PAC for mercury control

Dry sorbent injection is a well-proven mercury control technology used successfully in Portland cement manufacturing. In particular, this article discusses powdered activated carbon (PAC) injection for mercury emission control in cement plants to satisfy the National Emission Standards for Hazardous Air Pollutants (NESHAP) requirements.

■ by **Dr Prasanna Seshadri**, *PEC Consulting Group LLC, USA*

During OPC clinker production, the raw feed and fuel undergo physical and chemical transformations that produce intermediate solids, liquids and gases. Some of these species, especially those in gas phase, are classified as hazardous air pollutants (HAPs) due to their detrimental effect on both the environment and human health. The uncontrolled emission of these species into the atmosphere, especially those present in trace quantities, is a major concern. One such example is mercury (Hg), a trace pollutant and classified neurotoxin of global concern, especially in its vapour form.

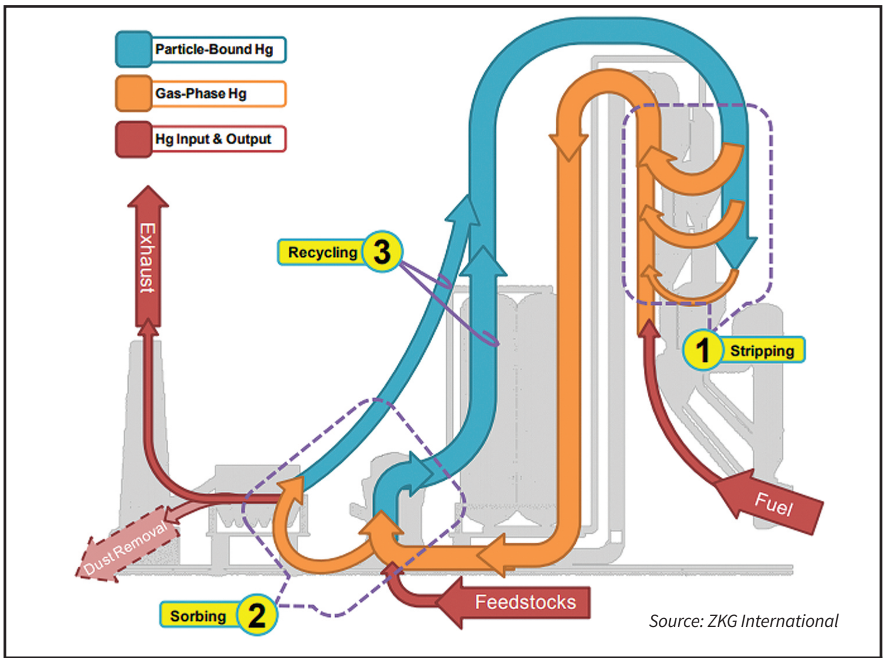


Figure 1: mercury pathways in the cement production pyroprocess

Mercury emissions in US cement plants

In the USA Hg is currently regulated under the National Emissions Standards for Hazardous Air Pollutants (NESHAP) 40 CFR Part 63 for OPC manufacturing plants, set out by the US Environmental Protection Agency (EPA). On 21 September 2017, the EPA set Hg emission limits of 55lb (25kg)/Mt of clinker produced in existing kilns and 21lb (9.5kg)/Mt of clinker produced in new kilns.[1]

Even though coal-fired power plants are the dominant source of Hg emissions in the US, cement plants are also a significant contributor, accounting for approximately 10 per cent of total atmospheric Hg emissions.[2] However, unlike coal power plants, Hg emissions in ordinary Portland Cement (OPC) manufacturing are from both raw materials fed to the kiln and the kiln fuel, especially coal-fired kilns. For example, limestone used for OPC manufacturing can have Hg concentrations in the range of 5-1121ppb,[3] while coal Hg can also range anywhere between a few ppb to over 1000ppb.[4] Due to the different processes in clinker production, mercury concentrates within the cement plant while only a small portion is continuously emitted. As a result, cement kilns can employ innovative and cost-effective Hg control methods that may not be practical or feasible for coal-fired boilers.

