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关于分解窑的水银排放控制

(3)

Precalciner Cement Kiln Mercury (Hg) Emissions Control

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Introduction

There is a growing level of concern about mercury emissions from cement kilns and interest in the industry in developing cost effective options for controlling these emissions. Cement plants have a wide range of mercury inputs and resulting emissions because of the wide variety of raw materials and fuels used in the process. Further, the current level of mercury emission control at cement plants varies from 0% to as high as 95% using existing particulate control systems. This is the third in a new series of GCI TechNotes that will examine this issue.

Mercury emissions are regulated based on concern for mercury entering the food chain and bioaccummulating to significant levels that could impact people eating fish. The following is a brief review of the factors that impact the issue of controlling mercury emissions from modern cement kilns.

引　言

由于人们对水泥窑排放水银的关注日益高涨，工业界才有兴趣发展节约且有效的办法来控制这些排放．　水泥厂因为在生产过程中使用的生料和燃料中可能含有不同程度的水银，因此会排放水银．　而且当前一些水泥厂对水银排放的控制程度由 0%至最高的 95%不等，使用的是微粒控制系统．　在新的一系例 GCI 工艺摘要中，这是探讨这个问题的第 3 篇。

水银排放的监控是基于人们的关注水银会进入我们的食物链，长时期的积累在生物系统里，对一些吃鱼的人会有影响．　以下是对那些影响到测试新法干窑，以肯定正确的[水银]排放率的因素作一个简短的复审。

It should be kept in mind that mercury control technologies are under active development around the world as pressure mounts to reduce the total anthropogenic source of mercury to the mercury cycle. Most of this development has been focused on controlling mercury emission from coal fired electrical power utility boilers.

应该记著水银的控制技术在全球范围内还是在活跃地发展，由于渴求减少因人为的原因造成的水银排放到全球的水银循环里. 大部分的发展是集中于，控制烧煤的火力发电厂锅炉的水银排放.

Not all of the observations made regarding mercury emissions and controls for those systems can be directly applied to cement kilns. Further, the unique operating environment inside a cement kiln may present innovative and cost effective control methods for cement kilns that are impossible or impractical to apply to coal fired boilers.

据观察所得，关于那些系统的水银排放控制，不是全部可以直接应用于水泥窑. 再则，水泥窑内的独特运作环境有可能发掘出，经济有效的方法使用于水泥窑，那是不可能或者是不实际应用于烧煤的锅炉。

Review of Control Options

During combustion, the mercury (Hg) in coal and other fuels is volatilized and converted to elemental mercury (Hg^0) vapor in the high temperature regions of the cement kiln. As the flue gas is cooled, a series of complex reactions begin to convert Hg^0 to ionic mercury (Hg^{2+}) compounds and/or Hg compounds (Hg_p) that are in a solid-phase at flue gas cleaning temperatures, such as HgO and HgS, or Hg that is adsorbed onto the surface of other particles. The presence of chlorine gas-phase equilibrium can favor the formation of mercuric chloride ($HgCl_2$) at system temperatures depending on the competition of alkali-chloride reactions. The presence of significant levels of sulfide in the form of iron sulfide (pyrite) in some cement kiln raw feeds may favor the formation of HgS.

检阅控制的选择

在焚烧中，煤碳中的水银和其他燃烧物料在水泥的高温带被挥发了，且转变成水银的原体(Hg^0)蒸汽. 待烟道气玲却后，一连串的复杂的反应开始把(Hg^0)转变成离子水银(Hg^{2+})化合物再/或水银合成物(Hg_p)，在烟道气的清洁温度下是固相，如氧化汞和硫化汞，或者是水银的原体吸附与其他的粒子上. 有氯气呈现时气相平衡在系统的温度里对形成氯化汞($HgCl_2$)有利, 取决于碱与氯反应的竞争. 硫化物以硫化铁(黄铁矿)形式出现达至足够的水平时，在一些水泥窑的生料里可能对形成硫化汞有利.

