CREATING A VIRTUALLY MERCURY FREE RAW MATERIAL

CHRIS POLING, SCB INTERNATIONAL, USA, OUTLINES A MEANS OF AVOIDING THE UNWELCOME VARIABLES OF THE WORLD OF CEMENT PROCESS ENGINEERING AND QUALITY CONTROL.

Making good quality Portland cement on a routine basis is no easy task. Raw material changes, process fluctuations, sampling techniques, equipment failures, operating errors and lab equipment limitations are all working to introduce unknown variables into the manufacture of Portland cement. The cost impact of poor quality or off specification Portland cement can be staggering. The cost of a simple colour change in a masonry run can result in the rebuilding of residential homes or commercial spaces. The cost of replacing miles of highway can be in the millions of dollars. The cost for a failed structural beam on a high rise, bridge or stadium can go even higher. There is no partial credit for trying to make on-spec Portland cement. It either exceeds ASTM specifications or it does not.

An engineering professor at my alma mater would unequivocally state the following in his very concise broken English: "You build bridge, bridge falls down, people die… and you want partial credit!" As cement plant operators we want to make the same thing every day, all the time, without regard for the variables referenced above. Additional variables are not welcome in the world of cement process engineering or quality control. Why create more variables when a viable alternative allows you to reduce them while saving money and managing risk? Dust shuttling introduces a variable we do not really want or need.

Cement kilns have recently been regulated to control their mercury emissions to a total of 55 lb mercury for every 1 million t of

Figure 1: Integral 5 tph industrial unit.

clinker produced. The mercury generated by cement kilns is primarily derived from the volatilisation of the mercury in the raw materials.

The hot gases from the cement kiln are often used for drying and conveying raw materials through the cement kiln process. Thus in a cement plant any sorbent injection must be done after the kiln (primary) baghouse or any sorbent which is mixed with cement kiln dust/bag filter dust (CKD/BFD) must be removed from the kiln process entirely. Failing to remove the spent sorbent or the CKD/BFD/sorbent mix will result in the absorbed mercury being re-volatilised in the process and increasing the buildup of mercury within the kiln process loop. The addition of a polishing baghouse along with sorbent injection system after the primary kiln baghouse is a significant capital investment. It requires a large footprint of space, an increase in the overall system fan capacity due to the additional pressure drop, and must remain operational as long as the kiln is operating.

The chemical nature of the cement kiln exhaust gases and the CKD/BFD tend to be alkaline, which allows for other technologies to be applied. The use of chemical reagents for the stabilisation of heavy metals from contaminated soils and water systems has been widely used as part of environmental cleanup. The injection of these same reagents into kiln exhaust gas streams has resulted in limited success, but has not been demonstrated as repeatable or economical as yet.

Mercury Capture Systems patented process utilises the inherent nature of CKD/BFD and other sorbents to absorb mercury. A patented process which removes over 95% of the mercury from the CKD/BFD, sorbents or other industrial dust such as coal flyash was produced. MCS captures over 99% of that mercury from the concentrated gas stream without the use of any other sorbent. The precipitate is concentrated as a particulate in a non-leachable form and non-hazardous form.

The MCS process

CKD/BFD is generated on a continuous basis as part of normal cement kiln operations. This dust has been found to function as a partial sorbent of mercury from the exhaust gas stream. Mercury concentrations in CKD/BFD have been found to vary from under 0.5 ppm to over 61 ppm. This mercury laden CKD/BFD is recycled into the process as a raw material, releasing this mercury back into the kiln and increasing the overall system concentration. Modern cement plants are equipped with a vertical roller mill (VRM) to grind the raw materials to the required fineness. The VRM uses the exhaust gases from the kiln for drying and conveying through the mill circuit.

During VRM operation, the fresh raw materials (primarily limestone and silica) absorb a portion of the mercury from the gas stream and an additional portion is absorbed by the CKD, keeping the stack gas emissions relatively stable. However, should the kiln baghouse temperature differential increase as little as 50˚F inlet versus outlet or should the raw mill be off, the vast majority of this built up mercury is released into the atmosphere over a very short period of time. Our data confirmed that this emission level increases from as low as 5 – 8 ug/m^3 to levels as high as 79 ug/m^3 from a stable kiln with either a baghouse temperature increase or a raw mill off situation. Our data further confirms concentration of mercury absorbed onto the CKD varies from 1 ppm to 41 ppm in the same kiln under the same circumstances. By eliminating this mercury from the CKD/BFD before it re-enters the kiln as a raw material, we have a significant effect on the overall system mercury and correspondingly reduce the level of mercury emissions from the stack.

