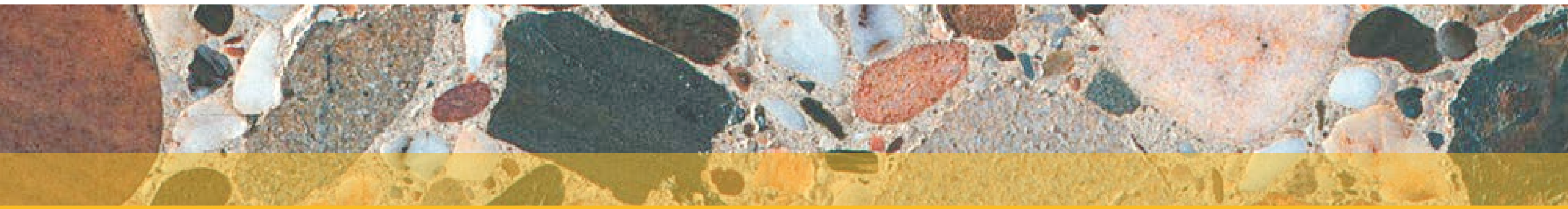
european cement research academy



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NEWSLETTER

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- Reduction of Mercury Emissions
  29–30 April 2015

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ECRA's research on carbon capture in the cement industry

Next steps towards an industrial-scale oxyfuel kiln

For more than five years ECRA has been working on carbon capture research with a strong focus on the technical and economic feasibility of this technology. This long term research project is currently in its fourth phase and the possibility of initiating an industrial-scale oxyfuel kiln is being examined. Opportunity studies for two potential sites are in preparation and will enable the Technical Advisory Board of ECRA to decide whether and how to proceed towards such a demonstration plant. ECRA benefits from its cooperation with the Norcem Brevik plant in Norway where different post capture technology providers test their equipment under realistic conditions. In addition, the ECRA academic chair, founded at the University of Mons in 2013, is an excellent source for findings from fundamental research in CO_2 capture and the different options for its reuse.

Most of the work packages in phase IV.A of ECRA's CCS project,"Further optimisation of an oxyfuel plant" have been finalised. The packages focused on a simulation study, an advanced cooler design, future oxygen supply and the experimental verification of the sealing potential. These work packages were intended to answer remaining questions which had arisen from the CCS project so far and prepare all necessary information for a potential next step towards a pilot plant.

An additional main focus was placed on a concept for an industrial-scale oxyfuel kiln, including its design, dimensioning and safety aspects. In particular, the question of the right size was to be answered as well as where the plant could preferably be located and how it could be built.

Steps towards an oxyfuel kiln

The outcome of its CCS project phases and work packages so far puts ECRA in the position to decide whether, and, if yes, under which circumstances this potential pilot kiln could be constructed. Against this background the Technical Advisory Board of ECRA agreed to proceed with the project stepwise and to identify a few potential sites at which such a kiln could in principal be built. Based on this, the concept for a pilot kiln will then be elaborated in considerably more detail, in particular with much more accurate cost estimates, as current estimates have been based on retrofitting existing equipment, which for many reasons will not be the best technical or economic approach.

Based on the work carried out, the optimum plant size is thought to be between 500 and 1,000 tonnes per day, depending on the specific site. In order to prepare ECRA for discussions with funding organisations such as the European Commission, the costs for such a kiln were estimated, taking into account not only the investment but also the expenditure for the test phase, i.e. the operation of the kiln. The major driver of the operational costs is oxygen, while the investment costs strongly depend on the plant environment and the equipment that needs to be installed or needs to be modified. In total, the budget required for a 500-tonne per day testing facility is between 40 and 60 million Euros, with an estimated uncertainty of ± 25 %.

These very high costs, not only for the demonstration kiln but for any full-scale oxyfuel kiln, constitute difficult circumstances for the future implementation of such a technology in the cement industry. While ECRA would be able to answer technical and economic questions, political guidance is necessary in order not to undermine the competitiveness of the plants which might apply such a technology.

Storage or reuse?

Whilst the storage of CO_2 is a difficult issue in many European countries, the question remains whether CO_2 cannot be reused instead of simply stored underground. ECRA has been cooperating with numerous partners for many years, and in 2013 it initiated a dedicated partnership with the University of Mons (UMONS), in which ECRA and UMONS sponsor the ECRA academic chair "From CO_2 to energy: CO_2 capture and reuse in the cement industry". Two PhD theses have in the meantime been assigned. The first thesis was started in 2013 with a focus on "CO_2 capture in cement production and reuse: Optimisation of the overall process". The second began in January 2014 with a focus on "The purification processes applied to CO_2 captured from the cement industry for conversion into methane and methanol". In addition, scientific studies have been carried out by undergraduate students.

