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Fate and transport of mercury in portland cement manufacturing facilities

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Fate and transport of mercury in portland cement manufacturing facilities

by

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Abstract

The USEPA’s 2010 mercury rule for non-hazardous waste burning portland cement manufacturing facilities will significantly reduce mercury emissions in the United States, but represents a substantial regulatory challenge for the industry. Development of mercury control technologies for these facilities is difficult due to widely varying levels of mercury inputs and transient emissions caused by a poorly understood mechanism of mercury loop concentration. Determination of mercury concentrations in baghouse dust and kiln feed samples from within the internal mercury loop represents another difficulty due to diverse analytical procedures. Little published literature exists on mercury sorption and desorption from these materials. Without this data, the potential for this loop to serve as a mercury control and removal mechanism is not possible. To advance knowledge of mercury fate and transport in cement manufacture facilities, this study highlighted data gaps and research needs, optimized a digestion method for determination of mercury in kiln feed and baghouse dust, and identified and tracked mercury desorption, sorption, and internal concentration at specific points within a facility demonstrating an internal mercury loop.

Chapter 1. General Introduction

Introduction

Mercury is recognized as a neurotoxicant by the United States Environmental Protection Agency (USEPA) and is listed as a chemical of global concern by the United Nations Environment Programme (UNEP, 2010; USEPA, 2010a). Within the United States (US), human exposure to mercury occurs most commonly through consumption of fish containing methylmercury. A portion of this mercury in fish can be attributed to atmospheric deposition of mercury emitted by anthropogenic sources (USEPA, 2010a).

Under the Clean Air Act (CAA), USEPA is required to address the annual emissions (i.e., estimated at 100 tons per year (tpy)) of anthropogenic atmospheric mercury released within the US. Utility coal boilers are the primary source of US atmospheric mercury, emitting half of the annual total US emission (i.e., 100 tpy), while cement manufacturing is also a major source, at 8 tpy (USEPA, 2009a). The USEPA's 2010 final rule on mercury emissions from cement manufacturing facilities is estimated to reduce emissions to 0.5 tpy (i.e., a 94% reduction) (USEPA, 2010b). This rule restricts mercury emissions from existing cement facilities to a 30-day rolling average of 55 pounds (lbs) mercury/million metric tons clinker and requires compliance on September 9, 2013. Facilities constructed after May 6, 2009 face a lower emission limit at 21 lbs mercury/million metric tons clinker and must be in compliance by the latter of November 8, 2010 or facility startup (USEPA, 2010c). The rule's aggressive nature, both in the level of emission reductions and in the short three-year compliance period, is estimated to force closure of a minimum of 10, and possibly as many as 18, of the 113 existing US cement facilities (USEPA, 2010d; Sullivan, 2010).

To manufacture portland cement, a kiln (typically fueled by coal) heats a mixture of 85% limestone, 13% clay or shale, and less than 1% each of corrective materials such as silica, alumina, and iron ore to an approximate temperature of 1,400°C (Alsop, et al., 2007; Bhatty, et al., 2004). This high temperature volatilizes mercury, causing it to leave the facility with exhaust gases. While volatilization of mercury is relatively constant and occurs in either the kiln or preheater portion of the facility, emission through the exhaust stack to the atmosphere is highly variable. Mercury emissions variability is due to a unique mechanism termed *'internal loop control'*. In many facilities, hot exhaust gases containing mercury travel through a raw mill (to dry incoming feedstocks) and through a baghouse (to capture exhaust dust). The relatively cool temperature and high surface area of materials in each of these facility components captures mercury. Baghouse dust and kiln feed (which is produced by the raw mill) are both inputs into the facility's kiln, creating an internal mercury loop that can concentrate the element by "hundreds of times" (Clark, 2009). However, this loop is broken whenever the feedstock mill is shutdown for necessary maintenance, causing a spike in the facility's mercury emissions (Schreiber, et al., 2005).

Exploitation of the internal mercury loop holds potential to reduce the control costs associated with the USEPA mercury rule. To advance the technical innovation required to achieve compliance with the rule, current knowledge must be summarized and data gaps and research needs identified in the areas of cement facility mercury fate and transport, cement-mercury emissions models, and current and proposed cement-mercury control strategies.

While the technological advancement required to meet the USEPA rule represents a complex challenge for the industry, analysis of the material samples required to study the internal mercury loop represents another difficulty. The diverse approaches used to determine the mercury sample mercury content include spectroscopic, radiochemical, and electrochemical methods (Clevenger, et al., 1997). Spectroscopic methods popular for liquid and solid samples include, but are not limited to, cold vapor atomic fluorescence spectrometry (CVAFS) and cold vapor atomic absorption spectrometry (CVAAS) (Morita, et al., 1998; Leopold, et al., 2010). Further complexity is encountered because these methods also diverge on whether the method used to extract mercury from the sample into an elemental vapor form is by wet digestion or thermal decomposition. For solid samples, these methods have various benefits and drawbacks, but kiln feed and baghouse dust samples are best suited to thermal decomposition. These materials are fine homogeneous powders (requiring no sample preparation for thermal decomposition), are assumed to have a homogeneous mercury distribution, and are believed to have low levels of interfering elements. Nevertheless, due to benefits such as lower detection limits, lower standard error, and possible remedies for interferences, many research entities are only equipped with liquid-based wet digestion analyzers.

USEPA digestion procedures are available for geologic and sedimentary solids, but unlike these materials, cement samples contain loop-concentrated mercury in addition to natural mercury concentrations. The form of mercury sorption (i.e., chemisorption or physisorption) that occurs in the loop is unknown; therefore, a digestion process that may be appropriate for geological materials may not be appropriate for kiln feed and baghouse dust. In order for a wet digestion method to be used for analysis of cement facility samples, USEPA digestion procedures must be optimized.

The internal mercury loop holds potential as a cement facility mercury control and removal mechanism. With knowledge of mercury's sorption and desorption behavior from raw meal and baghouse dust, it may be possible to develop novel control strategies that exploit this mechanism to achieve USEPA's emissions limit without use of comparatively expensive and inefficient 'tail-pipe' technologies (Paone, 2010). However, with one known exception that reports mercury concentration at specific points within a Slovenian facility (Mlakar, et al., 2010), published literature only reports stack emissions measurements or continuous emissions monitoring data (Schreiber, et al., 2005; Schreiber, et al., 2009a; Schreiber, et al., 2009b; Senior, et al., 2010). Facility observations are required to develop an understanding of the internal mercury loop. These observations will identify points of desorption, sorption, and internal concentration and lay the groundwork for future research that uses models to predict internal concentration levels at a facility.

With realization of the many issues created by cement manufacturing facility mercury emissions regulations, the objectives of the current research were: (1) summarize the current cement facility mercury issues, as well as highlight data gaps and research needs, (2) optimize a digestion method for determination of mercury in kiln feed and baghouse dust from cement manufacturing facilities, and (3) identify and track mercury desorption, sorption, and internal concentration at specific points within a facility demonstrating an internal mercury loop.

