Alternatives to ACI

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On 9 September 2010, the US Environmental Protection Agency (EPA) finalised regulations that dramatically lower emission limits for new and existing cement plants in the USA, but what are the alternatives to activated carbon injection (ACI) for lowering mercury emissions?

Among the pollutants with new or dramatically lower emission limits is mercury (Hg). Table 1 summarises these new limits for mercury.[1] Beyond the new limits, the EPA is requiring the use of mercury Continuous Emission Monitors (CEMs) to continuously monitor mercury emissions. All mercury CEMs must meet the requirements of Performance Specification PS 12A.

Control strategy development requires data

As a priority, the development of a control strategy requires plant specific data and not just any stack data. Mercury emissions from cement plants are well known to vary as much as and sometimes more than an order of magnitude over time. This is not because of changes in input concentrations but rather because of a build-up of recycling mercury in the system that periodically flushes, most often when the raw mill is unoperational for routine maintenance.

A CEM is required for initial data gathering to monitor mercury emissions over at least a few weeks and preferably over a month or more. As the data is being gathered, operating experience with the CEM will also play a key role in developing the long-term compliance strategy for the plant.

Further, while the CEM data is gathered, it is important to also obtain samples of all raw materials used in the kiln system as well as materials such as cement kiln dust (CKD) which are recycled in the system. Information on total and types or 'speciated' mercury from these samples should play an essential part in developing the emissions control and compliance strategy.

It is also very important to gather data that speciates mercury emissions. Not all CEMs can do this and none of them are designed to detect particulate-bound mercury. An excellent method for speciating mercury is ASTM D6784[2], also referred to as the Ontario Hydro Method. EPA Method 29 can provide only limited and unreliable speciation information. It is recommended that ASTM D6784 be performed while CEM data is being gathered with both the raw mill on and off. Once all of this data and raw material analysis has been performed, a model of the mercury inputs, cycling and emissions can be developed and used in creating an emissions control strategy.

Table 1: 2010 NESHAP Portland cement final mercury limits 40 CFR 63.1343(b)(1)

Source	*Operating mode*	*Mercury limit*	*Units*
Existing	Normal	55	lb/Mt clinker
Existing	Startup and shutdown	10	µg/dscm
New	Normal	21	lb/Mt clinker
New	Startup and shutdown	4	µg/dscm

Material substitution – control strategy number one

At first glance this control strategy would appear to be both self-explanatory and easy to understand and implement. However, this is not always the case. Mercury emissions from cement kilns and potential control techniques are highly dependent on the oxidation state of the mercury and the point in the process where the material is entering the kiln. Looking only at total mercury, a plant might find a substitute for a raw material that is the largest contributor of mercury to the system only to find no change in mercury emissions. It is quite possible that all of the mercury emissions are coming from a different material or point in the process and the primary mercury is in an oxidised form already being efficiently captured in the existing particulate emission control systems.

It is often assumed that all mercury

input into a cement kiln exits the stack with little or no capture efficiency. This is not true. Older technology wet kilns with electrostatic precipitators (ESPs) have been seen to capture up to 95 per cent of mercury input to the kiln. Modern precalciner kilns with inline raw mills have demonstrated high capture efficiency in the raw mill absorption process only to have the mercury flushed from the system while the raw mill is unoperational. Figure 1[3] provides an example of modelled mercury input rates to a kiln over time based on recycling load build-up and flushing that occurs during raw mill off periods.

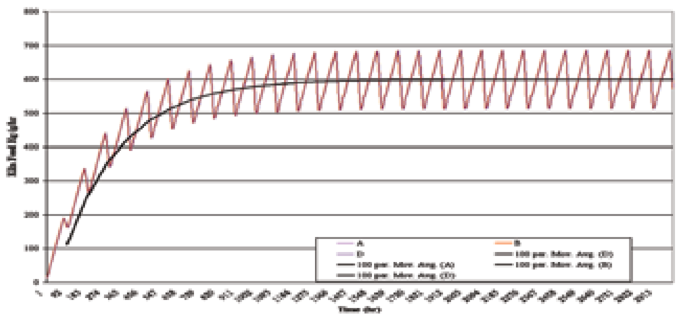
These types of facts strongly indicate that control techniques are not as straightforward as the EPA suggested activated carbon injection (ACI) method, nor need they be as expensive and environmentally detrimental as ACI.