However, Hg^0 oxidation reactions are kinetically limited and, as a result, Hg can enter the air pollution control device(s) as a mixture of Hg^0, Hg^{2+}, and Hg_p with varying ratios depending on the conditions in the kiln system. This partitioning of Hg into Hg^0, Hg^{2+}, and Hg_p is known as mercury speciation, which can have considerable influence on selection of mercury control approaches. For this reason it is critical that assessing the range of operating conditions and the resulting speciation of Hg in any given cement kiln be the first step in determining the most effective control technology. A control technology that works on one kiln system cannot be assumed to be effective on another。

不过水银的原体(Hg^0)它的氧化反应是受到动力的限制，其结果是水银能进入空气污染控制器(APCD)为一种混合体，水银原体(Hg^0)，离子水银混合物(Hg^{2+})和水银合成物(Hg_p)，具有不同的比率，视乎水泥窑的条件. 水银被分割成 Hg^0, Hg^{2+}, and Hg_p 是被称作水银物种，那对于选择控制水银的方法有相当大的影响力. 基于这个理由，在评定运作条件的范围是很重要，在任何一个指定的水泥窑里得出的水银物种，是确定最有效的控制技术的第一步. 一种控制技术使用于一个水泥窑时有效，并不能假设用于另一个水泥窑时也同样有效。

It is also critical to understand the role of CKD recycling in this process. Recycling CKD back into the kiln system can revolatilize mercury that has been captured, converting it from the particulate form to one of the more volatiles forms such as the chloride.

了解水泥窑灰在工艺过程里起的作用也是很重要. 窑灰循环回笼入水泥窑的系统里能再次把捕捉到的水银挥发，把它从粒子形态转变成一种或多种挥发的形态，例如氯气。

Some control of mercury emissions from cement kilns is currently achieved via existing controls used to remove particulate matter (PM), sulfur dioxide (SO_2), and nitrogen oxides (NO_x). This includes capture of Hg_p in PM control equipment and soluble Hg^{2+} compounds in wet scrubber systems. Available data on electric utility boilers also suggest that use of selective catalytic reduction (SCR) NO_x control enhances oxidation of Hg^0 in stack gasses and results in increased mercury removal in wet scrubbers. It is unlikely that the same would be true of SNCR NO_x control systems on cement kilns given the operating temperature of these systems. That said, the presence of excess ammonia in the stack gasses could impact available chlorides for reacting with and forming mercuric chloride.

时下一些对水泥窑的水银排放的控制是通过现有的，驱除尘粒(PM)、二氧化硫(SO_2)和氧化氮(NO_x)的控制装置来完成. 这个包括在尘粒控制装置里捕捉水银，于湿的洗涤系统里捕捉溶于水的离子水银. 根据有关电器多用途锅炉的可用数据，也令人想起用可选催化还原(SCR)氧化氮的控制，以增强烟囱里气流中水银的氧化作用，导致湿洗系统内铲除水银能力的增加. 对水泥窑使用可选催化还原(SCR)氧化氮的控制的办法，由于这些系统运作的温度[甚高]，未必会一样的精确. 此外，在烟囱气流里呈现过多的氨会影响到可用的氯化物使它起反应及形成氯化汞。

There are three broad approaches to mercury control: (1) activated carbon injection (ACI), (2) multi-pollutant particulate control, in which Hg capture is enhanced in existing/new PM control devices, and (3) multi-pollutant wet scrubber control, in which Hg capture is enhanced in existing/new SO_2, and NO_x control devices. Relative to these three approaches, this paper describes currently available data, limitations, estimated potential, and research and development needs.

有三种主要控制水银的方法:
(1) 活性炭注入(ACI) (2)多种污染物微粒制；在现有的、或者是新的微粒控制器内增强捕捉水银的能力. (3) 多种污染物湿洗控制；在现有的、或者是新的氧化硫和氧化氮控制器内增强捕捉水银的能力. 关于这三种方法，本文叙述目前可用的数据、极限、估计的可能性、研究和发展的需要。

Activated Carbon Injection Control of Mercury Emissions

以活性炭注入法控制水银排放

ACI has the potential to achieve moderate levels of mercury control. The performance of activated carbon is related to its physical and chemical characteristics. Generally, the physical properties of interest are surface area, pore size distribution, and particle size distribution. The capacity for mercury capture generally increases with increasing surface area and pore volume. The ability of mercury and other **sorbates** to penetrate into the interior of a particle is related to pore size distribution. The pores of the carbon sorbent must be large enough to provide free access to internal surface area by Hg^0 and Hg^{2+} while avoiding excessive blockage by previously adsorbed reactants. As particle sizes decrease, access to the internal surface area of particle increases along with potential adsorption rates.