Thesis Organization

This thesis discusses the fate and transport of mercury in cement manufacturing facilities. The thesis is organized in paper format and Chapters 2, 3, and 4 are written as journal articles. Chapter 2 reviews cement facility mercury fate and transport literature and identifies research and data gaps. Chapter 3 describes optimization of a wet digestion method for the determination of mercury in cement manufacturing facility baghouse dust and kiln feed samples. Chapter 4 details observations of mercury fate, transport, and internal concentration at a cement manufacturing facility. Chapter 5 provides overall conclusions for the material presented in Chapters 2, 3, and 4 and recommends future work.

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Chapter 2. Mercury Regulation, Fate, Transport, Transformation, and Abatement within Cement Manufacturing Facilities: Review

A paper to be submitted to *Critical Reviews in Environmental Science and Technology*

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Abstract

The USEPA's 2010 mercury rule, which would reduce emissions from non-hazardous waste burning cement manufacturing facilities by 94%, represents a substantial regulatory challenge for the industry (USEPA, 2010b). These regulations, based on the performance of facilities that benefit from low-levels of mercury in their feedstock and fuel inputs, will require non-compliant facilities to develop innovative controls. Development of these controls is difficult due to widely varying levels of mercury inputs and transient emissions caused by a poorly understood mechanism of mercury loop concentration. At present, a number of mercury control technologies are proposed; however, their effectiveness is limited by knowledge gaps. To achieve the USEPA's aggressive regulation with minimal harm to the industry, further research and data collection are required along with the development and assessment of control technologies. This review is subsequently intended to identify research and data gaps which might guide future efforts.

Introduction

While originally named hydrargyrum, Latinized Greek for "water-silver", the present name for the element mercury originates from Mercury, the Roman god. In similarity to the liquid metal's quick watery movement despite its heavy mass, this god was able to fly swiftly with winged sandals and a winged hat. In an unintended and unrealized likeness to Mercury, the god of thieves, the element also hides throughout the world and steals a human body's health (Swiderski, 2008). Prior to knowledge of mercury's neurotoxicity, the element was widely used in medicine. For instance, the elemental form was ingested so that mercury's heavy mass would clear digestive trouble and

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women consumed mercury during labor in hopes that the substance mass would help push out the fetus. Even Abraham Lincoln took mercury pills to cope with depression (Swiderski, 2008). In early use, mercury appeared widely useful, but history also presents many examples of the element's toxicity. For instance, the term '*mad as a hatter'* originated from mercury poisoning observed among men who treated pelts with mercuric nitrate when making felt hats. In 1971, Iraqi farmers received large quantities of wheat seed treated with an alkylmercury fungicide. The seed was received late in the growing season and drought conditions prevailed, so it was unlikely the seeds would sprout. Instead, the farmers ground the seed into flour and baked it into unleavened bread. In turn, alkylmercury contaminants were baked into the bread hospitalizing 6,530 and killing 459 (Swiderski, 2008). In a more recent example, after spilling one to several drops of dimethylmercury on her hand protected by a latex glove, Karen Wetterhahn, a Professor of Chemistry at Dartmouth College, fell into a coma and died 10 months later (OSHA, 1998).

Mercury is now recognized as a chemical of global concern by the United Nations Environment Programme, and is listed as a neurotoxicant by the United States Environmental Protection Agency (USEPA) (UNEP, 2010; USEPA, 2010a). The most common form of mercury exposure for people in the United States (US) is consumption of fish containing methylmercury. A portion of the mercury found in fish can be attributed to atmospheric deposition of mercury emitted from natural and anthropogenic sources (USEPA, 2010a). Current estimates indicate that half of atmospheric mercury can be traced to anthropogenic activities (Pacyna, et al., 2006). Under the Clean Air Act (CAA), the USEPA is proactively required to address the annual emissions (i.e., estimated at 100 tons per year (tpy)) of anthropogenic atmospheric mercury released within the US. Utility coal boilers are the primary source of US atmospheric mercury, emitting half of the annual total US emissions (i.e., 50 tpy), while cement manufacturing is also a major source, at 8 tpy (USEPA, 2009a). The USEPA's 2010 final rule on mercury emissions from cement manufacturing facilities is estimated to reduce emissions sixteen-fold down to 0.5 tpy (i.e., a 94% reduction) (USEPA, 2010b). This rule is far more aggressive than the USEPA rule requiring a 70% reduction of mercury emissions from coal-fired power plants which was vacated by the United States Court of Appeals for the District of Columbia Circuit (D. C. Circuit) in 2008 (USEPA, 2010c).

Successful future compliance with USEPA's mercury rule for cement facilities will require aggressive technical innovation. Unfortunately, few researchers are actively working with the industry to address this critical issue.

This article is subsequently intended to summarize the current cement facility mercury issues, as well as highlighting data gaps and research needs by addressing:

1. cement manufacturing,
2. mercury regulations for cement facilities,
3. the use of mercury concentration in inputs to predict average mercury emissions,
4. current knowledge about cement facilities relative to mercury fate and transport,
5. cement-mercury emissions models, and
6. current and proposed cement-mercury control strategies.

Overview of Cement Manufacturing Facilities

Emission of mercury from cement manufacturing facilities is highly variable and difficult to predict accurately. There are three fundamental stages: preparation of feedstocks, production of clinker, and preparation of cement. The second stage, production of clinker, is the most significant to understanding mercury fate and transport; however, the other two stages do provide contextual information.

Preparation of the feedstocks begins by quarrying raw materials that satisfy the stoichiometric requirements for cement production. The raw feed composition typically used for modern cement production consists of 85% limestone, 13% clay or shale, and less than 1% each of corrective materials such as silica, alumina, and iron ore (Alsop, et al., 2007). Following quarrying, feedstocks are crushed to a size below 50 mm and mixed in a pre-homogenization pile (Bhatty, et al., 2004). Production of clinker entails the majority of energy expenditure and chemical reactions required to produce cement. Both wet and dry processes are practiced; however, due to escalating fuel prices and inefficient energy use, wet facilities are being phased out. This review focuses on the dry process.

Figure 2.1 provides the various components of a typical cement facility. Cement manufacture begins when feedstocks enter the raw mill, creating a fine powder (so-called 'raw meal') in which 85% of material is smaller than 75 micrometers. Prior to entering the kiln, the meal is transferred to homogenizing silos that minimize variation in material (Bhatty, et al., 2004). Following homogenization, the meal is shuttled to the preheater and precalciner tower, marking the beginning of the chemical transformation of the meal into cement. Cyclone separators (called 'preheaters') in the tower intermix the raw meal with the near 1,000°C kiln exhaust gases to recover energy, preheat the meal and begin the chemical reactions producing cement. In fact, precalciners achieve greater than 90% calcination prior to the material entry into the rotary kiln (Alsop, et al., 2007). Within the kiln, temperatures reach approximately 1,400°C completing the process chemical reactions and producing calcium silicates, called clinker, with a diameter of 3-25 mm (Bhatty, et al., 2004). To maximize energy recovery, exhaust gas from the preheater tower is often routed to the raw mill, assisting in drying the incoming feedstocks. Following flow through the raw mill, exhaust gases are finally released into a baghouse, which also captures fine particles created when feedstocks are milled. In many cases, this dust is then recycled into the homogenizing silo and serves as a portion of the kiln feed. Preparation of cement completes the manufacturing process where clinker nodules are milled into cement. Following clinker milling, cement is ready for use as a binder in various concrete mixes.