Slipstream strategies

Slipstream strategies, also referred to as a 'mercury valve', for mercury control have been developed and used for about 10 years now, longer than that for thallium control. It was initially hypothesised that the extraction of a slipstream of CKD from an existing baghouse while the raw mill was down would be the most efficient way to break the mercury recycle loop and cut mercury emissions. Detailed dynamic modelling of a precalciner with an inline raw mill and subsequent testing demonstrated otherwise. It turned out that a continuous slipstream from the main baghouse under all operating conditions, raw mill on and off, was the most efficient method of controlling long-term mercury emissions. This technique has the potential to reduce mercury emissions 30-70 per cent below uncontrolled levels.

Diverting a small slipstream of continuously withdrawn dust from the main baghouse to the finish mills instead of back into the kiln system has numerous other operational and pollution control advantages. In addition to controlling mercury emissions, this technique can help to limit emissions of thallium and the associated dangerous levels of thallium that can build up inside a baghouse. Reductions in condensable particulate emissions are likely using this technique. Operational problems that arise from recirculating loads of chlorides, sulphur and alkalis are also often averted when this technology is implemented.

Figure 1: cement kiln modelled mercury feed rate



There are alternate slipstream strategies that can be used for kilns with specific kiln designs and operating conditions or in conjunction with other control strategies which will be discussed below.

Scrubber technologies without waste disposal

The EPA has suggested that in addition to ACI, wet scrubber technologies could be used to help control mercury emissions. While such technologies have been successfully implemented in the power industry this control method – like ACI – generally produces waste that requires disposal. After all the years of work that the cement industry has done to limit and often eliminate the need for industrial waste disposal, the author suggests that this 'promotion' of waste-creating technology by EPA is a huge disappointment.

There are effective alternatives to wet scrubbers which have added benefits and do not produce waste that cannot be used in the cement finish mills. The technology with the greatest potential for aiding in mercury control as well as in control of numerous other pollutants is a Circulating Fluidised Bed Absorber (CFBA). FLSmidth has an example of this technology called a Gas Suspension Absorber (GSA), see Figure 2.[4] Table 2 provides potential control levels using CFBA technology. As can be seen in these figures, the multi-pollutant potential of CFBA makes it a very attractive option for cement kilns working to comply with this new set of EPA emission limits. A CFBA system is the closest analogy of the existing high-efficiency absorber/scrubber already present in many cement plant inline raw mills. The ability to adjust CKD and reagent injection and recirculating rates provides a way to control emissions

