set-up.

Measurement requirements

According to the EU Directive the components dust, SO₂, NO_x, TOC, CO, HCl and HF have to be measured continuously in the exhaust gas of so-called co-incineration plants, i. e.

a cement kiln which uses secondary fuels.

In addition to these stack gas emissions the concentration of oxygen, the pressure, temperature and water vapour content of the exhaust gas has to be recorded continuously as well. These parameters are needed to standardise the measured concentrations at a temperature of 273 K, a pressure of 101,3 kPa, 10 % oxygen, dry gas.

Further to these continuous measurements periodic measurements of heavy metals, dioxins and furans, and – in some cases – polycyclic hydrocarbons or other pollutants have to be carried out regularly.

Calibration and functioning

According to Article 10 of the EC Directive the installation and functioning of the automated monitoring

equipment has to be controlled by an annual surveillance test (AST). Additionally a calibration has to be done by means of parallel measurements with standard reference methods (SRM) at least every three years. Based upon the results of these parallel measurements the analytical function of the complete monitoring equipment has to be calculated by a so-called regression analysis. Finally this mathematical correlation is fed into the emission data acquisition unit.

At least for cement kilns which burn waste the AST as well as the periodic calibration have to be carried out by the beginning of 2006 according to the new European standard EN 14181. This standard contains various new requirements that have an impact on the independent monitoring bodies (i. e. external laboratories) as well as on the plant operator.

A calibration of an automated measuring system (AMS) covers in principle the following items:

- Installation of the AMS
- Calibration of the AMS by means of parallel measurements with a SRM
- Determination of the variability of the AMS and the check of compliance with the required uncertainty

Additional tasks also for the plant operator

Apart from the fact that the plant operator will have to carry out procedures to maintain an ongoing quality of the AMS, he will in future be obliged to check the drift and the precision of the measuring devices regularly. In order to meet these requirements he will have to get accustomed to the application of control cards.

Additional seminar: Monitoring of Respirable Crystalline Silica

Crystalline silicon dioxide can appear in form of different mineral modifications, the most frequent of which is quartz and to a minor extent cristobalite. Both modifications are regarded to be harmful when respired. The main effect of the inhalation of respirable silica dust on human body is silicosis. Besides, an increased risk of lung cancer for persons with silicosis is suspected.

To protect the health of employees occupationally exposed to respirable crystalline silica at their workplaces, a social agreement between the related industrial sectors and labour unions was introduced in 2006 on a European level, supported by the European Commission. To assess dust exposure levels at workplaces, a monitoring is required. The demands of the European standards EN 689, EN 1232 and EN 481 are to be considered.

Because of the topicality of the issue ecra offers a seminar which will provide insight into the current status of the social agreement and relevant national and EU occupational hygiene provisions. An overview of the different techniques to collect dust exposure data complying with the given regulations will be presented. Diverse sampling systems as well as various analytical methods to determine quartz and cristobalite contents, e.g. by X-ray diffraction or infrared spectroscopy, will be introduced. Experiences and examples of results of measurements will be presented.

The seminar will take place on 26 June 2007 in Düsseldorf. The easiest way to register is via ecra website <http://www.ecra-online.org>.



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