Felix Bartknecht and Florian Greiter, SICK AG, examines the effects of mercury emissions from cement plants and possible solutions.

MONITORING MERCURY

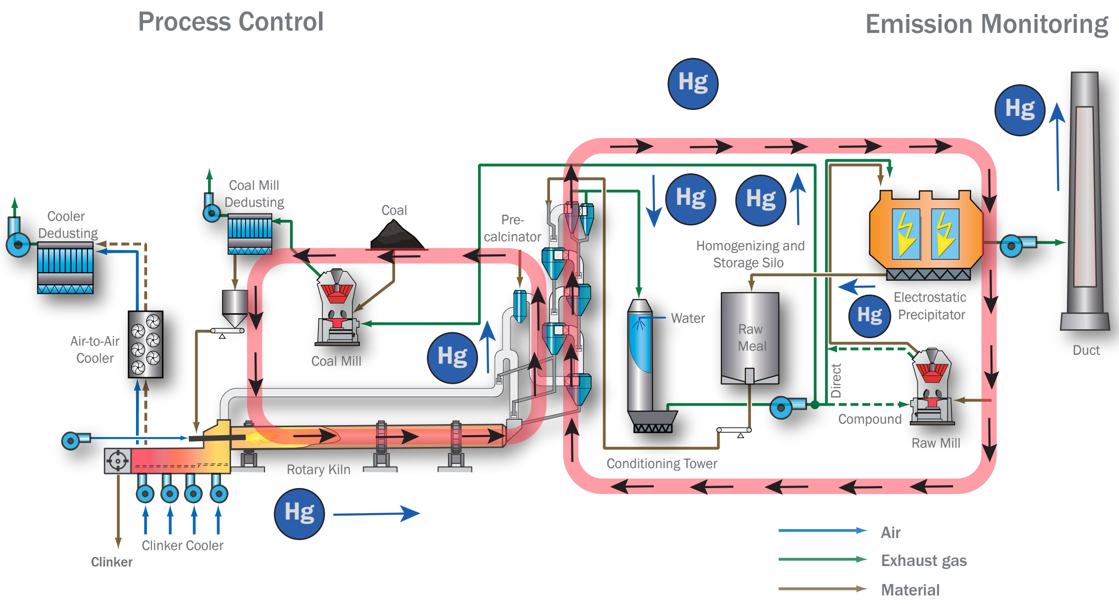
Introduction

It is hard to believe that mercury (Hg) was still being used to cure illnesses at the beginning of the 20th Century. Due to its deeply harmful properties, strict regulations now apply in a number of areas. Continuous measuring devices have been used to measure Hg emissions in waste incineration plants since the 1990s. More recently, the focus has been on Hg reduction from coal-fired power plants and cement plants, due to the magnitude of annual emissions from these facilities. However, pre-treating gases can drastically reduce actual levels of Hg. This is done through specific absorption methods, the use of wet scrubber technologies, or when plant operation modes are adjusted.

The dangers of Hg emissions

Hg and its compounds are extremely toxic for humans and the environment. It is an exceptionally volatile substance that can travel long distances in the atmosphere and enter the food chain, where it is accumulated in the form of methyl mercury. This extremely toxic form of Hg can cause cardiac and respiratory problems, as well as damage to the central nervous system.

When compared with previous decades, it is clear that Hg emissions have increased in the last couple of years. This is mostly due to small-scale gold mining or quarrying processes and the use of coal as main combustion fuel. The cement industry contributes approximately 10% of all manmade Hg emissions, with an average



Hg cycle: Hg emissions are higher in direct operation than in compound operations.

emission factor of 35 mg/t of cement produced, adding up to a total emitted quantity of 190 tpy. The growing demand for construction materials worldwide puts great focus on the cement industry and on Hg as a major pollutant. As a result, UN climate policies are now enforcing stricter requirements to keep emissions of this toxic substance to a minimum. In January 2013, a total of 140 countries signed up to the Minamata Convention in Geneva, Switzerland, pledging to limit the mining of Hg, cut emissions, and monitor waste.

Hg in cement production

In cement plants, gaseous Hg can be released by fuels containing Hg, such as coal, petcoke and waste fuels, or by raw materials, such as limestone or various additives. Even if the concentration in fuels and materials is very low, the total amount of Hg emitted is significant. The Hg from raw materials and fuels is volatilised in the clinkering process and exits the kiln system in the vapour phase. Elemental Hg can form various compounds when combined with other elements. As the Hg vapours cool down at colder spots inside the pyroprocess, the circulating Hg exists in the kiln system in both its elemental and oxidised forms.

