An Innovative Approach for Mercury Capture

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ABSTRACT

Mercury Capture Systems is an innovative method developed to remove mercury from cement kiln dust (CKD). *Mercury Capture Systems* gives flexibility to the cement industry, enabling the use of raw materials with higher mercury contents, such as coal combustion products (CCPs). Alternatively, the technology can be adapted to remove mercury from CCPs, potentially increasing CCP utilization.

Created as a cost-effective alternative to traditional activated carbon systems requiring a secondary baghouse, *Mercury Capture Systems* utilizes a chemical reagent. Results from a demonstration unit indicate nearly 90% of the mercury can be removed from CKD. A full scale industrial unit will be commissioned in the first half of 2013. Capital investment and operating cost estimates indicate the system will be about a third of the cost of a traditional powdered activated carbon system.

The United States Environmental Protection Agency (EPA) issued new National Emission Standards for Hazardous Air Pollutants (NESHAP) for cement plants, which take effect in September 2015. Every technology referenced to achieve compliance with the new standards requires significant capital investment, has a high operating cost, and creates a permanent high volume waste stream. These technologies include various forms of powdered activated carbon being injected into the gas stream and collected in a baghouse downstream on a steady basis. *Mercury Capture Systems* was developed as an alternative that produces less waste and costs less than powered activated carbon systems.

INTRODUCTION

Mercury and most of its compounds are toxic, and industry has looked at ways to control mercury emissions for quite some time. With upcoming mercury emissions limits for the cement industry, this paper discusses mercury control in power stations and introduces *Mercury Capture Systems* innovative new technology of volatilizing and capturing the mercury from CKD. The concept has been proven by a 113 kg per hour (250 lb per hour) Mercury Demonstration Unit. In June 2013, an industrial unit with a

capacity of 4.5 – 9.1 tonnes per hour (5 to 10 tons per hour) will be commissioned. This technology will give the cement industry more flexibility in raw material selection, potentially increasing the amount of CCPs used. Testing is scheduled for later in 2013 to use *Mercury Capture Systems* to reduce mercury contents of fly ashes and powdered activated carbon (PAC).

Mercury control has been developed for power stations, which have been regulated longer than the cement industry, whose regulations become effective in 2015 and limit existing kilns to 27.5 kg/1,000,000 tonnes (55 pounds of mercury per million tons) of clinker production[1]. Mercury can exist in its elemental form or in ionic compounds; the form of the mercury is referred to as speciation. The ability to capture and remove mercury from exhaust gas emissions has been effective through the use of various types of sorbents. The most prevalent sorbent for mercury emissions produced from coal fired power stations is PAC. The PAC injection rates for each system vary from 3.8 – 320 kg/MM am^3 (0.24 – 20 lb/MM acf)[2]. This rate is dependent on the coal source, mercury speciation, sulfur concentration and other exhaust gas characteristics. PAC injection represents a minimum addition of 36,290 tonnes (40,000 tons) of waste into landfills every year. Operating costs can range from $2.5 to $6 million per year, excluding disposal costs[2]. PAC injection may occur before the existing pollution control unit where it becomes mixed with fly ash or after and captured in a polishing baghouse.

What works for the power industry may not be the right fit for the cement industry. The mercury generated by cement kilns is primarily derived from the volatilization of the mercury inherent in the raw materials, as opposed to the power industry's source of mercury: coal combustion. Process differences provide another important distinction in mercury transport. Cement kiln operating temperatures and material flows allow for a significant internal mercury cycle within the system, while little cycling occurs within power stations.

Another key contrast is the handling of particulate matter from pollution control devices. CKD naturally absorbs mercury and is collected in the kiln (primary) baghouse; the CKD is recycled as a raw material contributing to the internal mercury cycle. In the power industry the fly ash is collected and removed from the process. Thus, in a cement plant any PAC injection must either be done after the kiln baghouse or any PAC which is mixed with CKD must be removed from the kiln process entirely. Failing to remove the spent PAC or the CKD/PAC mix will result in the absorbed mercury being re-volatilized in the process and a significant buildup of mercury within the kiln process loop. The addition of a second kiln baghouse to filter the PAC from the gas stream combined with the PAC injection system itself 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 PAC solid waste stream from the cement industry is estimated to be 116,811 tonnes per year (128,762 tons per year)[3].

