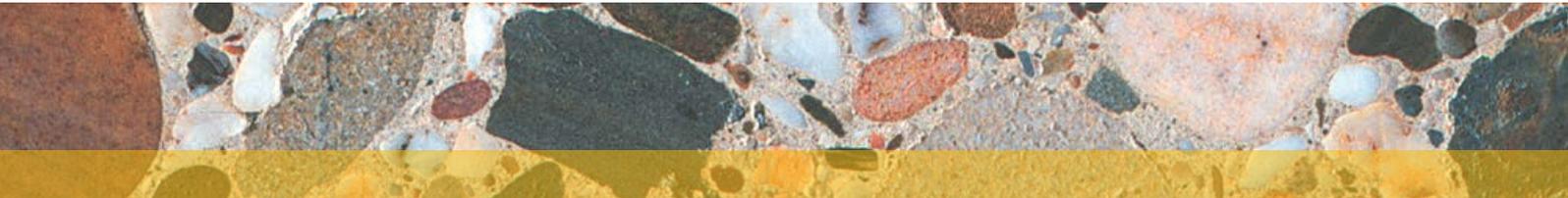




**ecra**

european cement research academy



**3 / 2019**

# NEWSLETTER

## Contents

- Mercury: Actions, balancing, limits and measures **p. 2**
- Calcined clay: A supplementary cementitious material with a future **p. 3**

## Upcoming ECRA seminars:

- Reduction of Mercury Emissions  
29-30 October 2019
- Blended Cements: Future Developments  
27-28 November 2019

# Mercury: Actions, balancing, limits and measures

Global efforts to reduce mercury emissions and detailed investigations on their origin and fate

**Mercury is a ubiquitous element which occurs naturally and is emitted through various anthropogenic sources. In the cement production process it is introduced naturally through both the raw materials and fuels. The respective concentrations are generally small and may vary from one raw material or fuel to another, from deposit to deposit or even within one quarry.**

Mercury has a high toxicity for human health and the environment. Its emissions are addressed at a global level by the Minamata Convention as a global and legally binding treaty. Initiated by the United Nations Environmental Programme (UNEP), it was opened for signature in October 2013 and came into effect in August 2017 after being ratified by over 50 countries/parties, among them the EU and most of its member states.

The import, export and production of mercury-containing products such as batteries, switches, some medical devices and cosmetics will be banned. Plans to reduce and eliminate mercury emissions from artisanal and small-scale gold mining will be established by countries promoting mercury-free alternatives. Plans to minimise mercury emissions from existing industrial mercury emitters such as coal-fired power plants, cement factories or waste incinerating plants are to be drawn up, while new facilities are to install Best Available Techniques (BAT).

## Mercury emission limits

Where emission limit values for mercury emissions resulting from clinker production are in place, they range with few exceptions between 0.05–0.10 mg/Nm<sup>3</sup>. In the EU, industrial mercury emissions are covered by the Industrial Emissions Directive (IED) which has been transposed into Member States' legislations, and are limited to 0.05 mg/Nm<sup>3</sup> over a sampling period of 30 minutes to 8 hours for kilns co-incinerating alternative fuels.

In the United States, mercury emissions for existing kilns are limited on a by-product basis to 27.5 kg per mil-

lion (metric) tonnes of clinker produced as a 30-day rolling average. Depending on the conversion factor, this corresponds to around 10–14 µg/Nm<sup>3</sup>. For new kilns, the limit is more stringent, with around 4–5 µg/Nm<sup>3</sup> (i.e. 11.5 kg per million tonnes of clinker produced).

## Origin and fate of mercury

While extensive investigations have led to a profound understanding of mercury's behaviour in the clinker burning process, the detailed understanding of its origin and fate in the context of contents in raw materials, fuels and products has recently taken a considerable step forward. Based on extensive data surveys in the German cement industry on a local and regional level as an example, the balances for the respective plants show that the mercury input through raw materials remains the largest source with more than 60 % of the total. This is despite the high share of alternative fuels of 65 %. About 60 % of the mercury output takes place through the products and about 40 % is emitted to air, (Fig. 1). The mercury contents in products are on average in the same order of magnitude as in the natural raw materials.

Continuous measurements at cement mill stacks (closed circuit grinding) have shown that the levels in the exhaust air lie very low in the range of

the limit of quantification of the method of measurement itself.