Cement plants are aware of this mercury concentration within their CKD/BFD and another option is dust shuttling. ASTM specifications allow CKD/BFD to be used as a Processing Addition up to 5% of the finished product provided all other performance characteristics are maintained. This allows some plants to reach NESHAP mercury emission limits, but will also result in the loss of a key ingredient in the raw material supply. Removing the CKD/BFD without replacing it as a raw material will result in lost clinker production and increased cost. CKD/BFD as a raw material has already been partially calcined and ground. Replacement materials will still need to be processed. No matter the plant, the cost for the CKD/BFD lies somewhere between the cost of the plant limestone and the cost of clinker. Dust shuttling of CKD/BFD may increase the insoluble residue and the Loss on Ignition of the finished product.

Through the use of Mercury Capture Systems technology, CKD/BFD can be returned to the kiln with over 95% of the mercury removed. The process has been designed to function independently, or as an integral part of the kiln system as shown in Figure 1. Dependent upon the mercury content of a plant's raw materials and the concentration of mercury within their CKD/BFD, the equipment may operate for as little as 40 hours each week to meet mercury emissions criteria. Likewise, some facilities may require the unit to operate 100% of kiln runtime to achieve targeted levels. By removing mercury from CKD/BFD, a kiln will be able to utilise different raw materials with higher mercury content but at a lower cost allowing them to reduce the cost per t of clinker, and yet still meet the mercury emissions standard.

Alternatively, by removing mercury from high concentration raw material streams the plant can benefit with lower cost raw materials as well as reduced mercury raw material inputs to the kiln.

Table 1. **Results from Thermal Desorber**

Feed material	Total Hg		Mercury removal efficiency
	Average desorber inlet ppm	Average desorber outlet ppm	
Cement kiln dust	2.16	non-detect	99.99%
Activated carbon	171.74	1.48	99.14%
Coal flyash	1.50	non-detect	99.99%

Table 2. **Capture rate across the Gas Reactor**

Total Hg		
Gas Reactor Hg inlet (ug/dscm)	Gas Reactor Hg outlet (ug/dscm)	Mercury capture rate (%)
13 502	215	98.41
5840	223	96.18
5384	383	92.89
4882	324	93.36
3564	244	93.15
2416	6	99.77
1111	94	91.54
707	13	98.22
334	9	97.30
265	9	96.64
175	5	97.05
126	16	87.34
302	21	93.21
1230	15	98.77
1650	14.5	99.12
2270	171	92.45

Dust shuttling emissions

One item which everyone agrees on when it comes to mercury is that it is hazardous and can be highly mobile. Elemental mercury will evaporate at room temperature for example. Studies completed by the The Hinkley Centre for Solid and Hazardous Waste Management in 2015 working with University of Florida and University of Oklahoma have indicated that the Mercury (Hg) on the bag filter dust (CKD/BFD) is far more mobile than previously reported.

'The total Hg concentration in the BFD ranged from 0.91–1.52 mg/kg (ppm) and was consistent in each season. More mobile and toxic SI-Hg counted 62 – 73% of total Hg in the samples, while the rest was in the NSI-Hg phase. The total Hg concentration in the BFD was higher than the 0.66 mg/kg (mean) in the cement kiln dust reported by Portland Cement Association (PCA).27' (Jun Wang, 2014)

Not only is Hg far more mobile but based on actual laboratory studies of BFD interacting solely with air it was found to release.

'The ball mill where clinkers are ground and BFD is added to the final product is in constant action. Thus, it creates good mixing between air and BFD. All the volatile Hg (NSI-Hg) can be possibly released from rotating and feeding air. However, there will be likely minimum oxidised Hg (SI-Hg) loss due to the low temperature profile (240˚F/116˚C) of the ball mill. Based on mass balance, there would be maximum 30 lb of additional Hg emitted from the ball mill per million t of cement produced, by adding 5% of BFD containing 1 mg/kg of Hg content to the ball mill, assuming conservatively all the 30% NSI-Hg is released. This is above the EPA limit of 21 lb per million t of clinker produced.6' (Jun Wang, 2014)

More recently this concern has arisen in Europe as part of the response to the Minamata Convention and specifically in regards to currently recommended practices such as dust shuttling.

'Dust Shuttling'. The selective bleeding off of mercury enriched dust from the cement manufacturing process, while a strategy for the prevention of mercury emissions from the stack, does not ultimately lead to the prevention of mercury releases from the cement production process. This is due to the lack of adequate management of these dust shuttling residues in the industry. To be clear, dust shuttling is not a mercury control strategy at all. Cement plants routinely recycle or shuttle their

Table 3. **TCLP of MCS precipitate**

Heavy metals	MCS precipitate			TCLP test result				Hazardous waste code
	Liquid	Solid	Unit	Result	Test limit	EPA limit	Unit	
Total mercury	ND	2360	ppm	0.0538	0.0002	0.2	ppm	D009
Metals SM3120 B								
Arsenic	0.043	147	ppm	ND	0.1	5	ppm	D004
Barium	0.054	141	ppm	0.627	0.1	100	ppm	D005
Cadmium	ND	49	ppm	ND	0.1	1	ppm	D006
Chromium	ND	166	ppm	ND	0.1	5	ppm	D007
Lead	ND	16	ppm	ND	0.1	5	ppm	D008
Selenium	ND	ND	ppm	ND	0.1	1	ppm	D010
Silver	ND	514	ppm	ND	0.1	5	ppm	D011