The chemical nature of the cement kiln exhaust gases are also very different from the coal combustion gases which allows for other technologies to be applied. The use of

chemical reagents for the stabilization of heavy metals from contaminated soils and water systems has been widely used as part of environmental cleanup. What we have done with *Mercury Capture Systems* patented process is to utilize the inherent nature of CKD as a mercury sorbent. That natural tendency combined with our cement process knowledge along with reagent technology has produced a viable system which removes 87% of the mercury from the CKD and captures over 90% of that volatilized mercury from the concentrated gas stream without the use of Powdered Activated Carbon. The residue is highly concentrated; initial testing has confirmed the captured metals are non-leachable. Additional testing on the residue is scheduled. Data from various trials indicate a 98% reduction in mercury from the vapor phase using the *Mercury Capture Systems* process.

THE PROCESS

Mercury Capture Systems was developed for emissions compliance in the cement industry through the volatilization and capture of mercury from CKD using a chemical reagent. The capital and operating costs are roughly a third that of a traditional PAC installation. The resulting residue will be on the order of kilograms (pounds) per year. Testing is scheduled in 2013 to adapt this technology to other industries. Materials like fly ash or bottom ash processed through the *Mercury Capture System* may have added value in the cement and concrete industries as raw materials with lowered mercury contents. Other industries such as iron processing may use *Mercury Capture Systems* to meet mercury emissions requirements. Using a nitrogen rich atmosphere, *Mercury Capture Systems* will be testing powdered activated carbon.

Cement kiln dust 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 have been found to vary from < 500 ppb to > 41,000 ppb. This mercury laden CKD 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 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, contributing to the internal mercury cycle. However, should the kiln baghouse temperature differential increase as little as 11.1˚C (20˚F) inlet versus outlet or should the VRM be off, the vast majority of this built up mercury is released into the atmosphere over a very short period of time. Our data indicates that this emission level increases from as low as 5 – 8µg/m^3 to levels as high as 79µg/m^3 from a stable kiln with either a baghouse temperature increase or a VRM off situation. Our data further confirms concentration of mercury absorbed onto the CKD varies from 1,000 ppb to 41,000 ppb in the same kiln under the same circumstances. By eliminating this mercury from the CKD before it is recycled 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 and another option which exists for them is dust shuttling. In performing this method, they remove the CKD from their kiln process and re-introduce it as an additive into their Portland cement finished product. ASTM specifications allow CKD to be used as a Processing Addition up to 5% of the finished product provided all other performance characteristics are maintained. This may allow some plants to reach EPA mercury emission limits, but will also result in the loss of a key ingredient in their raw material supply (CKD) which will have to be replaced. Replacement of the CKD will be accomplished through additional raw materials, all of which are at a much higher cost than recycling the CKD.

Through the use of *Mercury Capture Systems* technology, CKD can be returned to the kiln with nearly 90% of the mercury removed. Breaking the kiln's internal mercury cycle reduces the exhaust mercury emissions. The process has been designed to function independently using natural gas as a heat source, or as an integral part of the kiln system recovering waste heat. Dependent upon the mercury content of a plant's raw materials and the concentration of mercury within their CKD, the equipment may operate 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, a kiln might be able to utilize lower cost/higher mercury content raw materials thereby reducing the cost per ton of clinker, and yet still meet the mercury emissions standard.