## Mercury in the clinker burning process

The behaviour of mercury in the cement production process is mainly determined by the thermal conditions between the preheater, raw mill and dust precipitator. Mercury and its compounds enter the process through raw materials and fuels, evaporate due to their high volatility and leave the preheater with the hot gas stream. In raw mill-on operation, mercury compounds condense on the raw meal. Elemental mercury is adsorbed on the meal's surface to a smaller extent. Low temperatures and a high dust load favour the adsorption. It then again evaporates when raw meal and precipitated dust re-enter the preheater, thus forming a mercury cycle between the preheater, dust precipitator and raw mill where the kiln meal silo acts as a buffer (Fig. 2).

## Measures for mercury control

Where mercury emissions are too high, the first measure is – if possible – a careful selection of input materials to the cement production process in combination with a constant quality control of mercury contents in all used raw materials and fuels.

If despite careful input control mercury emissions are still an issue, the mercury circulation within the system can be limited by selectively shuttling precipitated dust. The removal efficiency is higher the lower the temperature in the gas stream is, and the higher the proportion of oxidised mercury is. This means that in most cases the water or air quench-

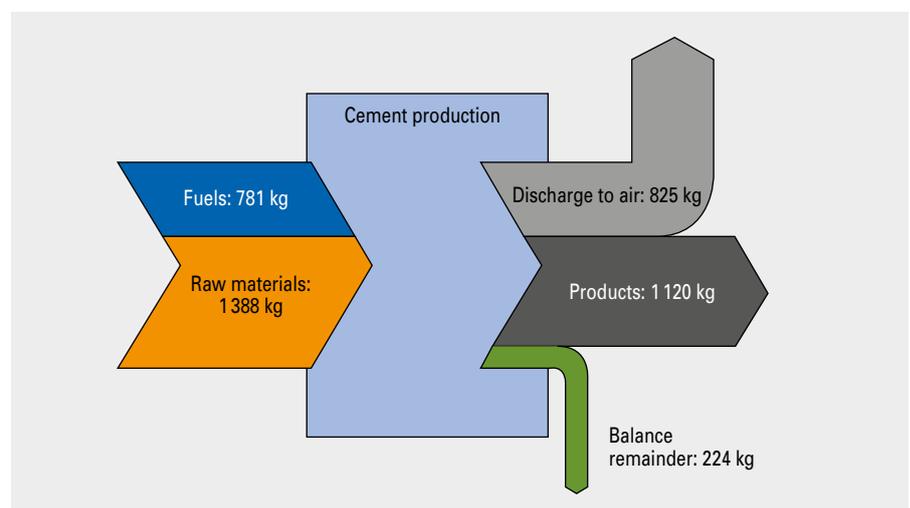


Figure 1: Mercury balance taking the German cement industry in 2017 as an example

ing of the exhaust gas has to be optimised and the temperature has to be reduced to below 140 °C. This leads to a significantly higher adsorption of mercury on the particles, so that with a given quantity of dust more mercury can be removed from the process. The removed dust can be used to specifically adjust the cement's properties

### Sorbent-supported dust shuttling

In cases where dust shuttling reaches its limits, it can be supported by the injection of sorbents with a high surface area or specific chemical properties into the gas stream upstream of a particulate matter control system to increase the rate of mercury bound to particles. In other industries, such as waste incineration, activated carbon is commonly injected. However, in the cement industry shuttled dust can be used in the cement mill but carbon-based sorbents may result in an undesired colouring of the cement or interference with air-entraining agents.