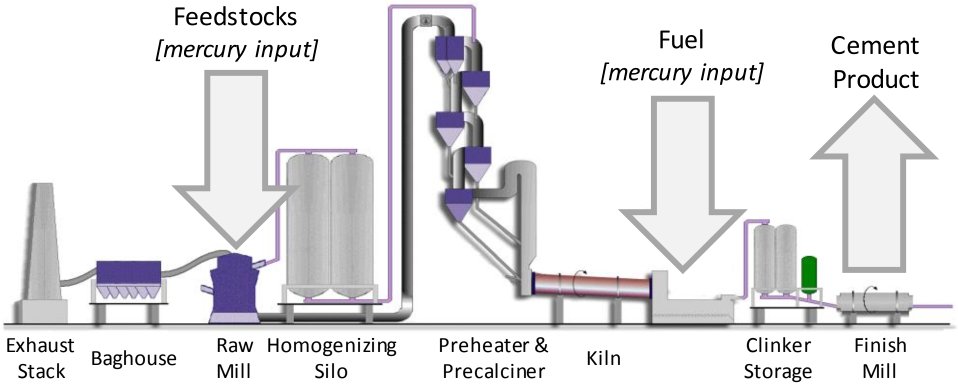

Figure 2.1. Overview of the Dry Cement Manufacturing Process

Cement Manufacturing Facility Mercury Regulation

The USEPA's 2010 rule on National Emission Standards for Hazardous Air Pollutants (NESHAP) From the Portland Cement Manufacturing Industry and Standards of Performance for Portland Cement

Plants restrict mercury emissions from existing cement facilities to a 30-day rolling average of 55 pounds (lbs) mercury/million metric tons clinker and requires compliance by September 9, 2013. Facilities constructed after May 6, 2009 face a lower emission limit of 21 lbs mercury/million metric tons clinker and must be in compliance by the latter of November 8, 2010 or facility startup (USEPA, 2010d). Although the 2010 rule addresses errors in USEPA's interpretation of the Clean Air Act (CAA), the regulation remains controversial due to additional interpretation errors found by the cement industry.

The CAA requires USEPA to set maximum achievable control technology (MACT) standards (referred to as "floor" requirements) on source categories that as a whole account for at least 90% of seven specified hazardous air pollutants (HAPs) (alkylated lead compounds; polycyclic organic matter; hexachlorobenzene; mercury; polychlorinated byphenyls; 2,3,7,8-tetrachlorodibenzofurans; and 2,3,7,8-tetrachloroidibenzo-p-dioxin). Portland cement facilities, that do not burn hazardous wastes, are one of these source categories due to their polycyclic organic matter, mercury, and dioxin/furan emissions. Application of MACT standards to mercury emissions from cement facilities requires emissions limits for new and existing facilities. New facilities are limited to emissions achieved by the facility with best mercury controls. Existing facilities are limited to the average emissions achieved by the top 12% of facilities in terms of mercury control. In this rulemaking, USEPA considered, but did not propose, a more stringent regulation that, instead of being based on a MACT floor, considers the cost of emissions reductions, non-air quality environmental and health impacts, and control technology energy requirements (USEPA, 2010d).

While USEPA's latest regulation does appear to follow the CAA, earlier regulations contained incorrect interpretations of the law. Portland cement manufacturing facilities are also subject to the CAA regulations for HAPs that pose the greatest potential health threat in urban areas. In 1999, USEPA issued a rule addressing non-volatile HAP metals, but not mercury. Mercury was not regulated because the USEPA reasoned that mercury emissions were due to mercury within raw materials. Since differences in emissions were not due to a control technology, USEPA concluded that a MACT floor could not be developed. D. C. Circuit held that this reasoning represented an error in USEPA's interpretation of the CAA stating "[n]othing in the statute even suggests that [US]EPA may set emission levels only for those listed HAPs controlled with technology" (D.C. Circuit, 2000). Instead, cement facilities whose mercury emissions are low simply because they have low-levels of mercury in their raw materials and fuel must be used to determine both the facility with best mercury control and the group making up the top 12%. In response, USEPA in 2006 established a new facility emissions standard of 41 micrograms per dry standard cubic meter of stack exhaust, or installation of a limestone wet scrubber exhaust cleaning system. USEPA did not create a MACT floor for existing facilities because the USEPA only had 2004 and 2005 performance data tests obtained from two wet scrubbers installed at cement facilities to control sulfur dioxide. At the time of rulemaking, only five of 19 facilities in the best performing 12% had this type of scrubber installed. USEPA reasoned a rule for existing facilities could not be created because the best performers' emissions could only be based on the mercury concentration of feedstock and fuel inputs. Over time, these apparent best performers would not be able to continually meet this performance standard due to variation of mercury concentration in facility inputs (USEPA, 2006). USEPA also considered developing MACT floors based on the emissions due to the input mercury concentration; however, they concluded that,

> "front end feed and fuel control of cement kilns is inherently site specific, and basing limits on kiln performance in individual performance tests which reflect only those inputs will result in limitations that kilns can neither duplicate (another kiln's performance) nor replicate (its own)" (USEPA, 2006).

Concurrent with the issuance of this ruling, USEPA began to reconsider the mercury standard due to "substantive issues relating to the performance of wet scrubbers and because information about their performance in the industry had not been available for public comment at the time of proposal" (USEPA, 2009b).

The D.C. Circuit March 2007 opinion on the appeal of Sierra Club regarding MACT floors for the Brick and Structural Clay Ceramics source categories holds significance in relation to the portland cement NESHAP. Key points from this opinion include:

- "Floors for existing sources must reflect the average emission limitation achieved by the best-performing 12% of existing sources, not levels the USEPA considers to be achievable by all sources;
- [US]EPA cannot set floors of "no control" … ; and
- [US]EPA cannot ignore non-technology factors that reduce HAP emissions". (USEPA, 2010d).

Based on these holdings, USEPA's 2006 reasoning that excluded a mercury limit on existing cement manufacturing facilities is also incorrect. In reflection of the 2007 opinion, the 2010 rule states:

> "we believe a source's performance resulting from the presence or absence of HAP in raw materials must be accounted for in establishing floors; i.e., a low emitter due to low HAP proprietary raw material can still be a best performer. In addition, the fact that a specific level of performance is unintended is not a legal basis for excluding the source's performance from consideration" (USEPA, 2010d).

With these interpretations of the CAA established, USEPA formulated the 2010 rule limiting mercury emissions from both existing and new cement facilities.

