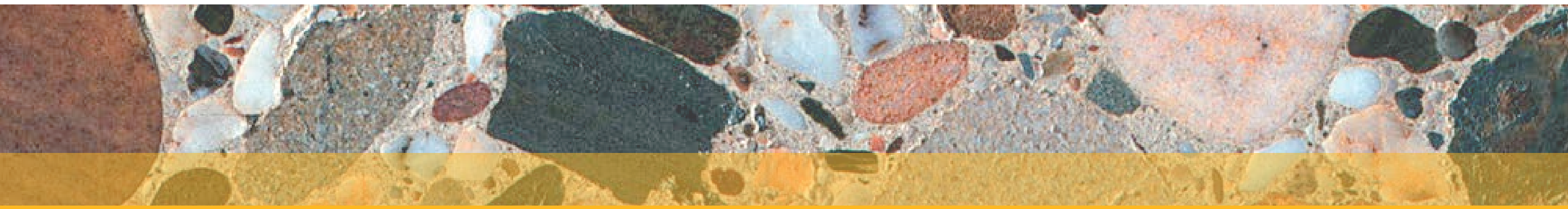
european cement research academy



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NEWSLETTER

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Current schemes for the determination of CO_2

Drafted EN standard published; Updated CSI Protocol V3.1 available; First emission reports in EU ETS phase III delivered

The European Committee for Standardization (CEN) has recently published a draft standard for the determination of greenhouse gas (GHG) emissions from stationary sources in energy-intensive industries. It includes a cement-specific part that is based on the Cement CO_2 and Energy Protocol of the Cement Sustainability Initiative (CSI Protocol), which is now available in version 3.1. More than 960 cement plants worldwide use the CSI Protocol for monitoring their CO_2 emissions and also their energy consumption. Cement plants located in the EU additionally have to report their annual CO_2 emissions within the framework of the European Emission Trading Scheme (EU ETS), phase III of which started in 2013.

The drafted EN standard describes methods for the monitoring and reporting of GHG emissions. It consists of six parts in total: one part on general aspects, and sector-specific parts for each of the five industries involved. Besides the cement sector, these are the lime, steel, aluminium and ferroalloys industries. The final publication of the standard is planned for 2016. CEN also plans to suggest the EN standard as a worldwide valid standard to be published in cooperation with the International Organization for Standardization (ISO).

The cement-specific part is based on the CSI Protocol (CSI is part of the World Business Council for Sustainable Development, WBCSD). The EU ETS is focused at plant level and reports the amount of direct GHG emissions (t CO_2) of an installation stemming from burning fuels and from the calcination of raw materials. The EN standard additionally formulates key performance indicators (KPIs) at product level, also considering indirect emissions from the consumption of electrical power. Such KPIs demonstrate the specific amount of emitted CO_2 or the consumed energy per ton of a product (e.g. t CO_2/t clinker or kWh/t clinker). This means that besides direct GHG emissions, the EN standard also encompasses the monitoring of indirect GHG emissions and energy consumption not only at plant level but also at product level. Furthermore, it enables the comparison of the specific emissions of a product (clinker or cement) over time as well as the comparison with product-specific emissions from other plants.

The standardisation project was funded by the European Commission. It received special attention during a visit by representatives of the Directorate-General for Enterprise during one of the verification plant tests (**Fig. 1**).

EN standard verification project

In 2013 and 2014 a total of four 48-hour field tests in two cement plants were performed to verify the different methods laid down in the cement-specific part of the EN drafted standard. A simple and a complicated test setting were chosen. Whilst in the simple test setting only fossil fuels and conventional raw materials were used, the complicated setting encompassed the use of alternative fuels and raw materials. ECRA participated by providing technical experts for the supervision of the field tests and the evaluation of the results.

Basically, GHG emissions can be determined by simplified or more detailed mass balance methods (assessing the amount of all relevant input and/or output materials multiplied with their specific emission factor) or by emission measurements at the stack (**Fig. 2**). The aim of the verification project was to compare five different methods.

The concluding evaluation taking all four field tests into account is not yet finalised. Some key findings from the first two field tests are:

1. Input and output mass balance methods proved their general

Figure 1: European Commission representatives visiting one of the verification plant tests.

Figure 2: The verification test at two cement plants included direct CO_2 emission measurements at the stack.

appropriateness for CO_2 emission reporting.

2. High reliability was achieved with the detailed output mass balance method. This method relies on precisely determining the clinker output of the clinker calcination process.
3. Stack CO_2 emission measurements were subject to relatively high uncertainty attributed to the volume flow reference measurements.

The field tests highlighted the importance of appropriate sampling procedures for achieving representative raw material and fuel samples (**Fig. 3**) and also that careful scale calibration is of high importance for uncertainty management. Furthermore, the relevance of the different

Figure 3: Sampling of alternative fuels during the verification plant tests.

