Contents

Current schemes for the determination of CO$_2$ .......................................................... p. 2
Stresses on refractories: Challenges and solutions ......................................................... p. 3

Next ECRA events:

- CO$_2$ Monitoring and Reporting: Latest Developments and Experiences in the Cement Industry
  12–13 June 2014

- Refractory Materials and High Temperature Corrosion in Cement Kilns
  24–25 September 2014
Current schemes for the determination of CO₂
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 CO₂ 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 CO₂ emissions and also their energy consumption. Cement plants located in the EU additionally have to report their annual CO₂ 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 CO₂) 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 CO₂ or the consumed energy per ton of a product (e.g. t CO₂/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 productspecific 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...
strategies to reduce damage caused by corrosive media

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 CO₂ 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 stress mechanisms of the refractory lining 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.

Figure 1: Refractory stresses: influencing factors

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


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 CO₂ 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 CO₂ from the use of urea arose in some member states. Usually, the CO₂ 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 CO₂ 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 monolithic. 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,
which in turn leads to complex inter-
actions 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 in-
creases the internal sulphur and 
chlorine cycles. These additional 
stresses, which act on the refractory 
linings, may result in shorter life-
spans. 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 short-
ening of individual kiln zones. Due 
to the changed formation of coatings 
and rings, the bricks installed in the 
kiln are subjected to further stress.

**Damage to the refractory lining and the plant**

The refractory lining is not complete-
ly gas tight or impermeable. Corro-
sive media are therefore able to 
penetrate the refractories. Carbonic 
species entering the atmos-
phere 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, Na₂SO₄, KCl, and the corro-
sion-promoting gases SO₂ 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 proper-
ties, becoming very brittle and 
susceptible to mechanical stresses.

With high alumina bricks, the salts 
lead to the formation of new mineral-
al phases, which considerably reduce the total 
thickness of the brick within a very short time.

Monolithic linings, by contrast, ex-
hibit fundamentally different damage 
profiles due to their more complex wall 
structure and the use of refracto-
ry castables. As soon as the prevalent 
partial pressure at the corresponding 
temperature leads to an oversatura-
tion in the local atmosphere, the indi-
vidual 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 corro-
sion 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 melt-
ing, 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 pene-
trate 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 atmos-
phere, nor lose their ductility due to 
infiltations. For these reasons, a 
trend towards the increasing use of 
high-grade spinel bricks – in particu-
lar magnesium 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 magnesium 
spinel bricks in kiln linings has in-
creased 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-contain-
ing 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.