The final mercury regulations for cement manufacturing facilities adheres to opinions from the D.C. Circuit and follows the CAA requirements to first create a MACT floor and second consider a standard more stringent than MACT. Due to transience in mercury emissions and a lack of installed continuous emissions monitoring systems, USEPA developed stack emissions data with a mass balance approach. This balance assumed that mercury inputs from fuel and feedstocks leave through the exhaust stack except when (1) mercury is removed with dust captured in the baghouse, (2) mercury is removed with dust from an alkali bypass, and (3) mercury is removed in gypsum generated by a wet scrubber (USEPA, 2009b). For 89 kilns in the US, USEPA obtained 30 days of daily mercury inputs, from fuel and feedstocks, and outputs, from the exceptions listed. USEPA selected 11 kilns, the best 12% in terms of mercury emissions, to establish a regulation for existing kilns, and selected the best performing kiln to establish a regulation for new kilns. USEPA's assessment of emissions attempts to determine the level of emissions control that is actually achievable and may not be obvious from the 30-day sampling effort. Since mercury control achieved at many cement facilities is based on feedstock and fuel mercury concentration, USEPA did account for the variability of mercury content in these inputs. The MACT floors restrict mercury emissions from existing cement facilities to a 30-day rolling average of 55 lbs mercury/million metric tons clinker and from facilities constructed after May 6, 2009 to an emission limit at 21 lbs mercury/million metric tons clinker. USEPA's beyond-the-floor considerations were rejected because they were either not cost-effective or were technically infeasible.

The rule does appear to follow the CAA and did satisfy environmental groups which disputed USEPA's previous rulings. On the other hand, the regulation is not without controversy. While the Portland Cement Association (PCA) disputed the proposed rule for multiple reasons, two issues received the majority of discussion from the USEPA and environmental groups: (1) an incorrect consideration of input mercury variability and (2) a rule subcategory argument for facilities with high limestone mercury levels.

PCA's review of input mercury variability found that one kiln in USEPA's set of best performers was producing oil well cement clinker instead of the typical product, Type I or Type II cement clinker. PCA asserted that this kiln should be removed from the data set, pointing out that the emissions from an identical kiln at the same facility had emissions seven times higher during the same data collection period. USEPA, upon receiving this data, revised the data set appropriately. PCA also proposed an alternative method to account for mercury variability in fuels. They argued that each facility purchases coal from their area open market. Instead of basing coal variability from the data collection period as in USEPA's approach, PCA calculated the 95% confidence level of coal shipments to utilities in the same market of best performing facilities (PCA, 2009a). USEPA viewed this as a request "for an upward adjustment of the MACT floors based on coal they might potentially use but never had used" (USEPA, 2010d). Furthermore, USEPA asserted that this approach "invites inflated estimates of variability based on hypothesized possibilities" and that "such an approach creates a perverse incentive to build in compliance margins based on seeking out more polluted inputs" (USEPA, 2010d).

The bulk of PCA's comment on the proposed mercury standard was devoted to a rule subcategory argument for facilities with high levels of mercury in limestone inputs. Under the proposed rule, two facilities appeared unable to meet the regulations even with installation of control technology. At these facilities, limestone had mercury concentrations of 1,121 parts per billion (ppb) and 653 ppb whereas USEPA's dataset reported median concentration of 21 ppb (USEPA, 2009b). Quoting a US House of Representatives report, PCA established that "[US]EPA may distinguish among classes, types and sizes within a category or subcategory" and that "MACT is not intended to require unsafe control measures, or to drive sources to the brink of shutdown" (PCA, 2009a). A judge's concurring opinion in a related case points out a CAA statutory conflict requiring MACT standards to be both based on the control "achieved by" best performing facilities and be "achievable" by all facilities (D.C. Circuit, 2007). The judge writes that "creating additional subcategories" is appropriate in situations when "the required technology cannot, given local inputs whose use is essential, achieve the 'floor'" (D.C. Circuit, 2007). PCA argued that the two noted facilities accurately fit the situation envisioned by the judge and called for a subcategory requiring 75% removal efficiency for facilities with limestone mercury concentrations in excess of 96 ppb, the outlier threshold identified by the PCA's statistical assessment of USEPA data (PCA, 2009a).

The USEPA was not receptive to PCA's subcategorization arguments. USEPA first noted that while it did have authority to create subcategories, this authority is not required by law, but is at their discretion. USEPA's review of the average mercury content of limestone found "a gradual continuum of mercury concentrations in limestone for all but two outlying plants", not a specific breakpoint therefore, USEPA saw no technical justification for subcategorization (USEPA, 2010d). Ultimately, USEPA did evaluate an 85% reduction standard for the two facilities, but found that based on 2008 production rates, the level of mercury that would be emitted by these facilities would total 1,020 lbs. In comparison, the rest of the industry would be permitted 1,012 lbs of mercury emission. USEPA believes that this disproportionate increase in mercury emissions would be an unwise use of its discretion.

Although PCA protested many portions of the mercury rule, environmental groups appeared entirely pleased. Submitted comments on the proposed rule by a group of six environmental groups gave USEPA "strong support" and mentioned that the agency "deserves applause" for a rule "that will provide meaningful protection from these polluters' toxic emissions" (Sierra Club, 2009). Additional comments from a seven-organization group urged the USEPA to "move quickly to adopt the Proposed Rule … and to reject the discussed alternatives" (NRDC, 2009). These responses starkly dissimilar to the reaction with USEPA's 2007 regulation which the groups called a "do-nothing rule" in which USEPA "ignored the law", "ignored the courts", and "ignored public heath" (Earthjustice, 2007).

USEPA's final mercury rule was developed in acknowledgement of relevant case law and appeared to follow the CAA. However, on November 5, 2010, the PCA filed a Petition for Reconsideration and

Administrative Stay with the USEPA and reportedly plans to file a challenge to the final NESHAP with the D.C. Circuit to address their contentions with the rule (PCA, 2010a). These petitions could substantially alter emissions regulations for cement facilities. For example, a March 2005 Clean Air Mercury rule scheduled to take effect in 2010 for the coal-fired power plants industry, was vacated by the D.C. Circuit in February 2008. This rule would have reduced mercury emissions from 48 tpy to 15 tpy; however, these emissions remain unregulated as USEPA awaits a response from the US Supreme Court concerning a petition for review of the circuit's vacatur (USEPA, 2010c).

The 2010 rule only addresses atmospheric emissions of mercury. Kiln dust, a potential mercury outlet, is at present listed as a "special waste" temporarily exempting it from the Resource Conservation and Recovery Act's hazardous waste regulations. USEPA is in the process of developing new regulations for the material. If the agency's proposed management standards are adhered to, the dust may remain a non-hazardous waste (USEPA, 2008). Mercury in the cement product is limited by American Association of State Highway and Transportation Officials (AASHTO) and American Society for Testing and Materials (ASTM) cement standards that permit up to 5% inorganic processing additions to portland cement (AASHTO, 2009; ASTM, 2009). The rule also does not affect an estimated group of ten cement facilities that burn hazardous wastes. These facilities are subject to a separate set of mercury emissions regulations through the NESHAP for hazardous waste combustors. Waste combustors typically do not generate a product output; therefore, this rule limits both feed mercury concentration to 3 ppm and mercury emissions to 120 micrograms per dry standard cubic meter at 7% oxygen (USEPA, 2005). This emissions limit is surprisingly less stringent than the newly proposed rule (converting to approximately 650 lbs mercury/million metric tons clinker); however, the industry believes that new regulations for hazardous waste burning facilities will be introduced in the near future (USEPA, 2010d).