On 26 November 2014 the first scientific event of the ECRA Chair was held at UMONS attended by more than 100 participants from around twenty different countries. Daniel Gauthier, the Chairman of the ECRA Technical Advisory Board, underlined the industry's view on carbon cap-

Daniel Gauthier, Chairman of ECRA's Technical Advisory Board, highlighted the role of carbon capture in the cement industry at the ECRA Chair event in Mons.

ture. He pointed out the challenges which the industry faces to further reduce its CO_2 emissions. While already existing measures like the increase of energy efficiency or the reduction of the clinker to cement ratio are widely applied and therefore limited in their contribution to further decrease CO_2 emissions, many so-called roadmaps see carbon capture as a coming breakthrough technology. For this reason ECRA has addressed the subject of carbon capture with its dedicated research project and has placed a special focus on its technical and economic feasibility. From today's point of view, carbon capture still remains much too expensive, but ECRA has decided to continue its research and is therefore now preparing the way for an industrial-scale oxyfuel kiln.

The event at UMONS not only addressed ECRA's carbon capture project. The EU Commission set CCS in the perspective of its research and funding strategy. Contributions on the post-combustion carbon capture project at the Norcem Brevik plant in Norway and current research on carbonate looping at the Politecnico University of Milan also highlighted the potential to capture CO_2 in the cement industry. The overall focus on the capture of CO_2 and its reuse was underlined by the example of using CO_2 as a feedstock in the chemical industry and a systematic approach taking into account the life-cycle analysis including the view on the still lacking political framework.

Challenging mercury: Emission limits and measures

Global abatement strategies to reduce mercury emissions

Mercury is a ubiquitous element which occurs naturally and is emitted through various anthropogenic sources. It is introduced into the cement production process, occurring in both raw materials and fuels. Concentrations may vary in a wide range from one raw material or fuel to another, from deposit to deposit or even within one quarry.

Due to its high toxicity for human health and the environment, mercury emissions are being addressed on a global level by the Minamata Convention on Mercury – a global and legally binding treaty targeting the reduction of mercury emissions. The import, export and production of products containing mercury, such as batteries, switches, some medical devices and cosmetics will be banned by 2020. Plans to reduce and eliminate mercury emissions from artisanal and small-scale gold mining will be established, promoting mercury-free alternatives. Plans to minimise mercury emissions from existing industrial mercury emitters such as coal-fired power plants, cement plants or waste incinerating plants are to be drawn up, while new facilities are to install Best Available Techniques (BAT).

Mercury emission limits

Emissions of mercury are regulated in many countries. Where emission limit values are in place, they range (with few exceptions) between 0.03-0.1 mg/m^3 as a daily average. In the EU, industrial mercury emissions are covered by the Industrial Emissions Directive (IED), which has been transposed into most Member States' legislations in the last two years. They are limited to 0.05 mg/m^3 for furnaces co-incinerating waste fuels, sampled over a period of 30 minutes to 8 hours. In the United States, new mercury emission limit values will come into effect from September 2015 on. Emissions for existing kilns will then be limited on a by-product basis to 27.5 kg per million (metric) tonnes of clinker produced. For new kilns, the limit is more stringent with 11.5 kg per million tonnes of clinker produced. These emission limits, based on a 30-day rolling average, are so low that the local cement industry is being required to examine new methods of mercury control.

Mercury in the clinker burning process

Extensive investigations have led to a profound understanding of the behaviour of mercury in the cement production process, which 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 and partly react with other gas constituents, and due to their high volatility leave the preheater with the hot gas stream, (**Fig. 1**). In raw mill-on operation a significant share of mercury compounds condense on the raw meal. To a smaller extent elemental mercury is adsorbed on the meal's surface. Low temperatures and a high dust load favour the adsorption. Adsorbed