Table 4: **MCS precipitate oxides and Hg**

MCS precipitate oxides & mercury	Value	Unit
Sulfur trioxide	46.40	%
Aluminum oxide	1.88	%
Calcium oxide	21.70	%
Carbon	9.26	%
Iron II oxide	14.00	%
Magnesium oxide	1.42	%
Phosphorus oxide	0.10	%
Potassium oxide	0.23	%
Silicon oxide	0.26	%
Titanium oxide	0.15	%
Mercury	441	ppm

cement kiln dust back into their kilns for economic reasons. Because this shuttled dust tends to be highly contaminated with mercury, compared to other inputs, dropping this practice or at least reducing the amount of mercury-contaminated dust that gets put back into the kiln is a strategy that can reduce mercury emissions out of the stack.

That said, plants must then handle this mercury-contaminated dust safely so that the mercury it contains doesn't just get released into the environment somewhere else.' (Zero Mercury Working Group, August 2015)

It is simply a matter of time before cement kilns which are shuttling dust are required to include monitoring of dust storage, dust metering systems, finish mill baghouses and potentially all the way to the final encapsulation in concrete. The writing is on the wall.

Independent industrial unit configuration

The Thermal Desorbtion Gas Reactor uses CKD/BFD, coal flyash, sorbents or any other industrial powder as raw feed. The feed material temperature is raised to 356˚C while generating very little nuisance dust. Elemental mercury and ionic mercury are volatilised and released from the feed. This creates a small concentrated heavy metal gas stream. The gas stream passes through a high temperature baghouse to the Gas Reactor. The reagents utilised in the Gas Reactor combine with the mercury and any other heavy metals on a molar basis. This reaction forms a precipitate that is separated from the gas stream and collected independently. The precipitate has been tested and confirmed to be non-leachable even with high concentrations of heavy metals.

The detailed flow chart shown in Figure 2 illustrates the functionality of the Gas Reactor. The Gas Reactor is a modified scrubber originally designed to remove particulate from an exhaust gas. Mercury Capture Systems applies this technology to create a particulate from a particulate free gas stream. The particles are collected and the unreacted reagent is returned to the Gas Reactor. As the reagent is spent additional reagent is added to the system to maintain efficiency. There is no liquid effluent generated. Air emissions consist primarily of water vapor and very low concentrations of H_2S.

Data results

Multiple materials have been processed using the Thermal Desorber. Materials have been primarily related to cement processing and precious metals recovery. The data in Table 1 is a summary of the percentage of mercury removed from these materials once the equipment is at optimal temperature.

The lowest average concentration of mercury found in cement kiln dust was from a wet process kiln measured at 0.4 ppm across multiple samples. The highest concentration of mercury in cement kiln dust was from a preheater/precalciner during raw mill off which measured 61 ppm. Activated carbon was found to have the highest overall initial concentration with some values as high as 240 ppm. The concentrated gas stream that was processed by the gas reactor measured up to 8388 ppm Hg at various times during the activated carbon work. Coal flyash tends to vary from 200 ppb Hg up to 1.5 ppm Hg.

The mercury capture rate across the Gas Reactor was measured using sorbent traps and is shown in Table 2. The average mercury capture rate is over 95% for inlet concentrations above 100 *u*g/dscm.

In addition to nearly eliminating mercury, reductions in chlorides in the feed stock from 25 – 50% after the Thermal Desorber have been routinely demonstrated.

All data has been generated using independent third party sorbent trap sampling with the samples either sent to an offsite laboratory for analysis or conducted in the field.

The mercury which was no longer present in the raw feed or the concentrated gas stream was found in the precipitate reservoir of the Gas Reactor. Samples of the precipitate generated by a common feed stream were sent for mercury, heavy metal analysis and TCLP testing as shown in Table 3.

Precipitate samples from another stream were sent for a general oxides analysis along with mercury and TCLP. All materials are in their solid particulate form and are captured in the reservoir and are presented in Table 4.

The TCLP data remains consistent and well below the EPA limit for hazardous waste.

Conclusion

Mercury capture system delivers:

- An essentially mercury free raw material in the form of CKD/BFD, coal flyash or other industrial dust.
- Captured mercury precipitate which can be analysed, tested and confirmed to be non-hazardous and non-leachable.
- Compact design which can be either independent from or integrated with the cement kiln.
- No need to waste dust or dispose of sorbents.
- No need to shuttle dust:
  - Allows the plant to maintain its current raw material grinding and clinker production balance using CKD/BFD.
  - Allows the plant to optimise itself for lower cost process additions.
  - Reduces finish mill variability – no mercury laden sorbents added to the mix.
  - Reduces potential liability associated with downstream monitoring or emissions.
  - No need for additional raw material processing to offset the shuttled dust.