Use of Mercury Concentration in Material Inputs to Predict Average Mercury Emissions

Continuous mercury emissions monitoring technology was not technologically mature at the time of data collection for the USEPA's rule. Instead, the agency estimated emissions by determining mercury levels in feedstocks and fuels collected over a 30-day period. Additional potential simplifications could estimate emissions by assuming 'typically observed' mercury levels in inputs or by assuming that emissions correlate with mercury levels in limestone, a facility's single largest input. Available data do not support these simplifications and demonstrates both a wide range of mercury concentrations in inputs and a poor correlation between limestone mercury levels and mercury emissions.

It is possible to find a ‘typically observed’ level of mercury in cement facility inputs. The limestone from cement manufacturing facility quarries has a mean mercury concentration of 43 ppb. However, even in this small set of 30-day data from 89 kilns, the concentrations range from 5 ppb to 1,121 ppb (USEPA, 2009b). Figures 2.2, 2.3, and 2.4 detail mercury concentration ranges for feedstocks, baghouse dust (a material generated by the facility but recycled as a feedstock), and fuels, respectively. With realization of the large range of possible levels of mercury input, it would be unwise to make any assumptions with regards to a facility’s emissions without first reviewing facility-specific data or conducting a sampling of mercury inputs.

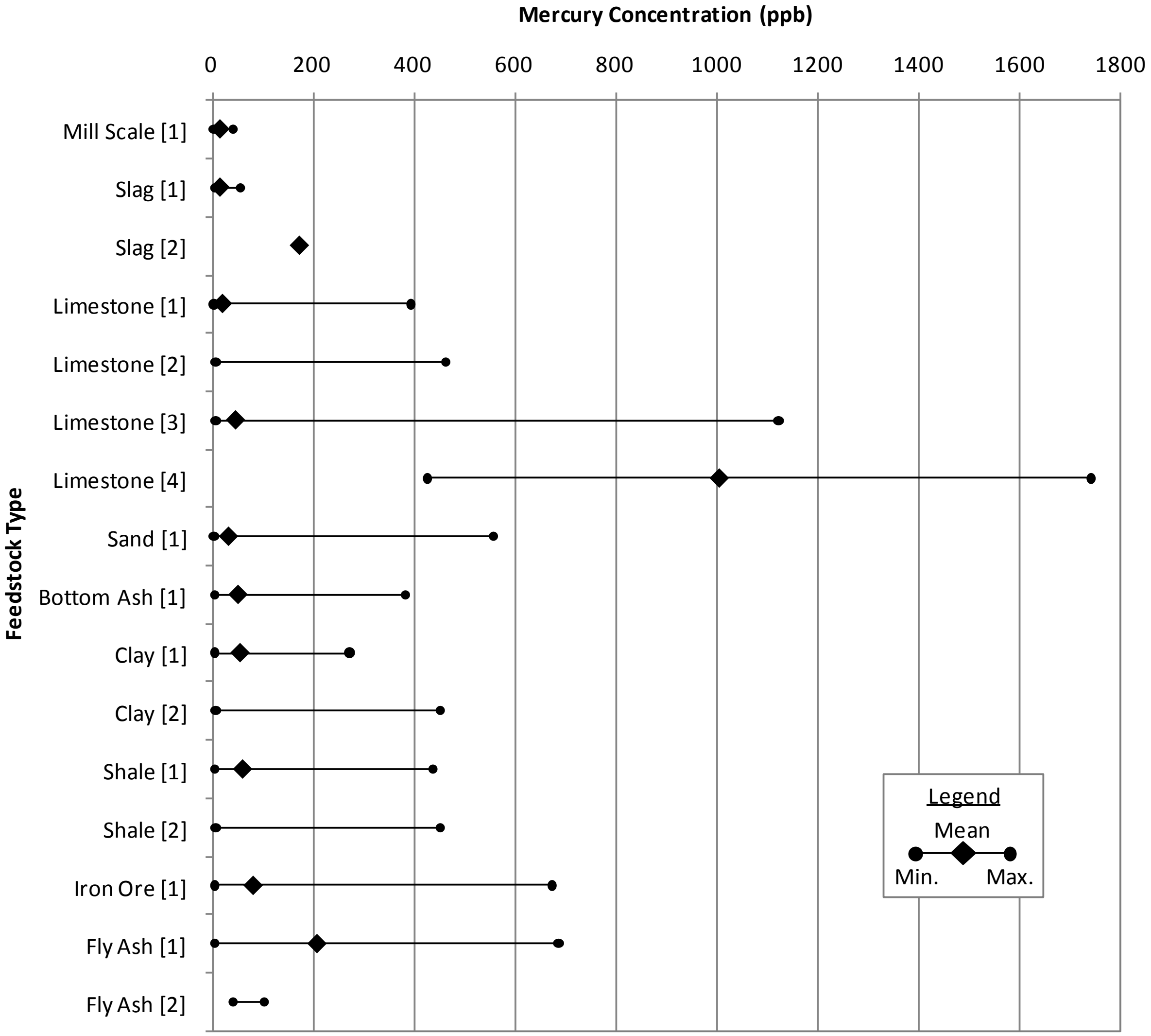

Figure 2.2. Observed Mercury Concentrations of Cement Manufacturing Facility Feedstocks ([1] Hills, et al., 2006; [2] Johansen, et al., 2003; [3] USEPA, 2009; [4] Lesslie, 2009; [5] USEPA, 1993; [6] Delles, et al., 1991; [7] Haynes, et al., 1982)

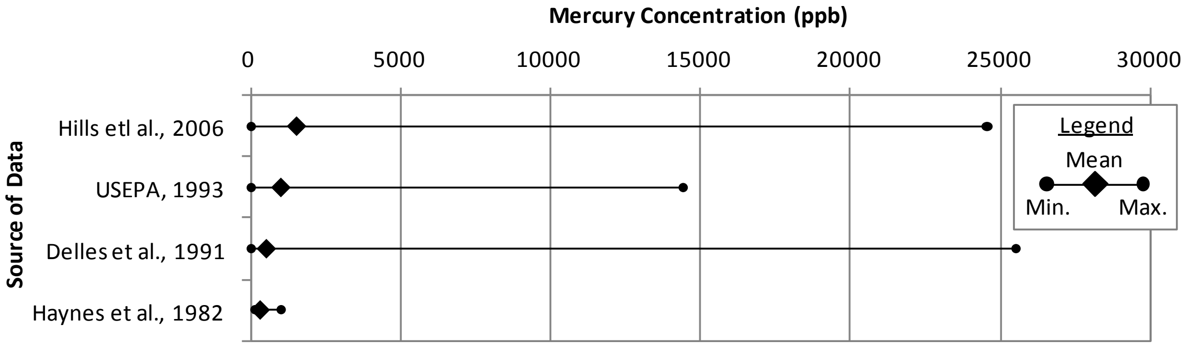

Figure 2.3. Observed Mercury Concentrations of Cement Manufacturing Facility Baghouse Dust