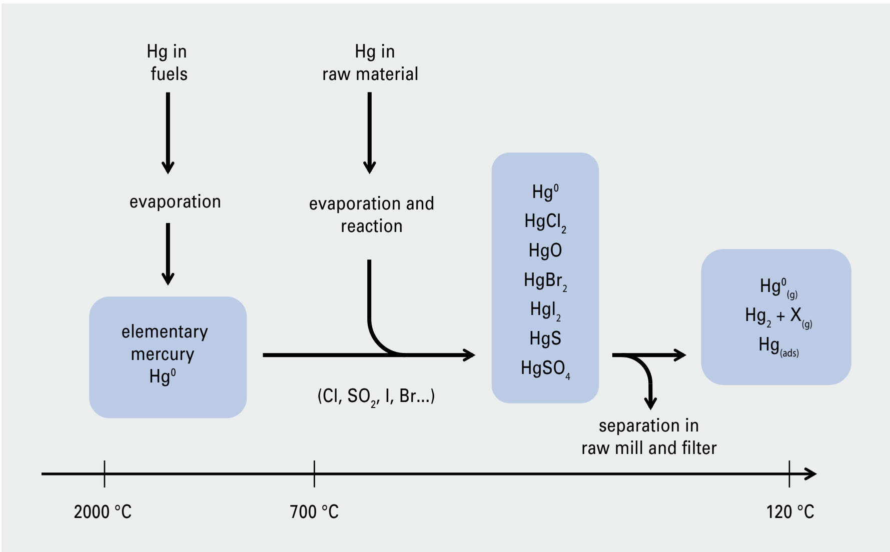

Figure 1: Behaviour of mercury and its compounds in the clinker burning process

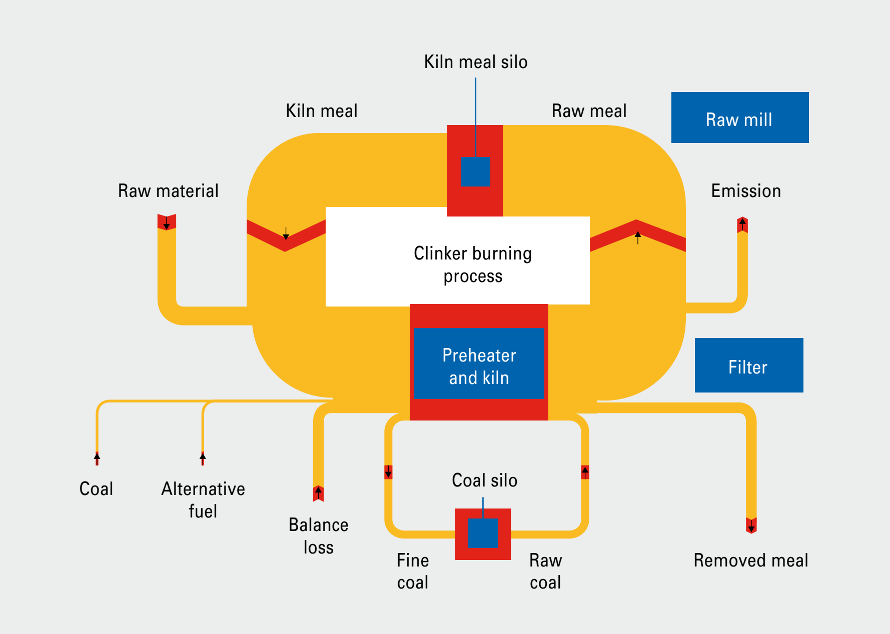

Figure 2: Mercury cycle balance in a clinker kiln

mercury then evaporates once more when raw meal and precipitated dust enter the preheater again, thus forming a mercury cycle between preheater, dust precipitator and raw mill where the kiln meal silo acts as a buffer, (**Fig. 2**).

Measures for mercury control

Within the process of implementing the Minamata Convention on a UN level, technical guidelines regarding BAT/BEP (Best Environmental Procedures) in relevant industry sectors are currently being developed. These guidelines aim at supporting governments, especially of developing/emerging countries, to later implement the Convention into national legislation. The draft guideline for the cement industry describes all known abatement techniques as well as monitoring/measurement techniques. The cement industry – represented by the Cement Sustainability Initiative (CSI) – is closely following the process. A major concern is that the assessment of the technologies does not sufficiently consider technical availability, industrial experiences and economic aspects. According to the guideline, the first measure is a careful selection of all input materials to the cement production process: While the composition of natural raw materials can hardly be influenced, a proper control of mercury contents in the alternative raw materials and fuels used is recommended.

Dust shuttling

If in spite of a careful input control mercury emissions are still an issue, a proven method is to limit the build-up of mercury cycles by the selective shuttling of precipitated dust. This is systematically applied in many cement plants in order to separate mercury from the process.

The efficiency of mercury removal is highest the lower the temperature in the gas stream and the higher the proportion of oxidised mercury. Therefore, in most cases the water or air quenching 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 dust particles. Accordingly, with a given quantity of dust, more mercury can be removed from the process. However, depending on the gas atmosphere, measures against corrosion have to be considered.

Sorbent supported dust shuttling

In cases where dust shuttling is technically restricted, the guideline mentions that it may be supported by the injection of sorbents into the gas stream upstream of a particulate matter control system. Their high surface area or specific chemical properties may increase the rate of mercury bound to particles. Activated carbon, for example, is commonly injected in power plants or waste incineration plants. However, in the cement industry, the technology is applied in very few plants and so far only in order to limit peak emissions in mill-off operation. As shuttled dust is often used as an additive in the cement mill, it has to be ensured that the cement quality is not harmed by the sorbent.

Oxidised mercury is adsorbed on dust and sorbents to a higher extent than elemental mercury, thus oxidising agents such as bromine or sulphur can even further enhance the sorbents' adsorption capacity. However, if shuttled dust is used in the cement mill, again a possible impact on the product quality needs to be considered. Sorbent injection in the clean gas would require an additional polishing filter, making this technology unacceptable costly.

Based on published results from lab-scale tests, alternative concepts to remove mercury from the process have been suggested recently by technology suppliers using a separate thermal treatment of precipitated dust in a separate installation. Mercury is re-volatilised and subsequently separated again by the use of sorbents. The scale of this installation would be smaller than a separate tail-end activated carbon injection system with a separate polishing filter for the entire exhaust gas stream. These techniques are not yet applied on an industrial level today. Therefore, because of the lack of experience these technologies are far from being be seen as BAT/BEP.

All measures suggested have to be seen in the light of the efforts to reduce mercury emissions on a global scale. Existing measures show that the cement industry already has proven means at hand to cope with the challenges faced. Beyond this it is constantly developing and investigating techniques to achieve sustainable mercury abatement.

ecra
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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