Hg emissions from kilns are heavily influenced by the raw material grinding operation. As shown in Figure 1, when the raw mill is operating, Hg transformation follows a path of vaporisation, followed by vapour-to-solid sorption and recycling of the captured dust as kiln feed. This internal loop increases overall Hg concentration in the raw meal by several factors compared to the original amounts fed to the system. This concentration loop provides internal Hg control that only functions while the raw mill is operating. However, operation of a cement facility requires weekly mill maintenance, typically around 20h/week, while the kiln continues to produce clinker. Therefore, when the mill is off, stack Hg emissions will significantly increase and require additional downstream control measures to meet NESHAP requirements. Technology choices are manifold and vary based on plant operating conditions.

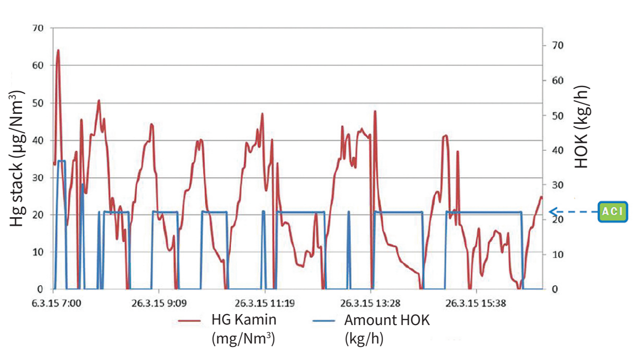
Mercury control technologies

Range of options available

The options for Hg control include a wide range of technologies, some of which are successfully adapted to other industries, especially coal-fired power plants. Additionally, technologies have been developed specifically for OPC manufacturing plants, taking into account operational parameters such as raw material and fuel properties, kiln type and raw mill operation. These include dust purging/shuttling, sorbent injection and the effective use of other pollution control technologies, such as a wet scrubber, to also aid in Hg capture. Dry sorbent injection (DSI) is a particularly effective technology that is actively practised in the coal-fired power industry and the use of powdered activated carbon (PAC) as a sorbent is gaining traction in other heavy industries such as cement plants.

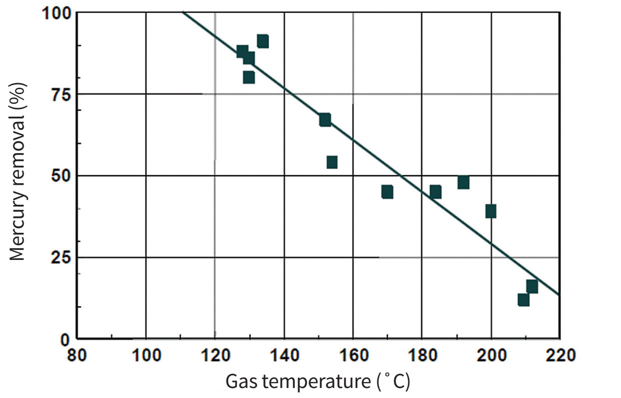
Activated carbon is extremely efficient, and its use also eliminates the need

Figure 2: mercury reduction with activated carbon (HOK™) injection and dust shuttling



Source: Roland Melerski, Lafarge Wössingen, ECRA Seminar, 2015

Figure 3: gas temperature vs mercury adsorption capacities on sorbent



Source: B Kirchartz, VDZ, 1994

for liquid chemicals used in scrubbing systems that may pose a site hazard and would require additional processing for hazardous waste disposal.

Activated carbon injection

Reducing Hg emissions by PAC injection has been successfully demonstrated as a competitive technology at a growing number of cement plants. While dust shuttling is the most common form of control measure used in OPC plants, dust shuttling combined with activated carbon injection can achieve higher Hg removal efficiencies than dust shuttling alone, especially when additional control is required to meet emission standards. The performance of activated carbon is related to its physical and chemical characteristics, which play a significant role in the removal of Hg and possibly other trace species. PAC has a relatively-higher surface area and pore volume compared to a lot of other sorbents used for gas separation. This allows for low injection rates to achieve moderate to high Hg capture efficiencies.