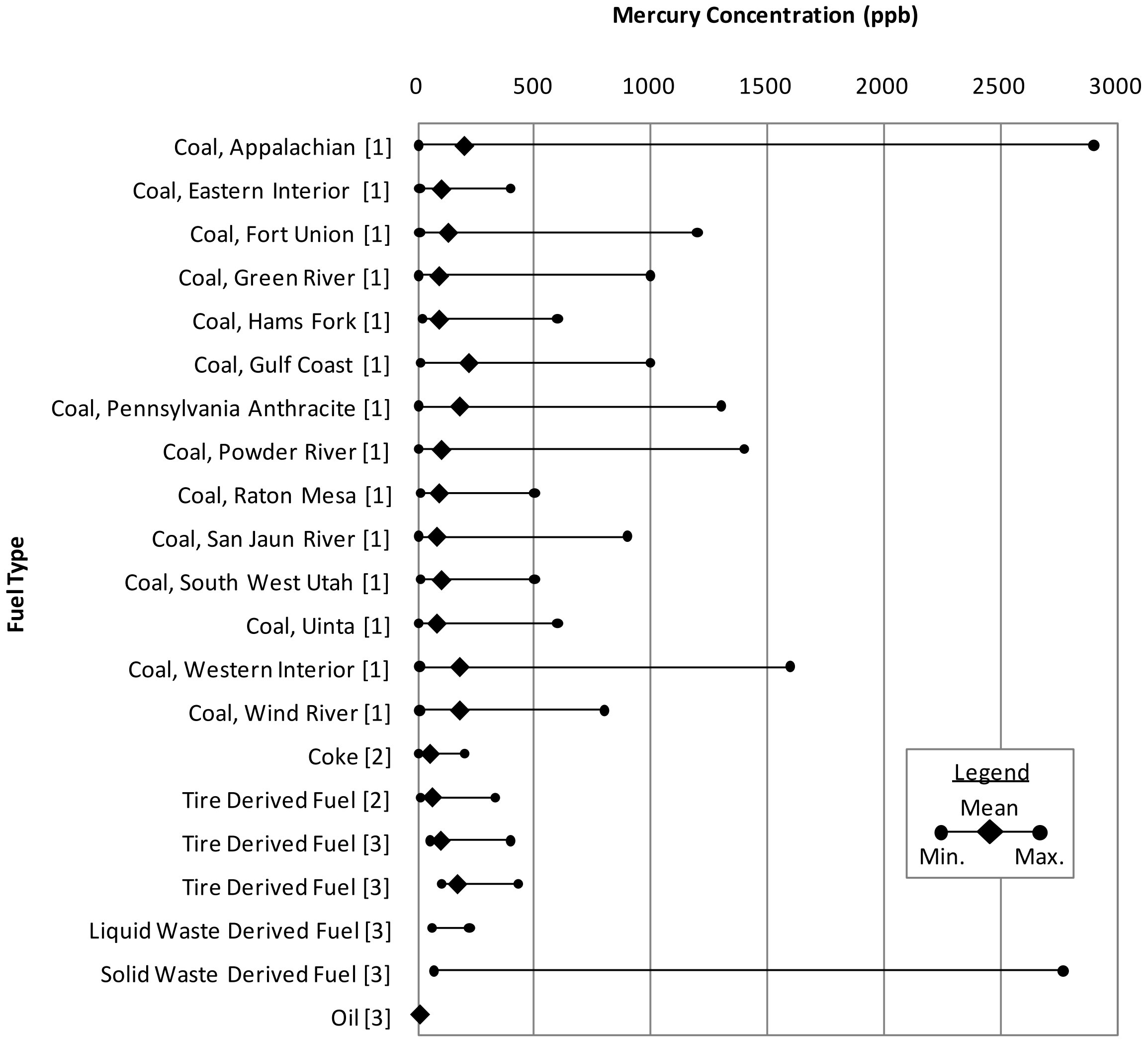

Figure 2.4. Observed Mercury Concentrations of Cement Manufacturing Facility Fuels ([1] O'Neil, et al., 1999; [2] USEPA, 2002; [3] Hills, 2006)

A simple approach in estimating mercury emissions is by assuming a correlation with observed limestone mercury concentrations. As shown in Figure 2.5, review of USEPA's data set in its entirety does appear to support such a conclusion, with a 97% linear correlation between limestone mercury concentration and mercury emissions. However, this correlation is highly leveraged by data from two facilities with abnormally high limestone mercury concentration. Eliminating these facilities from the dataset reduces the correlation to 14% (as shown in Figure 2.6).

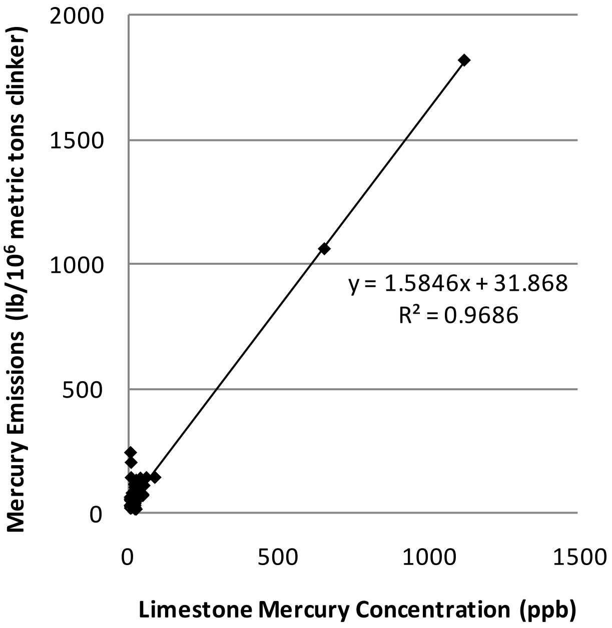

Figure 2.5. Linear Correlation of Limestone Mercury Concentrations and Mercury Emissions (Mercury Concentrations and Emissions Data from PCA, 2009a)

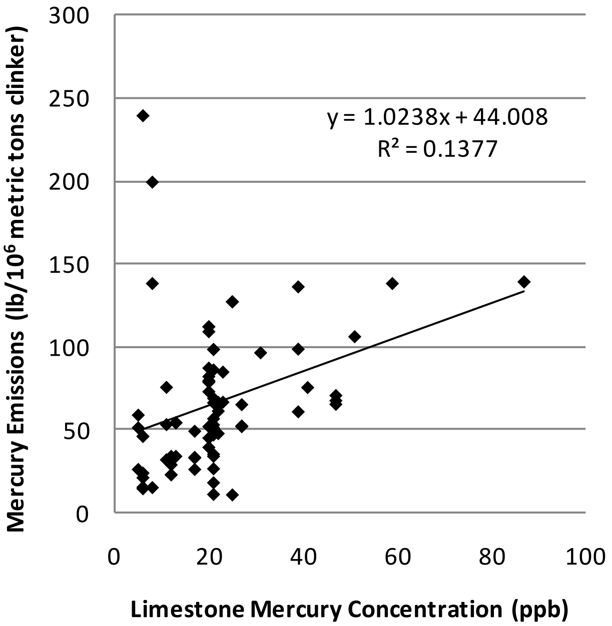

Figure 2.6. Linear Correlation of Limestone Mercury Concentrations and Mercury Emissions with two High Mercury Concentrations Facilities Removed (Mercury Concentration and Emissions Data from PCA, 2009a)

Based on Figure 2.6, this simplification of 'typically observed' input concentrations or correlation between limestone mercury concentrations and emissions should be avoided. Instead, both available USEPA data and unpublished data collected by the industry should be reviewed. At the time of writing, facility-specific data were not widely available. Research that collects and publishes data balancing inputs and emissions at cement facilities would be valuable to advancing technological development in this area.