活性炭注入法能做到中等程度的控制. 活性炭的表现关系到他的物理与化学的特性. 通常，我们对它的物理性能感兴趣是它的表面面积，它的微孔大小和微粒大小的分布. 水银的捕捉能量通常是随着表面面积和微孔数量的增加而增加. 水银和其他的吸着物【注1】能否穿入微粒的内部是与微孔的大小分布有关. 炭吸着剂的微孔必须有足够的尺寸，来提供通道，给水银原体和水银混合物，渗入内部的表面面积，同时避免过多而被以前残留下来的吸附反应剂阻塞. 当微粒的尺寸变小时，进入内部表面面积的微粒与吸收率相应增加。

Carbon sorbent capacity is dependent on temperature, the concentration of mercury in the flue gas, the flue gas composition, and other factors. In general, the capacity for adsorbing Hg^{2+} will be different than that for Hg^0.

炭吸着剂的能量是与温度、烟道气里的水银浓度、烟道气的成分和其他因素有关. 通常，吸附水银混合物的能量与吸附水银原体有别.

The selection of a carbon for a given application would take into consideration the total concentration of mercury, the relative amounts of Hg^0 and Hg^{2+}, the flue gas composition, and the method of capture (electrostatic precipitator (ESP), or baghouse). An important factor for some cement kilns will be the levels of hydrocarbons and the need to account for their sorption on to the carbon reducing the capacity of the carbon to adsorb mercury. In addition, bench-scale research shows that high SO_2 concentrations diminished the adsorption capacity of activated carbons. Both of these issues could prevent ACI from being an effective control on some cement kilns.

为某一样用途而选择一种炭, 会需要考虑到全体的水银集中度、相应的水银原体和水银混合物的量、烟道气的成分和捕捉的方法（例如；静电除尘器或袋屋）. 一个重要的因素，对于一些水泥窑就是碳氢化合物的水平，需要考虑到它们吸着于炭之后，炭的吸附水银的能量就会减小. 另外，扩大的试验显示出，高浓度的二氧化硫会缩小活性炭的吸附能量. 这两个问题足以摒弃活性炭作为一个有效控制有些水泥窑水银排放的方法。

There has been only limited testing of ACI on low concentration mercury gas streams as are typical of cement kilns. Most of this work has been done on power plant boilers achieving control efficiencies of 25-95% depending on the type of coal being burned and a wide number of other factors. In many cases these plants already had some mercury control via the particulate control systems in place and enhanced control via ACI was as low as a 10% improvement.

曾经有过对活性炭的有限测试；用于测试典型的水泥窑低浓度的水银气流. 大部分应用于发电厂的锅炉，达到的控制效果为25-95%，视乎燃烧的煤碳种类和广泛的其他因素. 在许多例子里这些发电厂已经有些对水银的控制，通过已经安装了微粒控制系统，而且用活性炭增强也只有10%的改进。

ACI has the further disadvantage of requiring the disposal of the mercury contaminated spent carbon. Whether the carbon is cleaned and reactivated for reuse or disposed of, the ultimate fate of the mercury needs to be assessed to insure that the mercury will not be reintroduced into the global mercury cycle through some other means.