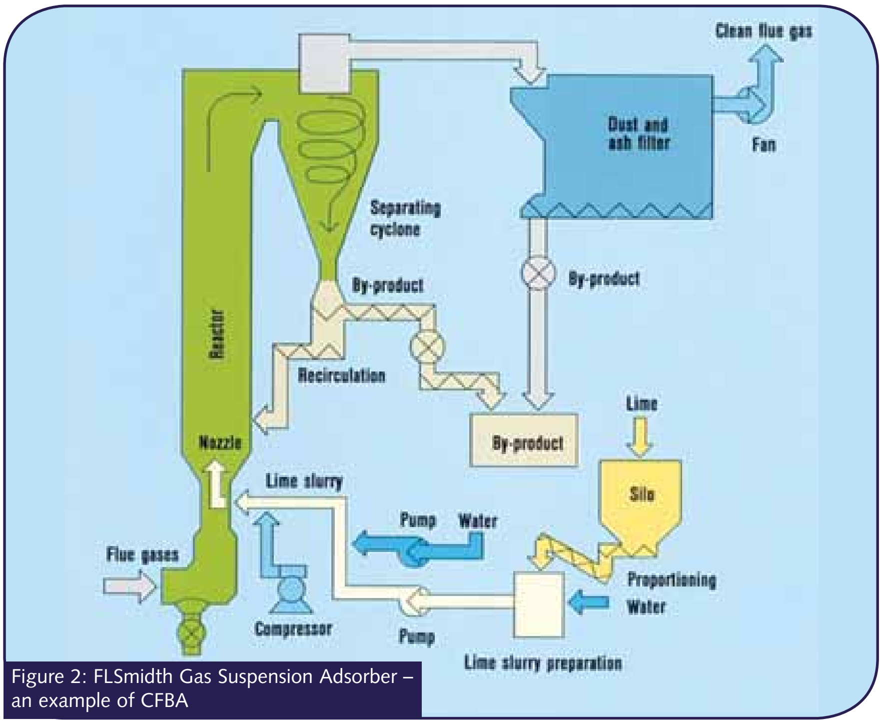


Figure 2: FLSmidth Gas Suspension Adsorber – an example of CFBA

while raw mills are out of action for maintenance. By using the plant's own CKD as a reagent in the CFBA and moving a slipstream from the unit's particulate control system to the finish mills a cement plant can dramatically reduce emissions and still avoid the generation of industrial waste requiring disposal.

Mercury oxidation state control

The ability of a system other than ACI to control mercury emissions is largely dependent on the mercury oxidation state. Elemental mercury must be oxidised for CFBA, or slipstream controls with a baghouse to control mercury emissions. The shifting of mercury oxidation states inside the cement kiln system is a complex issue and that is one of the reasons that mercury speciation during stack and process sample testing is recommended. The extent that the oxidation state of the mercury exiting the kiln system can be controlled may determine the success or failure of any of the alternatives to ACI. If a plant is planning on or considering the use of SNCR for NO_x control this also needs to be taken into account, since a SNCR system may shift the oxidation state of the mercury in favour of being captured by particulate control systems. SCR systems have been shown to oxidise elemental mercury.[5] Table 3[6] provides a summary of the forms of mercury that are potentially found in the cement kiln system. It is easy to see that if the mercury can be shifted to the oxide or sulphide, capture should be fairly straightforward.

While many of the oxidation shifting strategies are proprietary and/or under development there is one that has already been patented and tested on power plants. The reagent is sodium tetrasulfide and injection of this material within the critical temperature regime in the APCD system has proven an effective method of shifting the mercury oxidation state and enhancing capture efficiency.[7] Other reagent systems that may prove more effective and viable on cement kilns are under development.

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Conclusion

Many cement kilns are going to need to invest in enhanced emissions controls to comply with the new EPA limits on existing and new cement kilns. One of the most challenging of these emissions controls will be for mercury. The author believes that the EPA's knee-jerk response suggesting Activated Carbon Injection is a costly solution that will require the cement industry to backtrack on years of reducing solid waste disposal and shift the mercury from one medium (air) to another (land). Gossman Consulting Inc feels it is disappointing that the EPA advocates such a backward approach to emissions controls.

Table 2: CFBA potential control levels

Compound	*Potential control level (%)*
SO_x	95-98
Fine particulate and condensibles	50-90 improvement
Hg	50-95
HCl	95-98
THC	50-90

The cement industry has the opportunity to move beyond the EPA approach of moving a pollutant from one medium to another and instead develop innovative controls that are consistent with the production of high-quality cement while minimising environmental impacts. Many of these technologies have the advantage of controlling multiple pollutants and enhancing the reliability of the cement kiln operation.

In many cases these technologies can be used together to further increase the overall mercury removal efficiency. Gossman Consulting Inc advocates that ACI should be the technology of last resort for any cement plant needing to control mercury emissions.

References

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Table 3: mercury forms

Compound	*Formula*	*Melting point (°C)*	*Boiling point (°C)*	*Water solubility*
Mercury	Hg	-39	357	Low
Mercuric chloride	$HgCl_2$	276	302	High
Mercuric oxide	HgO	500 (decomposes)	N/A	Insoluble
Mercuric sulphide	HgS	584 (sublimes)	N/A	Insoluble