Current Knowledge on Mercury Fate and Transport Within Cement Facilities

Mercury emissions and fate from cement facility can be assessed with an overall mass balance. Although this balance provides insufficient knowledge for control technology development, it does provide a starting point for model development. As described by Figure 2.7, existing preliminary mass-balance models pair mercury inputs with outputs of exhaust, dust removal, and clinker (Schreiber, et al., 2009b). Dust removal and clinker are both potential output streams. As discussed earlier in Section 2, many facilities recycle baghouse dust back to the manufacturing stream, which eliminates this output. Most mass balances assume clinker is free of mercury due to the barrier of the kiln's high temperature (Schreiber, et al., 2005; USEPA, 2009b). However, one study reported an average mercury concentration of 5.2 ppb with a 122% standard deviation for a clinker sample (Mlakar, et al., 2010). The mercury present in clinker may be that of mercury silicates (e.g., $HgSiO_3$ or $Hg_6Si_2O_7$), a set of stable mercury compounds with unknown decomposition temperatures (Schreiber, et al., 2005). Over long periods of operations, a mass balance approach is valid, but in the short-run, a known … but poorly understood … mechanism of mercury loop concentration creates substantial variation in stack emissions and internal material concentration. As illustrated by Figure 2.8, this mechanism, termed *'internal loop control'*, and mercury emissions variations can be explained by subdividing the facility into three stages: stripping, sorbing, and recycling.

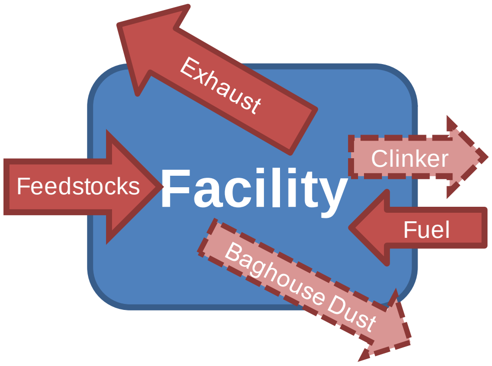

Figure 2.7. Cement Manufacturing Facility Mercury Mass Balance

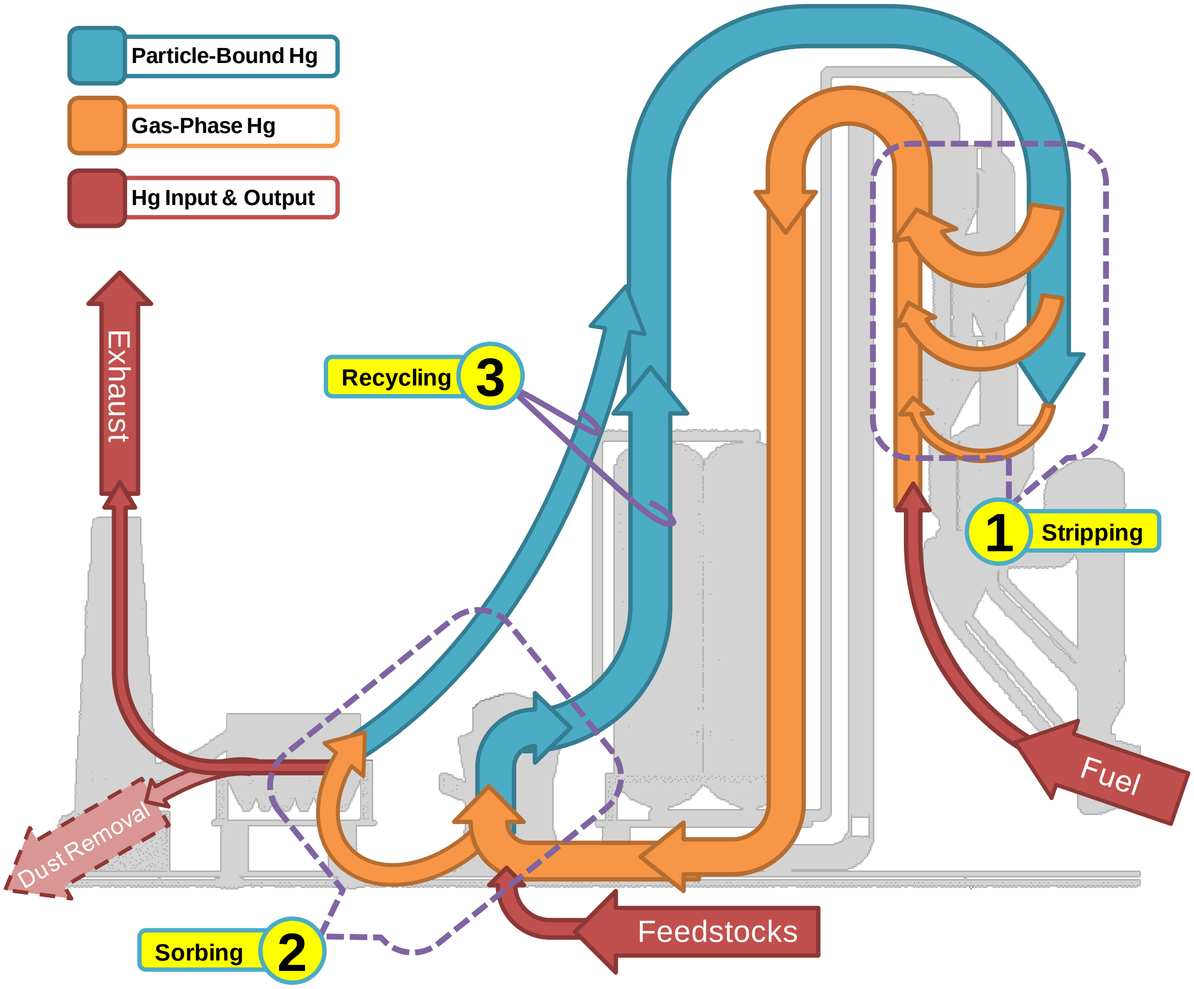

Figure 2.8. Mercury Transport and Fate within a Cement Manufacturing Facility

In the ‘stripping’ stage (see #1 in Figure 2.8), mercury in kiln feed (i.e., the ‘blue’ stream) volatilizes while falling through the preheater tower. In addition to cinnabar (HgS), the major form of mercury in feedstocks, different mercury compounds are physisorbed and chemisorbed on the feedstocks’ surface when the gas emissions are internally looped to preheat the raw meal. The different sorption forms and widely varying boiling points of mercury compounds assumed to exist in the facility (listed in Table 2.1) cause desorption to occur in the multiple preheater stages. Observation at one facility found between 58% and 82% stripping in the first preheater in terms of material flow and 97% stripping in the second preheater (Mlakar, et al., 2010). At the time of writing, no additional measurements of mercury desorption from kiln feed were available. Plant observation research that tracks desorption at various preheater stages will help to make hypotheses of the mercury species within a facility. In addition lab scale evaluations of mercury species and desorption dynamics will benefit internal mercury transport models and aid development of control technologies.