EVALUATION AND SUPPORTING DATA

DEMONSTRATION UNIT CONFIGURATION

Mercury Capture Systems technology has been verified with the Mercury Demonstration Unit and using CKD from several different cement plants. Our Mercury Demonstration Unit raises the temperature of CKD and other powders to temperatures above 356˚C (673.8˚F). Elemental mercury and ionic mercury are volatilized at this temperature. Once the mercury has released from the CKD and become part of a small concentrated gas stream, it passes through a heated duct to

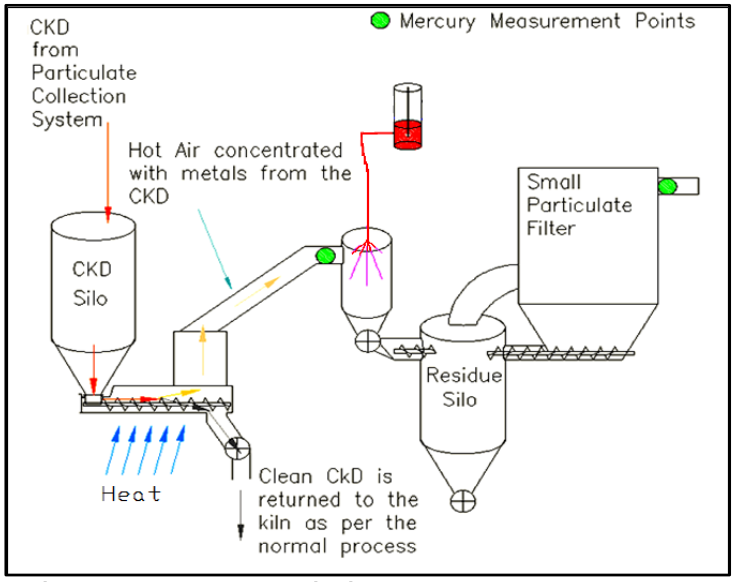

Figure 1: Conceptual Flow

a spray chamber. It enters the spray chamber passing through a fog of chemical reagent, which reacts with and converts the mercury into a solid particle. The particle drops out of stream and is collected as part of the residue at the bottom of the chamber. This residue may be in liquid form or dry form dependent upon temperature, volume of chemical reagent and overall system design. Testing thus far has produced both residue forms.

A detailed design was completed to support the conceptual flow chart shown as Fig 1. While the industrial version will utilize waste heat and/or a gas burner, the Mercury Demonstration Unit was built to operate on electricity. The unit was completed in January 2012 and system balancing occurred over the next five (5) months until late May of 2012. At the completion of the system balancing, we were able to maintain design airflow, temperatures, and material flow on a repeatable and continuous basis. Testing in May through July 2012 (Fig. 2) confirmed the ability of the unit to volatilize mercury from CKD into a gas stream traveling through the spray chamber.

DATA RESULTS

Date	**Unprocessed CKD Mercury Concentration (*µg* / g)**	**Processed CKD Mercury Concentration (*µg* / g)**	**Percent Reduction**
5/31/2012	26.000	2.323	91.0%
5/31/2012	19.547	2.323	88.1%
7/12/2012	34.994	6.107	82.5%
7/12/2012	39.788	4.357	89.0%
7/12/2012	41.937	4.500	89.3%
7/31/2012	36.159	5.154	85.7%
7/31/2012	37.907	5.006	86.8%
7/31/2012	39.370	5.327	86.5%
Average	34.463	4.387	87.3%

Figure 2: CKD Concentration Reduction

We also measured the mercury concentration across the spray chamber while injecting only water, no reagent, (Fig. 3) to confirm mercury volatilization.

Run	**Gas Inlet (*µg* / g)**	**Gas Outlet (*µg* / g)**
1	2.55	1.99
2	1.02	1.24
3	1.03	1.13

Figure 3: Mercury Concentration Across Spray Chamber – <u>water only injection</u>

In July and August of 2012, trials continued using CKD and the chemical reagent. All testing was performed by an independent laboratory; testing methods are presented at the end of this paper. Testing results indicated a significant drop in the concentration of mercury across the spray chamber when injecting the chemical reagent (Fig. 4). At the same time these tests confirmed that injection of water alone provided no significant change in the concentration of mercury within the gas stream (Fig. 3). Portable hand-held mercury analyzers were used to provide instantaneous indication of mercury concentrations. However, the portable hand-held units were only capable of measuring a gas concentration up to 0.999 ppm. Anything above this value registered as 0.999 ppm, and then the unit would require a 30 minute regeneration cycle as it was effectively saturated. Mercury concentration determined by the hand-held units is not as accurate as the mercury concentration determined from the sorbent traps.