GHG defined in the Kyoto Protocol (besides CO_2 e.g. CH_4 and N_2O) was assessed and showed no significant contribution of non-CO_2 GHG.

CSI Protocol Spread Sheet V3.1

After the publication of the final ISO-EN standard in 2016 the CSI may potentially adapt its already existing calculation tool for CO_2 emissions from cement plants accordingly. Currently more than 960 cement plants worldwide use the CSI Protocol for internationally harmonised CO_2 determination. In December 2013 the CSI published the updated version 3.1 of the CSI Protocol Spread Sheet (www.cement-co2-protocol.org/v3). This update implements the correction of two calculation formulas in the Company Sheet and a tool for data transfer to the CSI Protocol Spread Sheet. First companies started to use this updated Protocol version for their 2013 reporting for the GNR ("Getting the Numbers Right") project. In the past the GNR data had been fundamental for describing the benchmark methodology that was the basis for the EU ETS allocation of emission allowances free of charge.

First reports within EU ETS phase III

The third period of the EU ETS started on 1 January 2013. Cement plants have to apply the new requirements laid down in the Monitoring and Reporting Regulation (MRR). European cement plants had to deliver their reports on direct CO_2 emissions in 2013 based on new regulations for phase III (2013-2020) by the end of March 2014. Compared to phase II, cement plants have to follow more stringent formal regulations, e.g. regarding sampling plans, internal written procedures, the documentation of control activities and the approval of the equivalence of plant laboratories compared with accredited laboratories. Furthermore, the implementation of the new harmonised rules meant that in some countries further minor emission sources had to be included which had not been reported before in phase II (e.g. fuels for room heating or emergency power equipment). Just a few weeks before the delivery deadline a discussion on reporting CO_2 from the use of urea arose in some member states. Usually, the CO_2 used for producing urea stems from ammonia production plants that already have to report these emissions within their EU ETS reports. In such cases reporting by the cement plant would mean double accounting. Further guidance on this issue is expected to be published this year for 2014 CO_2 emission reporting.

Stresses on refractories: Challenges and solutions

Strategies to reduce damage caused by corrosive media

Refractories are a major cost factor in cement plants. The right choice of refractories and the understanding of their wear are therefore important not only for process reasons but also for economic reasons. Corrosion is one factor that degrades refractories. Its speed and severity depend on a number of aspects which in the end define the actual corrosion mechanism. The kiln atmosphere itself is determined by the raw material and fuel composition and the kiln operation, including in particular the use of a bypass system. As a consequence the right choice of refractories with respect to their chemical and mechanical stress is a key factor in every cement plant.

The raw materials and fuels contain different amounts of sulphur and chlorine compounds which are introduced into the kiln system. By means of suitable measures, for example, bypass systems, many process and plant-related problems can be solved, but not all can be completely eradicated.

Stress mechanisms of the refractory lining

The refractory brick lining is implemented in various ways. In the static areas of the plant, such as the preheater and the clinker cooler, today's refractory linings mainly consist of monolithics. The plant's dynamic area – i.e. the rotary kiln itself – is lined with refractory bricks. All the areas named are subjected to thermal, chemical, and mechanical stresses, and particularly to combinations of these three stress mechanisms (**Fig. 1**).

The individual stress types never occur alone, but in combination,

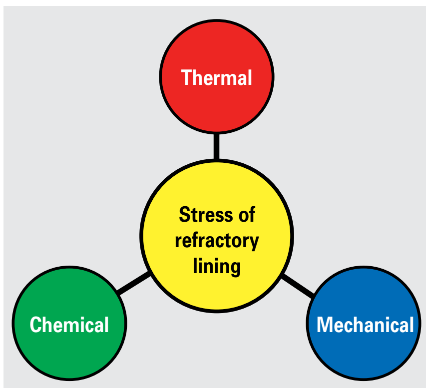

Figure 1: Refractory stresses: influencing factors

which in turn leads to complex interactions and damage mechanisms. In addition, they mutually influence each other, thereby increasing or accelerating the respective damaging process. Depending on the types of raw materials and fuels used, higher amounts of chlorine, sulphur, and alkali compounds are introduced into the kiln system, which thereby increases the internal sulphur and chlorine cycles. These additional stresses, which act on the refractory linings, may result in shorter lifespans. Moreover, with the use of alternative fuels, a shift of the kiln's temperature profile can frequently be observed at the kiln burner, with a corresponding lengthening or shortening of individual kiln zones. Due to the changed formation of coatings and rings, the bricks installed in the kiln are subjected to further stress.