活性炭还有一个缺点，就是需要处置被水银污染了的炭. 不管那些炭是清洁的或者是再活化再用或处置，水银的最后的结果需要被评定，以保证不会通过其他途径再被引入全球的水银循环中。

Mercury Emission Control via Control of Particulates in ESPs or Baghouses

ESPs and/or baghouses (fabric filters) can be an effective control for mercury from cement kilns if two critical conditions are met. First, the mercury must be in the particulate form. This may occur naturally in the system or may require reagents added to the right point in the process to oxidize or catalyze the oxidation of the Hg to HgS and/or HgO. One US wet process plant has demonstrated 95% control of mercury emission through their existing ESP system. High levels of pyrite in their raw materials may be a factor in producing this relatively high level of control. (Theoretically, efforts to reduce SO_x emissions by controlling pyrite in the raw feed could increase mercury emissions.) One experimental system (not in a cement kiln) uses UV light to shift the oxidation state of mercury.

通过静电除尘器或袋屋对微粒的控制来控制水银排放

静电除尘器再/或袋屋(织物过滤)对水泥窑排放的水银会是一种有效的控制办法，如果符合两个重要的条件. 第一，水银必须于微粒形态. 这也许自然地发生于系统里，或者会需要加入试剂，于水银原体氧化或催化氧化过程中的恰当位置，使它变成硫化汞再/或氧化汞. 美国的一家湿窑的水泥厂子证明了，他们通过现有的静电除尘器，控制水银的排放达95%. 在他们的生料里含有高水平的黄铁矿可能是达至相对地高度控制的因素. （理论上，尝试控制在生料中的黄铁矿来减少二氧化硫的排放，会增加水银的排放.）有一个实验性的系统 （不是在一个水泥窑）用紫外线光来转移水银的氧化状况。

The second critical step in the process is to remove a portion of the mercury-containing dust from the air pollution control system in such a way as to maximize the mercury removal and not place that portion of the dust back into the kiln system. In older wet process plants this has been done routinely by removing the dust from the final one or two stages of the ESP systems. Precalciner plants with in-line raw mills have a more complex scenario to consider. For plants that currently recycle all of their cement kiln dust, the mercury is simply returned to the system and recirculates until the concentration gets high enough that a portion is emitted out the stack in some form.

第二个于工艺中的重要步骤是，从防止空气污染的系统里消除一部分含有水银的灰尘，作为加大消除水银的一个方法，而且不再把那部分的灰尘回笼到窑的系统. 在使用旧式湿窑的厂子里，从静电除尘系统的最后一道或两道里，清除哪些灰尘是例行的工作. 新法干窑的厂子有在线生料磨的，会有更复杂的局面要考虑. 对那些厂子目前在循环再用窑灰的，水银就简易地回笼至系统里，再循环使用直至它的浓度达到相当高时，部分是以多种形态从烟囱里排放出去。

It is critical to break this cycle. Without breaking this cycle the speciation of the emissions may have limited or no meaning relative in determining the most effective control technology.

打破这个循环的很要紧的事. 如果不打破这个循环，排放的物种会受到限制，或者对确定最有效的控制技术没有意义。

A program to **speciate** mercury in dust samples taken during raw mill on and off conditions should be a first step in characterizing an operation to see if particulate control of mercury emissions is a viable option. It needs to be kept in mind that under current normal operations where all CKD is recycled back into the system that the mercury concentration in stack gasses and in the dust will be highly dynamic. The system probably never reaches a steady-state operation relative to mercury input and output. (This implies that there is no way to accurately determine mercury emissions with a stack test.)

作一个程序来找出【注2】，于生料磨运作时和停止时，采取的窑灰样板里的水银，应该是作为鉴定一个[窑系统]的运转的第一个步骤，以观察微粒控制水银排放是否是一个可行的选择. 需要记著，在通常运作的境况下，所有窑灰都被回笼到系统里，使得水银的浓度在烟囱的气流里和在窑灰中会非常活跃. 这个系统很可能永不达至一个静止状态相对于水银的输入和输出（这个意味著一个烟囱的测试是无法可正确地确定水银的排放.）

Modeling of cement kilns with in-line raw mills suggests that removing a small portion of the captured dust when the raw mill is operating (and possibly when it is not on line as well) can break the recycle loop and may control mercury emissions with efficiencies in excess of 90% depending on speciation and a number of other factors including baghouse blowback cycles, baghouse (or ESP) operating temperatures, types of bags, etc. With the raw mill operating there is likely a very high level of sorption of mercury onto particles in the raw mill and in the baghouse (or ESP) – one set of tests on a precalciner showed sorption efficiencies of 98.5%. It has been typical to operate baghouses at higher temperatures when the raw mill is down and in the just mentioned case efficiencies dropped to 90%. This drop in efficiency is likely to have been due to the increase in the baghouse operating temperature from 100 °C to 175-200 °C.

