Capturing mercury in CKD

by Christopher Poling, Mercury Capture Systems, USA

As cement plants are faced with the need to drastically reduce mercury emissions, technological advances enable the lowering of such emissions from cement kiln exhaust stacks and other sources.

While cement plants use common compliance methods such as reducing mercury inputs, dust shuttling and sorbent injection to reduce mercury emissions, capturing mercury directly from a gas stream is fundamentally different from any control method available today.

Developed over the past five years by a team of cement professionals, Mercury Capture Systems (MCS) eliminates over 99 per cent of mercury within cement kiln dust (CKD), allowing the CKD to remain within the kiln system, eliminating the need for dust shuttling and its potential long-term liabilities. As well as helping adhere US cement plants to the 2015 NESHAP regulations, it also opens up new opportunities in raw material use for the forward-thinking cement producer.

In addition the process can be applied to coal fly ash, activated carbon, clay and other industrial dusts which are currently unusable by cement plants due to their high mercury contents.

The use of MCS results in a virtually mercury-free raw material and an insoluble concentrated form of mercury, which can be safely cast into concrete, disposed of or sent for recovery.

Figure 1: MCS Thermal Desorbtion Gas Reactor (November 2014)

The first-generation Thermal Desorbtion Gas Reactor (TDGR) was built in the last 18 months and is designed to function independently of its parent cement kiln (Figure 1). It can process between 5-20tph of material, depending on the material input temperature and moisture content.

The ancillary equipment required as part of the demonstration work consisted of a dust storage silo, transfer equipment, dust collector, discharge cooling and a bypass mercury condenser. For installations integrated with a cement kiln or power plant, only the thermal desorber, gas reactor and a small dust collector are required.

The average result from the initial start-up run confirmed over 99 per cent of the mercury was removed from the CKD (Figure 2).

Applying this precise process to any industrial dust generates very similar

Figure 2: average mercury reduction using CKD and MCS process

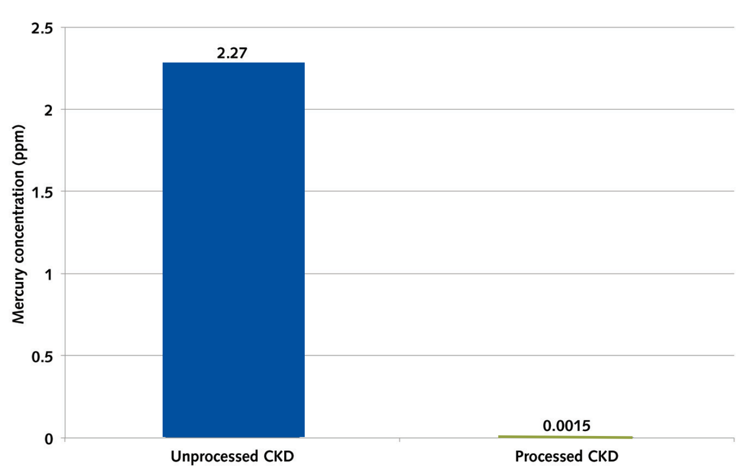

Figure 3: MCS gas reactor

reductions. The mercury is removed from the material. The material can then be used in the kiln without contributing to mercury stack emissions.

The mercury, which has been desorbed and contained in a concentrated gas stream, is sent to the MCS Gas Reactor (Figure 3). The Gas Reactor is essentially a modified particulate scrubber with a constantly-recirculating stream of reagent catalyst. In the normal configuration, vaporised mercury is carried into the scrubber and then removed from the gas stream through contact with an aqueous reagent catalyst solution. As part of the MCS process, mercury particulates are formed when the reagent catalyst comes into contact with the mercury in the gas stream. The generated mercury particulate is then collected in the reservoir tank. The unspent reagent catalyst solution is filtered and re-introduced to the scrubber. The chemical reaction occurs on a molar basis, which allows the reagent solution to be continuously recycled back through the gas reactor until it has been fully reacted.

The gas stream was measured before and after the gas reactor (Figure 4). All testing was performed by a third-party laboratory using a combination of handheld Jerome mercury analysers, total mercury sorbent traps and speciated mercury sorbent traps. The results were impressive. Since the handheld units are only capable of measuring up to 0.999ppm in the gas stream, the upper value was not measurable after the units exceeded their maximum saturation. The handheld units showed a mercury reduction of 88 per cent. The sorbent traps measure the gas stream only and are much more accurate. The results are even more impressive with mercury reduction exceeding 99 per cent.

According to MCS data collected over the past five years, thermal desorption generates both ionic and elemental mercury. The reagent catalysts have demonstrated very effective results in capturing both forms of mercury directly from a gas stream.

What does this mean for a cement kiln? Eliminating 1ppm of mercury from 18,000t of raw material or CKD will lower the mercury input to a kiln by 32lb/year. This is the same as processing the CKD generated by a plant during its raw mill-down days. This indicates that the MCS process can be tailored for any plant and may run continuously or as required to lower the mercury inputs to a kiln.

MCS vs dust shuttling

Dust shuttling was originally proposed as a low-cost option for cement kilns by the US Environmental Protection Agency (EPA). This is reportedly an easy way to reduce the mercury input to a kiln by transferring the CKD directly to the finish mill for intergrinding with clinker and including the mercury directly into the resultant concrete. All studies have confirmed that once the mercury is within the concrete it is encapsulated.