### Oxidising agents

Since oxidised mercury is adsorbed on dust and sorbents to a higher ex-

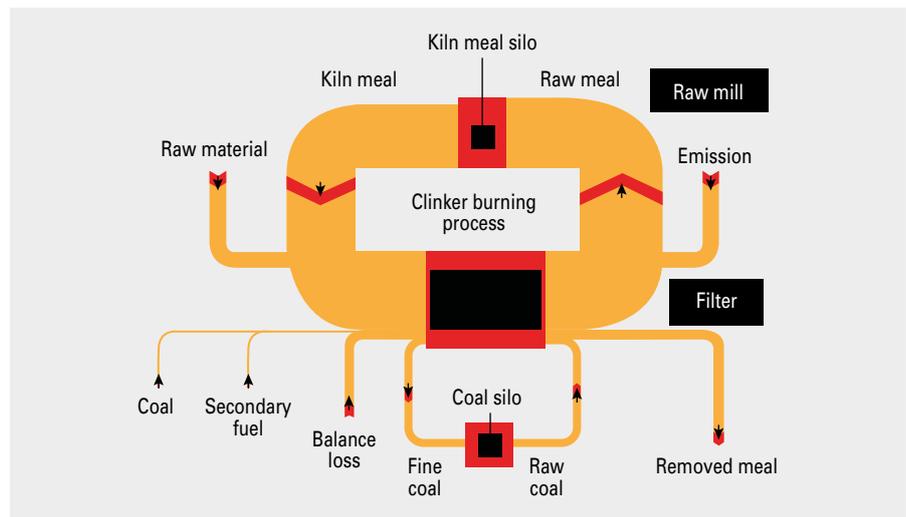


Figure 2: Mercury cycle balance in a clinker kiln

tent than elemental mercury, oxidising agents such as bromine or sulphur can even further enhance sorbents' adsorption capacity. Possible consequences for product quality due to the oxidising agent still need to be investigated.

### New concepts for mercury separation

Alternative concepts which have been realised in recent years twice in Eu-

rope on an industrial scale suggest a separate thermal treatment of precipitated dust. In a separate installation mercury is re-volatilised from the precipitated filter dust and subsequently abated in a small-scale polishing filter. With this technology, mercury input to the product is practically avoided, but small amounts of mercury-loaded activated carbon have to be discharged as hazardous waste.

## Calcined clay: A supplementary cementitious material with a future

Interest in calcined clays is increasing, especially in growth markets for cement

**The reduction of the clinker factor continues to be an important step towards lowering the emissions of CO<sub>2</sub> caused by the production of cement. This is also underlined by the International Energy Agency in the current Technology Roadmap (Fig. 1). Increasing attention is being paid to calcined clay as a potential supplementary cementitious material (SCM), because widely used clinker substituents, such as slag and fly ash, are envisioned as being significantly less available than clays for the rising demand worldwide. Nevertheless, an equivalent replacement of, for example, coal fly ash as a pozzolana still seems a long way off.**

Current predictions envisage a rise in cement consumption worldwide from the present annual figure of around 4.2 billion tons to about 5.2 billion tons by 2050. To be able to produce cements in the future with a

further reduced clinker factor there is a pressing need for new, reactive cementitious materials. Because of their broad availability, the current focus is on those clays which can be activated to form pozzolanic material by suitable heat treatment (calcination).

### Successful research projects

During the past 10 years several research projects have been carried out to investigate the fundamental suitability of ceramically low-grade clays as pozzolanic materials. These clays in particular are economically interesting for the cement industry, as

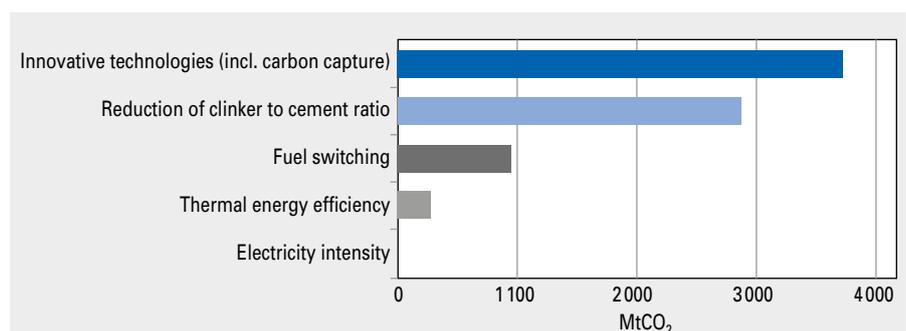


Figure 1: Global cumulative CO<sub>2</sub> emissions reductions [1]

many cement plants have direct access to them. By using burning conditions matched to the different clay compositions it is possible to achieve sufficient pozzolanic properties according to the European Standard with all clay varieties tested. Furthermore, the interactions between the pozzolana and the clinker components were investigated systematically and optimised. It is possible to produce concretes containing cements with 20 mass % of calcined clay with nearly the same fresh and hardened concrete properties as concretes made with Portland cement. Higher proportions of clay (40 mass %) can lead to losses in workability caused by the higher water demand of the calcined clay. However, this behaviour could be offset with superplasticizers. The chloride migration resistance and the resistance to carbonation (Fig. 2) and freeze-thaw are in the range normally found in concretes made with other pozzolanic or latent-hydraulic binder constituents.