Test	Date	Mercury Analyzer	Gas Inlet Concentration	Gas Outlet Concentration	Unit	Percent Reduction
1	07/10/12	Portable	0.999	0.206	ppm	79.4%
2	07/10/12	Portable	0.999	0.100	ppm	90.0%
3	07/10/12	Portable	0.999	0.122	ppm	87.8%
4	07/10/12	Portable	0.999	0.220	ppm	78.0%
5	07/12/12	Portable	0.613	0.221	ppm	63.9%
6	07/12/12	Portable	0.999	0.231	ppm	76.9%
7	07/12/12	Portable	0.999	0.239	ppm	76.1%
8	07/12/12	Portable	0.999	0.232	ppm	76.8%
9	07/12/12	Portable	0.999	0.205	ppm	79.5%
10	07/31/12	Portable	0.999	0.049	ppm	95.1%
11	07/31/12	Sorbent Trap Section II	2,415.785	5.626	µg/g	99.8%
12	07/31/12	Portable	0.999	0.057	ppm	94.3%
13	07/31/12	Portable	0.999	0.228	ppm	77.2%
14	07/31/12	Portable	0.999	0.210	ppm	79.0%
15	07/31/12	Sorbent Trap Section II	706.600	12.584	µg/g	98.2%
16	08/01/12	Portable	0.800	0.100	ppm	87.5%
17	08/01/12	Portable	0.999	0.060	ppm	94.0%
18	08/01/12	Portable	0.956	0.100	ppm	89.5%
19	08/01/12	Portable	0.387	0.104	ppm	73.1%
20	08/01/12	Portable	0.512	0.101	ppm	80.3%
21	08/01/12	Portable	0.687	0.109	ppm	84.1%
22	08/01/12	Portable	0.999	0.120	ppm	88.0%
23	08/01/12	Sorbent Trap Section II	21.093	0.608	µg/g	97.1%

Figure 4: Mercury Concentration Across Spray Chamber Injecting Reagent

Sorbent trap sampling was conducted independently with the samples sent to an offsite laboratory for analysis. This was done both to confirm the data generated by the handheld units as well as to determine the actual value for the upper inlet concentration. Both the hand-held units and sorbent traps were hampered by a small portion of the particulate getting past the spray chamber and being measured by the analyzers. By examining only the gas fraction of the sorbent traps (Section II), the reduction was even more promising; nearly 100% mercury capture was realized (Fig. 4).

The mercury which was no longer present in the gas stream was expected to be found in the residue within the spray chamber. Samples of this residue generated by a common CKD stream were taken and sent off site for analysis. Results are shown in Figure 5 and confirm capture of the mercury.

Sample	Dry Residue Mercury Concentration	Solid & Liquid Residue Mercury Concentration	Units	
1	101.1		µg/g	ppm
2	105.7		µg/g	ppm
3	103.8		µg/g	ppm
4		21,100,000	ng/l	ppt
5		15,100,000	ng/l	ppt
6		11,900,000	ng/l	ppt

Figure 5: Residue Concentration

The results shown in Figure 6 indicate that an overall mass balance may be achievable, but more work is required as the residue sample is cumulative over the test period.