对那些有在线生料磨的水泥窑做的模型分析令人想起，在生料磨运作时移除一小部分捕捉到的窑灰（而且有可能也在停止运作的时候）能打破这个循环圈，而且有可能控制水银的排放效果超过90%，视乎物种和其他的一些因素，包括袋屋的回吹周期，袋屋（或静电除尘器）运作的温度，袋的种类等. 生料磨在运作中很可能在生料磨内，和袋屋（或静电除尘器）内有很高的吸收水银上微粒的能力 – 对一个预分解炉进行一套测试，显示吸收效果达98.5%. 当生料磨停止运作时袋屋在高温下运作是典型的，与刚才说过的情况那样效果降低至90%. 这个效果下降是很可能因为袋屋的运作温度从100 ° C提高到175-200 ° C.

Spray Tower/Wet Scrubbing of Mercury Emissions

Wet spray tower/slurry systems remove gaseous SO_2 from emissions by absorption. For SO_2 absorption, gaseous SO_2 is contacted with a caustic slurry, typically water and limestone or water and lime. Gaseous compounds of Hg^{2+} are generally water-soluble and can absorb in the aqueous slurry of a wet scrubber system. However, gaseous Hg^0 is insoluble in water and therefore does not absorb in such slurries. When gaseous compounds of Hg^{2+} are absorbed in the liquid slurry of a wet system, the dissolved species are believed to react with dissolved sulfides from the flue gas, such as H_2S, to form mercuric sulfide (HgS); the HgS precipitates from the liquid solution as sludge.

The capture of mercury in wet scrubbers is likely dependent on the relative amount of Hg^{2+} in the inlet flue gas and on the PM control technology used. Electric utility boiler data reflected that average mercury captures ranged from 29 percent for one unit burning subbituminous coal with an ESP plus wet scrubber to 98 percent in a unit burning bituminous coal with a fabric filter baghouse plus a wet scrubber. The high mercury capture in the fabric filter baghouse plus wet scrubber unit was attributed to increased oxidization and capture of mercury in the baghouse followed by capture of any remaining Hg^{2+} in the wet scrubber. For cement plants with SO_x scrubbers this has particular potential. A system of **bleeding** the APCD particulate control system followed by a scrubber system for SO_x that coincidentally captures $HgCl_2$ may provide very high levels of mercury emission control on cement plants with the right chemistry.

喷淋塔/湿洗水银排放

喷淋塔/浆料系统以吸收功能移除排放中的二氧化硫的气体. 为了吸收SO_2，SO_2气体是与苛性的浆料接触，典型地为水与石灰石或水与石灰. 水银混合物的气体一般都溶于水，而且能被吸收入在湿洗系统内水样的浆料里. 不过，水银气体是不容于水的，因此不会被吸入到浆料里. 当水银混合物的气体被吸入湿系统的液体浆料时，这个被溶入的种类相信会与来自烟道气内溶入的硫化物产生反应，如H_2S, 而形成硫化汞(HgS)；这个硫化汞从液体的溶液沉淀下来成泥状物。

在湿洗器捕捉到的水银是很可能取决于烟道气入口处，相应的水泥混合物Hg^{2+}的分量和使用的微粒控制技术. 电气多用途锅炉的数据反映出平均捕捉到水银的范围由29%，对一个单位燃烧中的次烟煤，用静电除尘器加上湿洗器，到98%对一个单位燃烧中的烟煤，用织物过滤袋屋加上湿洗器，是归咎于增加氧化和在袋屋内捕捉水银，接着于湿洗器内捕捉任何残留的水银混合物. 水泥厂设有二氧化硫的洗涤器的有这个独特的可能性。用一个移除部分窑灰 【注3】的的系统；微粒控制系统后跟着就是氧化硫的湿洗系统，这个组合会巧合地捕捉硫化汞，在一些水泥厂子里有恰当的化学作用，这个系统对水银排放可能提供很高水平的控制。