### LC<sup>3</sup> Consortium and conferences

For some years now the LC<sup>3</sup> Consortium, headed by EPFL in Lausanne, has been developing composite cements with the combined use of calcined kaolinitic clays and limestone for local markets in developing and emerging countries. Due to this combination, these ternary cements are able to reduce some workability problems caused by the increased water demand of the calcined clay, and some benefits can be drawn from the carboaluminate formation. Some investigations confirm binder properties which are thoroughly fit for specific purposes, e.g. unreinforced concrete, even with a clinker replacement of up to 50 mass % (e.g. with 35 mass % of calcined clay and 15 mass % of limestone powder).

While the 1<sup>st</sup> International Conference on Calcined Clays for Sustainable Concrete (ICCCSC) in 2015 was mainly focussed on fundamental issues concerning the activation of clays, at the 2<sup>nd</sup> ICCSC in 2017 there was already a significant trend towards practical application and process engineering topics. The participating countries were Brazil, Cuba and India, where an important potential of this new type of cement can be seen in its use for comparatively simple components for infrastructural development (e.g. masonry blocks and frost-free road surfaces). Particularly advantageous is the fact that the expected growth markets for cement

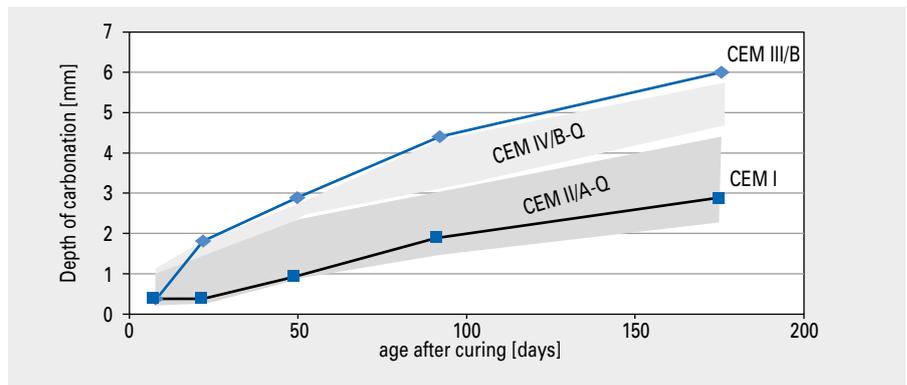


Figure 2: Ranges in depth of carbonation of concretes with CEM II/A-Q (20 mass % calcined clay) and CEM IV/A-Q (40 mass % calcined clay), related to typical CEM I and blastfurnace cement (CEM III/B)

sales and the largest accessible deposits of suitable clays are to be found geographically in the same regions.

The 3<sup>rd</sup> ICCSC, which took place in October 2019 in New Delhi, India, aimed to follow up on the scientific studies and experiences of the application of calcined clays in cement and concrete construction.

### Situation in Europe

Several cements with up to 55 mass % of calcined clay are still part of the European cement standard EN 197-1, but have only been produced on a small scale until today due to different reasons such as restrictions on use and lacking experience. One of the objectives of the current revision of the standard is a further reduction of the clinker factor by the production of cements with SCMs. Therefore, CEM II/C cements with 36 to 50 mass % SCM, for example, should be standardised. It is to be expected that cements with calcined clay as a main constituent will become more important. For this reason there is a need for further research to develop suitable composite cements for the European market.

A current research project deals among other aspects with the investigation of impure clays containing high levels of limestone. On the one hand, through carefully controlled calcination in the temperature range for calcining limestone the residual lime content is available for supporting the hydration of the cement. On the other hand, calcination at higher temperature can lead to the formation of reactive phases like Belite through reaction of the free lime with mineral phases containing SiO<sub>2</sub>. In a second test series, the clays have been treated with additives such as lime, gypsum or bypass dust before

the calcination step to determine their effects on pozzolanic activation. A clay sample doped with 9 mass % CaO calcined at 1200 °C shows an increasing amount of X-ray amorphous phases, and a respective higher amount of reactive Al and Si could be detected in comparison to a clay without additives.

XRD investigation on the hydration products of pozzolanic cements with the doped calcined clays reveals an increase in alite hydration of the clinker. This positive effect on the clinker hydration was also reflected in an up to 5 % higher relative compressive strength after 28 days of hydration.

Finally, an energy evaluation of different methods of calcining (rotary kiln, flash calciner, fluidised bed) will be conducted in cooperation with plant manufactures. Predictions about energy consumption of the production of cements with calcined clays can therefore be made, dependent on the technology used.

### Source:

- [1] International Energy Agency, IEA. *Low-Carbon Transition in the Cement Industry: Technology Roadmap*. Paris: International Energy Agency, IEA 2018



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