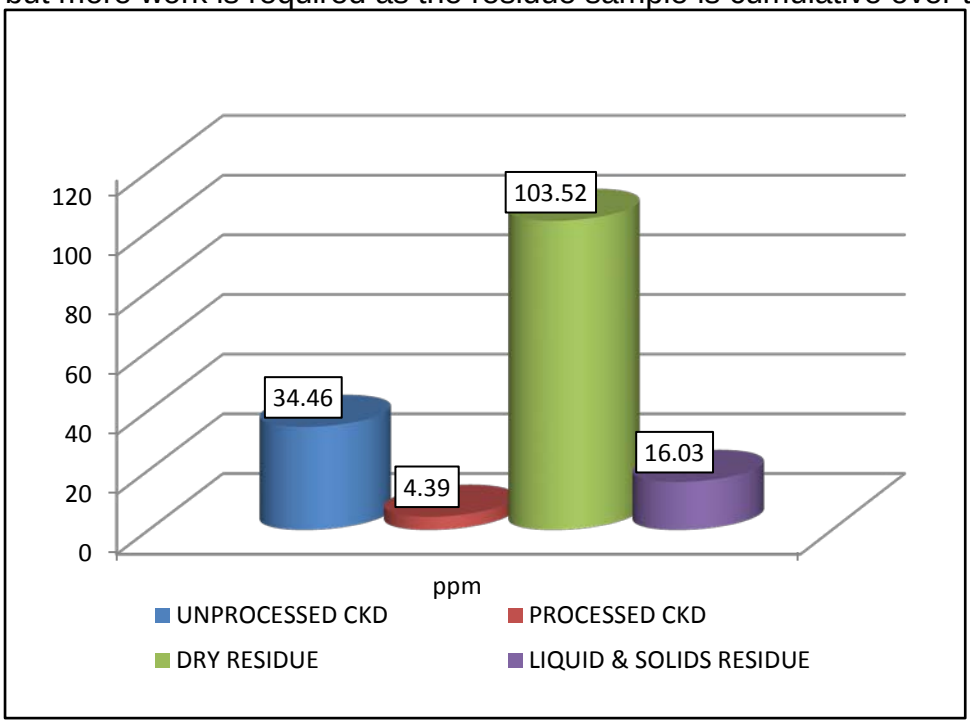

Figure 6: Average CKD & Residue Concentrations

NEXT STEPS

The next steps in the implementation of this technology involve:

1. Commission industrial unit by June 2013. This standalone unit will process 4.5 – 9.1 tonnes per hour (5 to 10 tons per hour). The industrial unit will be installed at a cement plant for full scale testing.
2. Complete classification of the generated residue and potential for market uses of this highly concentrated material.
3. Continue efficiency improvements to reduce volume of reagent, optimize residence time at temperature, minimize system airflow, and generate additional data.
4. Conduct complimentary trials to increase the concentration of mercury within the CKD itself.
5. Modify the technology to allow for similar testing of powdered activated carbon, fly ash etc. The goal is to regenerate PAC and make fly ash viable for concrete or as a raw material in a cement kiln.

CONCLUSION

The Mercury Demonstration Unit confirmed the ability of *Mercury Capture Systems* to remove mercury from CKD. At least 87% of the mercury was volatilized from CKD, and 98% of mercury was removed from the exhaust gas stream. Removing the mercury from the CKD removes the mercury from the internal cycle in the kiln system and lowers a cement plant's mercury emissions.

The industrial units for *Mercury Capture Systems* will have a lower capital cost than traditional PAC systems. *Mercury Captures Systems* will also have a lower operating cost than PAC systems. The volume of waste generated will be on the order of kilograms per year rather than tonnes (pounds rather than tons).

Mercury Capture Systems technology is transferrable to other industries. The technology can be used to decrease mercury emissions or remove mercury from raw materials used in cement plants, such as fly ash. *Mercury Capture Systems* is customizable and will assist the cement industry in controlling mercury emissions and may prove useful for power stations, and similar heavy industries.

SAMPLING AND ANALYTICAL METHODS

Several sampling and analytical approaches have been employed to determine Hg emission levels in the field and during the Mercury Demonstration Unit phase of this project. These include:

- USEPA Method 30B Sorbent Trap Collection and AA Spectrometry
- USEPA Method 17 Particulate Collection
- Selective Extraction

- Gold Film Sensor Mercury Vapor Analyzer

A brief description of these approaches:
USEPA Method 30B was developed to measure total vapor phase mercury (Hg) emissions primarily from coal fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. The sorbent traps, in this case, filled with specially prepared charcoal are inserted into the flue gas stream and a measured known volume of flue gas was extracted over the two sections of charcoal. Analysis for was conducted using an Ohio Luminex Model 915 Mercury Analyzer.