Conclusion

While ACI and wet scrubbing may provide control of mercury emissions from cement kilns, the lowest cost option appears to be the use of the existing particulate control system in conjunction with **a small bleed** of dust from the primary air pollution control system. Plants that have an ESP, may find that the dust in the final stages of the ESP is even more enriched in mercury and that this simplifies the process of creating a “break” in the mercury recycle loop. For example, if it is found that this dust represents 1% of the total feed to the kiln system and is enriched to a factor of 100 times the average level of mercury in the system relative to raw feed; removal of that dust would effectively remove all the mercury from the system. This dust could then be sent to the finished cement blending silos with no appreciable impact on product quality. Investigation of the speciation and enrichment of mercury in the dust being captured in various stages of the ESP or bagouse with the raw mill both on and off is recommended as the first step in developing a dynamic model and from that a mercury control strategy for any cement plant wishing to reduce mercury emissions.

结　论

虽然活性炭和湿洗可能为水泥窑提供水银排放的控制，这个廉价的选择似乎是, 用现有的微粒控制系统, 与从主要的防止空气污染的系统里移除小部分窑灰【注4】的做法相结合[即上述方法之1]。有静电除尘器的厂子，可能发现在除尘器的最后一节里的水银更加多了，那是简单创造一个“打破”水银循环圈的过程. 举个例子，如果被发现这窑灰代表全部喂入窑系统里生料的1%，相对于生料而言，系统里平均的水银的水平被增强了100倍【注5】；那么移除那些窑灰即是有效地移除所有在系统里的水银. 然后这些窑灰被输送到水泥产品的混合筒仓，对产品的质量不会有可察觉到的影响［即上述方法之2]。 对物种的调查，以及于生料磨运作时和停止时，增强在静电除尘器在的不同阶段里，或者在袋屋中捕捉到的窑灰内的水银含量，是被推荐作为发展一个动态模型的第一步，而且也是任何水泥厂意欲降低水银排放的控制战略[即上述方法之3]。

【注 1】**Sorbates –** a general term used to refer to materials that are involved in "sorption". They are usually fine particulates that other materials stick to.

是一个常用的术语，指物料起“吸着”的作用. 通常是幼细的微粒，其他得物料可以吸着在上面。

More notes below …..

【注2】**Speciate －** in this case for mercury emissions the verb is used to describe the process of investigating which of the different compounds that mercury can form are actually found in the emissions or in the dust. Typical mercury species include elemental, oxide, sulfide and chloride. Each of these compounds has different physical and chemical characteristics which can influence what strategy is used to control the mercury emissions.

在叙述水银排放的情况时，这个动词是用来叙述调查的过程，实际上于排放中或者窑灰中找到的水银能形成那个不同的化合物. 典型的种类包括水银原体、氧化物、硫化物和氯化物. 每一种化合物有它不同的物理和化学的特性，能影响到用的是什么控制水银排放的策略。

【注 3】**Bleeding －** in this case referring to the removal of some of the CKD from the system. In many plants they recycle all CKD from the air pollution control system. Bleeding a small portion of that out of the kiln system is an important part of controlling mercury emissions.

这里指从系统里移除部分窑灰. 许多水泥厂他们都循环再用所有来自防止空气污染系统的窑灰. 从窑的系统里移除一小部分[窑灰]是控制水银排放的一个重要部分。

【注 4】**A small bleed of dust －** the removal of a small portion of the dust that is normally recycled back to the raw material feed system of the kiln.

意即；从平时回笼入水泥窑喂料系统的窑灰里移除一小部分。

【注5】In the dust it is at much higher concentrations than it is found in normal raw materials - it can be over 100 times higher.

窑灰比一般的生料有非常高的[水银]浓度 － 有可能超过100倍那么高。

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