PAC is also available as halogenated PAC, which is used to capture Hg from gas streams when it is present in its elemental form (Hg^0). Research has shown that the oxidised form of Hg (Hg^{2+}) is preferentially adsorbed on solid surfaces, while the elemental form is not so easily captured. Elemental Hg is poorly adsorbed on most surfaces, including cement kiln dusts, and would need to be oxidised prior to capture. Impregnating PAC with a halogen enables oxidation of the Hg in the gas stream and subsequently it is captured on the PAC surface. A study[5] conducted by Cabot Norit Activated Carbon Corp shows that its sorbent with improved halogenation achieves up to 88 per cent Hg and at a reduced rate of activated carbon sorbent injection (44 per cent reduction by weight).

PAC injection normally requires a secondary dust collection unit to minimise dust loading in the gas stream. Carbon injected into the duct can capture Hg both in flight as well as in the dust collector as the sorbent builds a dust cake. In many cases, carbon captured in the dust collector hoppers can be reused (or even regenerated) multiple times until the material reaches saturation. The rate of carbon injection varies depending on raw mill operation and can be anywhere between a few pounds to over 40lb (18kg)/h. While this configuration is highly efficient and can achieve over 95 per cent total Hg removal (as shown in Figure 2)[6], it also increases the plant's capital expenditure due to the addition of the secondary dust collection device.

Like any other technology, the use of PAC in certain plants may not yield desired results or prove to be a cost-effective option for Hg control as observed in the case of testing carried out for kiln gases. Since carbon capacity depends on factors such as temperature, overall Hg concentration and flue gas composition, overall efficiencies may vary depending on plant operating conditions. For example, as shown in Figure 3, sorbent adsorption capacity is most efficient between gas temperatures 120-140˚C and is drastically reduced when temperature exceeds 160˚C.

Additionally, competing species such as SO_2 and SO_3 may affect capture efficiencies as they are present in significantly-higher concentrations and can also get adsorbed at a much quicker rate than Hg. However, technology advancements have enabled the development of "tolerant" activated carbon-based sorbents[4] where the effect of SO_2/SO_3 in the flue gas was negated and over 90 per cent Hg control was achieved at reduced rates of carbon injection.

Conclusion

While every OPC plant presents its own set of challenges for emission control, multiple options are available to meet the plant's requirements for meeting environmental regulations.

In terms of Hg control, more than a few options are actively practised in the cement industry, including PAC injection. PAC possesses the required physical properties and can be chemically modified to capture elemental and oxidised Hg in the gas stream. It is a fairly-efficient technology that is well established in the coal-fired power industry and can also be an economic option in certain cement plants. ■

REFERENCES

[1] US GOVERNMENT (2018) '40 CFR Part 63 – National Emission Standards for Hazardous Air Pollutants From the Portland Cement Manufacturing Industry Residual Risk and Technology Review' in: *Federal Register*, 83 (143), p35122 – https://www.govinfo.gov/content/pkg/FR-2018-07-25/pdf/2018-15718.pdf

[2] KNOTTS, J AND GUENIOUI, K (2017) 'The mission against mercury' in: *WC*, August, p93-96.

[3] US GOVERNMENT (2009) '40 CFR Part 63 – National Emission Standards for Hazardous Air Pollutants From the Portland Cement Manufacturing Industry – Proposed Rule' in: *Federal Register*, 74 (86), p21135-21192 – https://www.govinfo.gov/content/pkg/FR-2009-05-06/pdf/E9-10206.pdf

[4] HILLS, LM (2006) *Mercury and Lead Content in Fuels: A Literature Review*. Skokie, USA: PCA, 11p.

[5] SATTERFIELD, J (2017) Effective mercury sorbents in: *ICR*, April, p84-86.

[6] BARTKNECHT, F (2018) 'Continuous Process Gas and Mercury Emission Monitoring' in: *Proceedings 8th International VDZ Congress*, Düsseldorf, Germany, 26-28 September.