The question has always been how much of the mercury actually gets into the concrete? A recent study by the University of Florida entitled: "Characterization of Vapor Phase Mercury Released from Concrete Processing with Baghouse Filter Dust Added Cement", which was published by the American Chemical Society, indicates that up to 70 per cent of the mercury absorbed onto CKD never makes it to the actual concrete. The study went on to indicate mercury monitors would eventually be required for cement finish mills which are incorporating mercury-laden CKD.

In addition to the potential cost for monitoring, potential liability and the implied newly-regulated mercury emission point, there is also the subject of cost and quality. Dust shuttling removes a raw material from the kiln which must be replaced by other raw materials. The CKD has already been processed, calcined, and chemically recombined. The cost of CKD is effectively the same as clinker and also carries the same carbon footprint. Cement kilns are striving to reduce the clinker/cement ratio through the use of various cementitious process additions and intergrinding limestone. Dust shuttling does not contribute to a reduced carbon footprint and is a relatively high-cost process addition.

MCS can eliminate the need for dust shuttling by providing a low-cost, virtually mercury-free raw material back to the cement kiln on a routine basis.

Mercury capture effectiveness:
what does this mean to a cement plant?

- Analysis of mercury concentrations within various cement kiln dusts have shown a range of 0.250-41,000ppb Hg.
- 1000ppb Hg removed from 1t of CKD represents 0.0020lb Hg

$$1000\text{ppb Hg} = 1\text{ppm Hg} = \frac{1\text{lb Hg}}{1{,}000{,}000\text{lb CKD}} = \frac{1\text{lbHg}}{500\text{t CKD}} = \frac{0.0020\text{lb Hg}}{0.0020\text{lb Hg/1t CKD}}$$

- Cement kilns produce up to ±20tph of CKD

$$\frac{0.0020\text{lb Hg}}{1\text{t CKD}} \times \frac{20\text{t CKD}}{1\text{ raw mill down hours}} \times \frac{905.9\text{h raw mill down hours}}{1\text{ year}} = \frac{32\text{lb Hg}}{1\text{ year}}$$

MCS vs sorbent injection

Sorbents are increasingly being used through direct injection into the cement kiln baghouse to raise the amount of mercury that is absorbed by the CKD. Many of the current sorbents are now reportedly concrete-friendly and in most cases, the total volume of used sorbent is relatively small, which reduces quality concerns.

As part of the MCS development process, SCB International Materials has successfully reduced mercury levels in a gas stream prior to a cement kiln baghouse by 55 per cent using its reagent catalysts along with an existing downcomer water injection system. There was no need for additional sorbents and additional testing confirmed a 25 per cent increase in the mercury concentration within the CKD. More work will be conducted on this process.

For plants that are planning to use sorbent injection, the MCS process will still work to clean the combined CKD/sorbent stream. MCS Thermal Desorption has been proven effective at concentration levels as high at 61ppm Hg.

Combined MCS processing

The combined MCS process would allow any cement kiln to remove the mercury from its CKD, protecting clinker consistency, cement quality and customer relationship. When the system is not being used to process CKD, it could be employed to remove mercury from alternative raw materials. As a result, the cement plant can use high-mercury fly ash or process spent sorbents into raw materials at low cost. This would reduce the plant cost per tonne, while increasing the range of the available raw materials it is able to use in its production process.

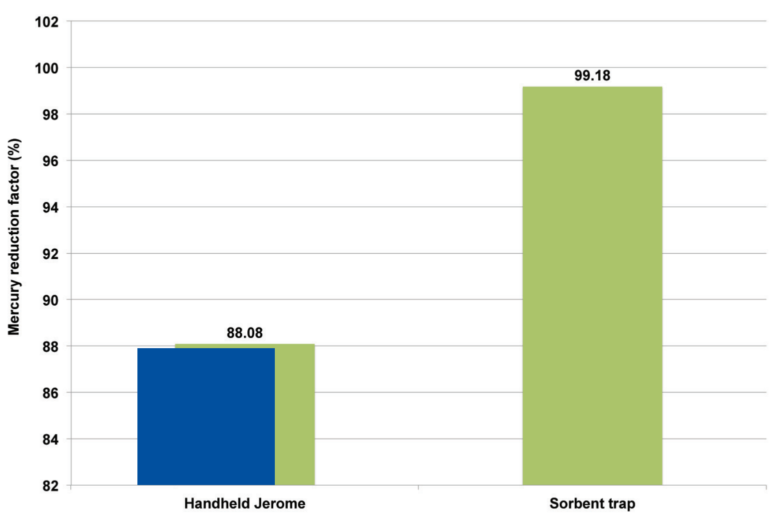

Figure 4: average mercury reduction across the MCS gas reactor

Conclusion

Mercury Capture Systems is an innovative method developed to reduce mercury emissions from cement kiln exhaust stacks and other emissions sources. The technology can be adapted to remove mercury from coal combustion products, spent powdered activated carbon and other raw materials without the use of additional sorbents. Test results confirm the ability to capture both elemental and ionic forms of mercury. Mercury Capture Systems uses a chemical reagent catalyst that not only affects mercury but also all heavy metals.

The process employs thermal desorbtion to separate mercury from CKD and forms a non-leachable sulphide in a separate gas reactor. This allows the CKD, essentially free of mercury, to be recycled and used anywhere within the process. Results from the TDGR confirm 99 per cent mercury removal from CKD and a corresponding 99 per cent reduction in mercury from the gas steam. This breaks the mercury cycle within a cement plant and allows cement kilns to meet the upcoming NESHAP regulations, which will be in place in September 2015.