Hg measurement technologies

Hg mass balances are needed for a continuous clinker quality control and to check emission values. There are a number of devices available to ensure users get accurate measurements of emissions or process gases. However, not all of these are suited to meet the complex UN requirements. Different technologies are available to measure Hg in process and emission gases, all of them based on devices that extract part of the gas stream in order to determine Hg concentrations. All systems consist of a heated gas extraction probe and a sampling filter to reduce dust ingress into the measurement system. Depending on the device, the sample may be diluted with ambient air or nitrogen in order to reduce cross-sensitivities during gas analysis. Afterwards, oxidised Hg is converted into elemental Hg, as only elemental Hg can be detected by analyser technologies. This conversion is done with the wet chemical method, using a solution of stannous chloride, a heated bromide converter, or a high-temperature thermal converter, using temperatures of more than 1000°C to crack all Hg compounds. Next, an accumulation of Hg is sometimes needed. This can be done by using gold foil, which is alternately charged and discharged with Hg, in order to concentrate the amount of detectable Hg. In addition, reference gas can be used to eliminate potential cross-sensitivities. Finally, Hg concentration is measured by using different spectroscopy technologies, whereby atomic absorption spectroscopy (AAS) and atomic fluorescence spectroscopy (AFS) have won strong recognition.

SICK measurement technology

SICK has developed an Hg measurement device, based on a high-temperature thermal converter, primarily to reduce overall running costs, to keep maintenance at the lowest level, and because the high-temperature converter showed the best performance during tests. The MERCEM300Z Hg measuring system monitors Hg emissions in flue gases, with high reliability within the smallest measuring ranges. Due to its rugged housing, MERCEM300Z is suitable for use in harsh industrial environments. The complete extractive system is designed to meet national and international regulations and directives. There is no need for a dilution, accumulation, or separation step, which has a significant impact on overall running costs.

SICK uses an internal cross-sensitivity correction, based on the Zeeman effect. Using this effect, the continuous Hg measurement device, MERCEM300Z, generates the measuring and reference signal, using an Hg electrodeless discharge lamp and a static magnetic field. Using the same source to generate measuring and reference signals, cross-interferences are compensated immediately. The device combines thermal conversion at temperatures of around 1000°C, with the fast measurement of trace or low Hg concentrations directly inside the heated converter. This enables the device to supply reliable and continuous readings for actual flue gas concentrations. Continuous measurement directly inside the hot converter, combined with AAS, is patented.

There is no chemical conversion, no particulate converter, and no gas cooling that may quickly distort the measurement result. Using Zeeman cross-sensitivity correction gives the benefit of a direct Hg measurement, with low operating costs and low maintenance requirements. MERCEM300Z is certified according to EN 15267 and it can measure total Hg (oxidised and elemental) concentration with an approved measurement range from 0 – 10, up to 0 – 1000 µg/m³. Thus the device can be used for emission and process gas monitoring applications without any hardware changes.

Furthermore, this is a flexible device that uses measurement gas lines with a length of up to 65 m. The optional sample point switching function enables measurement at multiple extraction points, using only one analyser. It is a cost-efficient solution to check Hg removal efficiency of e.g. wet scrubber systems.

The cyclical behaviour of Hg

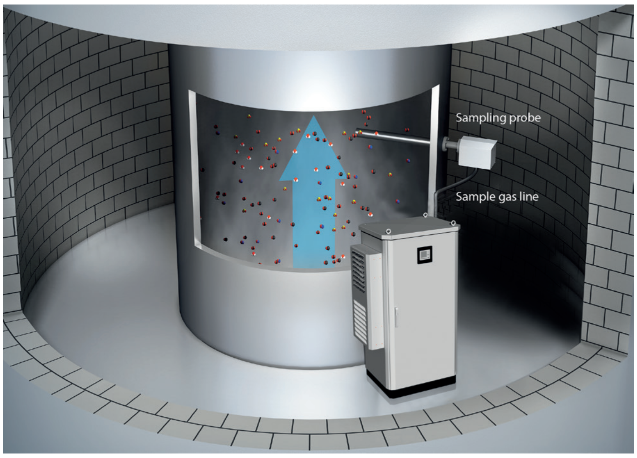
Hg is cyclical within the cement manufacturing process. Almost all of the Hg from raw materials and fuels is vaporised as elemental Hg in hot combustion zones. The elemental Hg often combines with other elements in the gas streams to form various Hg compounds, which adsorb more readily into dust than elemental Hg. As exhaust gases are used to pretreat fuels and raw materials, this leads to different Hg cycles, e.g. filter dust and fuel mill cycles. When the raw mill is off during direct operation, the preheater exhaust gas goes directly to the main filter. This means that a big share of waste heat is not utilised in other ways, leading to high gas temperatures, high stack emissions, and a higher concentration of Hg being adsorbed to the filter dust. In addition, there may be an increase in Hg concentration in the fuel mill cycle, if waste heat is used to dry coal or coke. That is why cement plants often utilise the kiln exhaust gases for raw material drying. This is usually accomplished in a mill, where there is extensive contact between the exhaust gases and the ground raw materials. Combined with lower gas temperatures, this creates a high degree of Hg adsorption on the dust particles. The adsorbed Hg is then returned to the kiln feed silo with the raw mill product, creating a high-concentration Hg cycle, while temporarily reducing total Hg stack emissions.