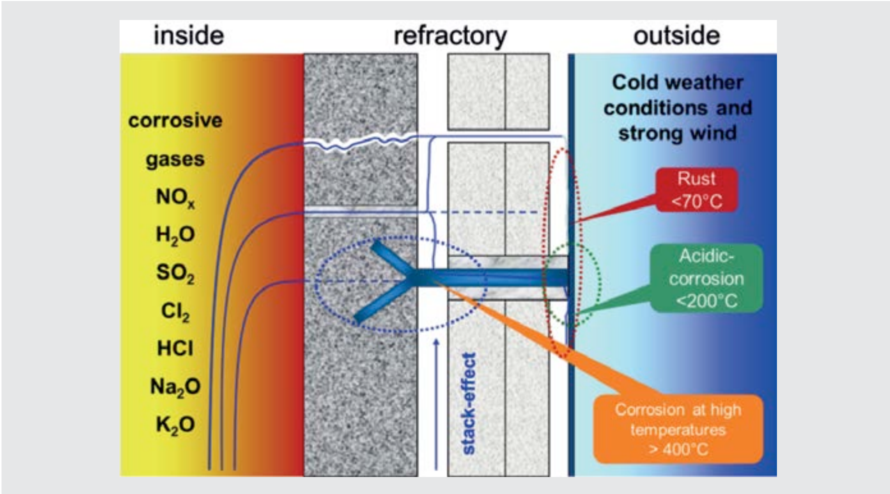

Figure 2: Mechanism of anchor and shell corrosion

Damage to the refractory lining and the plant

The refractory lining is not completely gas tight or impermeable. Corrosive media are therefore able to penetrate the refractories. The corrosive gases occurring in the atmosphere of the hot area of the kiln penetrate the refractory lining where they condense, forming salts of alkali chlorides and alkali sulphates, which can lead to various types of damage.

At the gas temperatures existing in the kiln, the calciner, and the lowest cyclone stages, vaporous salts such as NaCl, Na_2SO_4, KCl, and the corrosion-promoting gases SO_2 and HCl diffuse into the refractory lining. The bricks installed in the kiln are thereby infiltrated, and the open pores are filled with the salts. As a result, the bricks can lose their ductile properties, becoming very brittle and susceptible to mechanical stresses.

With high alumina bricks, the salts lead to the formation of new minerals, resulting in high volume increases. The reduced ductility and simultaneously increased internal stresses frequently cause spallings, which considerably reduce the total thickness of the brick within a very short time.

Monolithic linings, by contrast, exhibit fundamentally different damage profiles due to their more complex wall structure and the use of refractory castables. As soon as the prevalent partial pressure at the corresponding temperature leads to an oversaturation in the local atmosphere, the individual gaseous compounds condense or desublimate at the transition to and within the insulating layer.

The high porosity of the insulating layer hereby supports the capillary transport of the liquid condensates in the direction of the outer wall, until they solidify completely. Due to the mechanisms described, different mixtures of liquid and solid salts, plus newly formed minerals are created within the refractory lining's cross-section, causing direct corrosion of the metal anchors, as well as spalling of the upper layers of the brick lining.

Because of process-related fluctuations in temperature (up to ΔT of 150 °C), previously crystallized salts are remobilized due to renewed melting, which promotes further mixing of the various salt compounds within the refractory lining. Depending on the local concentration levels of the different salts, eutectic melts are formed, which increasingly attack the anchors and simultaneously penetrate even deeper into the refractory material (**Fig. 2**). Moreover, if the temperatures at the walls of the plant (cyclone walls or kiln shell) fall below the dew point, acid formation and corresponding corrosion is possible.

Strategies to reduce damage and increase refractory lifetimes

In order to prevent the formation of new minerals and the associated spallings, high alumina bricks should, if possible, not be installed in severely stressed areas of the rotary kiln. Instead, brick grades should be used which neither react with the condensing salts of the kiln atmosphere, nor lose their ductility due to infiltrations. For these reasons, a trend towards the increasing use of high-grade spinel bricks – in particular magnesia spinel bricks – has been observed in many plants with a high utilisation rate of alternative fuels.

With the increasing use of alternative fuels, the percentage of magnesia spinel bricks in kiln linings has increased in recent years. SiC castables can be used to prevent or at least reduce the infiltration of salts. Under normal operating conditions these castables form a glassy surface which prevents the infiltration of salts into the lining. Furthermore, concepts for monolithic linings should be adapted so that practically gas-tight or encapsulated linings are installed.

In areas with particularly high wear, such as both kiln and cooler inlets, precast and tempered refractory blocks made of low-cement castables are being employed to an increasing extent. Blocks made of SiC-containing castables have particularly long lifespans, and are preferably used for the cooler bullnose and side walls, and also in the transition from the kiln inlet arch to the inlet chamber.

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