USEPA Method 17 was developed to measure particulate matter (PM) emissions from a wide range of sources and is similar to USEPA Method 5 in operation. The difference between the two methods is found in where the filter media is placed. In the case of Method 5 the filter is located outside the flue gas stream in a heated compartment. Flue gas and particulate matter are isokinectically extracted via a properly sized nozzle and heated probe before being directed to the filter media. Method 17 has the filter media at the end of the probe (unheated) and just after the nozzle. In this manner the particulate matter is collected under stack conditions. It is most useful where high PM levels exist. A pre-filter thimble, which has a higher PM volume collection ability, can be added to the sampling train just prior to the filter itself. This allows for collection of several grams of material that is not embedded into the glass fiber filter media. Samples (PM only) were sent to Frontier Global Laboratories and selective cold extraction was performed to determine Hg concentration at six separate phase levels.

The RA-915+ mercury analyzer employs differential atomic absorption spectrometry technique, which is implemented using the direct Zeeman effect (Zeeman Atomic Absorption Spectrometry using High Frequency Modulation of Light Polarization ZAAS-HFM). A glow discharge mercury lamp is placed in a permanent magnetic field, whereby the 254-nm mercury resonance line is split into three polarized components, only two of those, o^+ and o^-, which are circularly polarized in the opposite directions, being detected for analysis. After passing through a polarization modulator, which modulates the polarization at a frequency of 50 kHz which triggers the line components in turn, the radiation then passes through a multi-path cell, whose equivalent optical length is about 10 m. The unit is equipped with narrow-band high reflectivity mirrors, where the cell isolates just the 254-nm resonance line and suppresses all the non-resonance and stray radiation. A logarithm of the intensity ratio of o^+ and o^-, which is proportional to the mercury atom concentration in the cell, is determined upon detecting the radiation by a photo-detector and subsequent analog-digital conversion of its electric signal by a built-in microprocessor.

The Jerome 331XL and 405 hand-held portable Mercury Analyzers use gold film sensor technology and are highly specific for mercury, eliminating interferences such as water vapor and hydrocarbons. It has a detection range of 0.5 - 0.999 µg/m^3 with an accuracy of +/-10 per cent at 1µg/m^3. Its response time is 12 seconds in sample mode and two seconds in survey mode.

Surface Plasmon resonance (SPR) is the resonant, collective oscillation of valence electrons in a solid stimulated by incident light. The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. SPR is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nano-particles.

Selective Cold Extraction
Sample Preparation
Aqueous samples for total mercury determination are oxidized to 1-100% (v/v) with 0.2 N bromine monochloride. The level of preservation is dependent on the amount of turbidity and particulate matter in the samples. Samples are then allowed to react/digest for at least 24 hours at room temperature prior to analysis. Aqueous samples for dissolved mercury determination are filtered through a 0.45 micron pore size cleaned filtration units prior to oxidation with 0.2 M bromine monochloride. Soil/Sediment samples are homogenized and digested at room temperature for at least 4 hours with 8ml of concentrated hydrochloric acid and 2ml of concentrated nitric acid. Samples are then diluted to a final volume of 40 ml with a 5% (v/v) solution of 0.2 N bromine monochloride.

Sample Analysis
Aliquots of the oxidized samples are neutralized with hydroxylamine-hydrochloride (NH_2OH-HCl) to destroy free halogens then added to a bubbler. Stannous chloride ($SnCl_2$) is added to the bubbler to reduce the Hg(II) to volatile Hg(0) and the bubblers are sealed. Blanked gold traps are placed at the end of soda lime pre-traps, and the bubblers are purged with nitrogen (N_2) for 20 minutes, purging the Hg(0) onto the gold trap. The gaseous mercury amalgamates to the gold traps, which are then heated and introduced into an atomic fluorescence detector using argon as the carrier gas. A chart recorder is used to record the detector signal. Peak heights are then measured and entered manually into the Laboratory Information Management System (LIMS) for calculation of the final mercury concentration.

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