Hg abatement technologies

There are various ways to reduce the Hg emissions of a cement plant. First, it is possible to select raw materials, additives, and fuels with lower Hg concentrations. In addition, plant operators can reduce fuel consumption by upgrading a plant with state-of-the-art-technology, to improve efficiency in thermal energy usage. However, operational measures, also called primary abatement technologies, and the possibility of using additional equipment, such as flue gas treatment systems, can also reduce Hg emissions.

A widely used operation procedure is dust shuttling, also known as dust purging or dust bleeding. Plant operators remove the Hg-laden filter dust from the kiln system, without returning it to the combustion zones, where Hg has the possibility to evaporate again. This breaks the Hg cycle. Often the filter dust can be used later on as a cement additive. Due to its high volatility, Hg removal

Left: MERCEM300Z for measurements outdoors at temperatures from -20 – 50°C. Optimised industrial design for measurements in harsh ambient conditions near to where the sample is taken – with integrated air conditioning. Right: MERCEM300Z Indoor: for measurements in air-conditioned rooms at temperatures from 5 – 35°C. With a compact standard design, it is possible to arrange additional cabinets on the left-hand side.



MERCEM300Z measures using hot extraction. The flue gas is extracted using a sampling probe and is transported to the analyser via a sample gas line. All components in contact with the sample gas, such as the probe, sample gas line, and converter in the analyser are heated above the dew point.

efficiency is highly dependent on gas temperatures. Therefore, dust shuttling is most effective during direct operation, when the raw mill is off, as the collected dust comes directly from the preheater, which can have significantly higher Hg concentrations. When cement producers do not extract, but instead feed the filter dust back to the kiln system, the consequences are high Hg emissions. Dust shuttling is a simple measure that can significantly reduce Hg emissions by up to 40%.

Sorbents can be used to enhance the adsorption of Hg from the exhaust stream. These specially developed materials are injected into Hg-laden gas streams, typically ahead of the main filter. The sorbents, e.g. activated carbon, can capture a large percentage of Hg in the gas stream and can be shuttled with the filter dust. Of course, lower temperatures enhance Hg removal efficiency, so selective catalytic reduction systems or wet scrubbers can be beneficial. The collected dust can either be used as a cement additive or must be disposed of, because activated carbon often makes the final concrete unsuitable for infrastructure applications. Real-life applications show that when certain sorbents are injected into the gas streams, Hg removal efficiency of up to 95% can be reached when dust shuttling is applied.

Modern cement plants go one step further, making use of the high volatility of Hg on the dust particles and treating the filter dust by heating it up with waste heat. Thereby, filter dust can be desorbed and reused, while sorbents are used to enrich the Hg content in a special Hg exhaust gas stream. This way Hg can be removed from the system very effectively by breaking the Hg cycle.

Conclusion

In order to control Hg emissions, advanced quality control and Hg mass balances have to be made. It is necessary that the Hg measurements are well executed so they represent real process conditions. Due to high fluctuations in Hg concentration in the exhaust stream, e.g. due to the effect of direct and compound operation, a continuous measurement of this exhaust stream is needed. Analysers therefore must be applied that can be used for very low and very high measurement ranges. The MERCEM300Z from SICK is suitable for process and emission monitoring applications, and it has shown its practicability, mainly due to low maintenance demand and reliable performance. Using this analyser, the total and oxidised Hg can be measured. In addition, taking the information from continuous Hg measurement, cement producers can control the industrially proven Hg mitigation measures. By doing so, cement producers have the opportunity to minimise Hg emissions, while complying with local emission regulations.

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