Table 2.1. Properties of Mercury Compounds Assumed to be Found in Cement Manufacturing Facilities (Paone, 2010)

	Hg^0	$HgCl_2$	$HgSO_4$	HgS	HgS	HgO
Name	Elemental Mercury	Mercuric Chloride	Mercuric Sulfate	Mercury Sulfide (Red)	Mercuric Sulfide (Black)	Mercuric Oxide
Melting Temperature (°C)	-38.9	277		344		
Boiling Temperature (°C)	357	304		583	446	
Decomposition Temperature (°C)			450			476

Although desorption does not occur in a single stage, all mercury is transferred to the gas phase prior to reaching the kiln's exit (with possible exception of mercury silicates). The kiln's high temperature reduces mercury to the elemental state (Hg^0) (Schreiber, et al., 2005). With exhaust cooling, a number of mercury transformations are possible (as illustrated in Figure 2.9). Although formation of many mercury compounds is possible, an equilibrium calculation indicates that below 480 to 590°C, the oxidized mercury species mercuric chloride ($HgCl_2$) should be the dominant mercury species observed (Senior, et al., 2003). Schreiber's 2009 compilation of US facility stack measurements does show high levels of oxidized mercury in comparison to elemental mercury (see Figure 2.10). However, determination of whether these observations are of mercury chloride requires additional mercury transformation modeling and mercury species identification work.

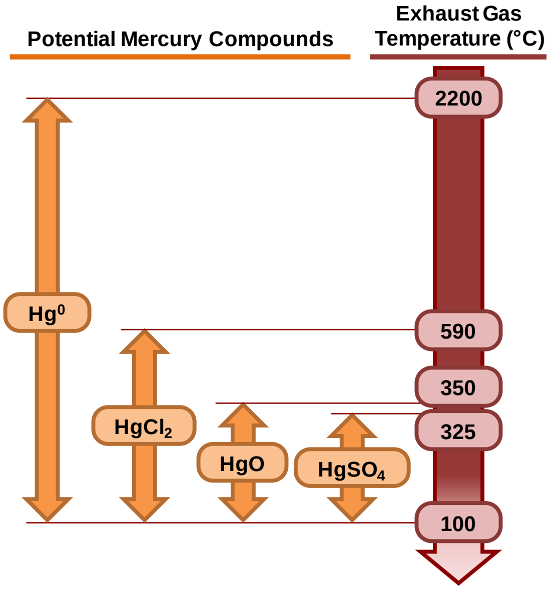

Figure 2.9. Potential Mercury Compounds in Cooling Kiln Exhaust Gas (Temperature Ranges Identified in Schreiber, et al. 2009a)

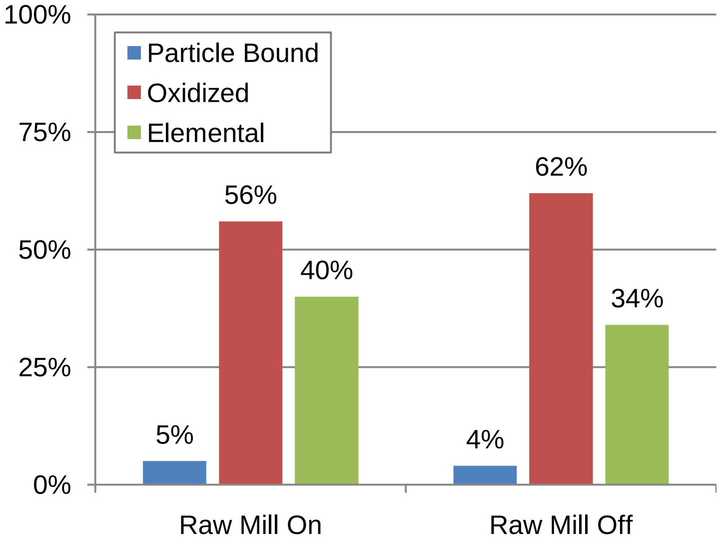

Figure 2.10. Comparison of Mercury Speciation Percent in Exhaust Gas for Different Process Factors (Adapted from Schreiber, et al., 2009a)

Exhaust gas containing desorbed mercury exits the preheater tower and flows towards the raw mill, transporting mercury from stage #1 (stripping) to stage #2 (sorbing) as shown in Figure 2.8. Stage #2 contains both the raw mill and baghouse; however, gases first enter the raw mill. This mill operates at between 90°C and 120°C and causes condensation of gaseous mercury onto cool feedstock particulates. It is also possible that electrostatic attraction exists since the fracturing nature of the mill severs electrovalent bonds in feedstocks creating particulates with charged surfaces. A change in arrow color from orange (i.e., gas-phase mercury) to blue (i.e., particle-bound mercury) denotes this sorption phenomenon in Figure 2.8. A portion of particle-bound mercury in the raw meal flows to the silo and transitions to stage #3. A smaller stream composed of mercury bound on fine particulates and gaseous mercury flows into the baghouse (as illustrated by the smaller side loop). The dust cake, found on baghouse fabric, is another material that captures gas-phase mercury by sorption onto the dust particles. Typically, dust is recycled and serves as a feedstock for the kiln transferring the dust to stage #3. Although measurement of mercury concentration on baghouse dust and raw meal do confirm that mercury sorbs in stage #3, there is no knowledge of the factors that optimize this sorption. Observations at representative facilities could help to identify the dynamics of internal mercury accumulation and determine which particles are favored for sorption. Lab scale mercury sorption dynamics tests could aid in further development of control technologies that exploit *'internal loop control'*.

Stage #3 completes an 'internal mercury loop'. The blue-colored streams of raw meal and baghouse dust flow through the silo and serve as feedstocks for the kiln. As long as the facility continues to operate with the mill on, mercury continues a process of stripping, sorbing, and recycling that can increase mercury concentration on the raw meal by "hundreds of times" (Clark, 2009). This loop provides internal loop control of mercury with reported system removal efficiencies in excess of 90% (Schreiber, et al., 2005). Completion of this mercury loop adds complication to an already imperfect explanation of speciation. The mercury compounds that sorb onto raw meal and baghouse dust are not necessarily broken down into elemental form upon entry into the preheater tower. Instead, these compounds may simply vaporize and flow in reverse away from the kiln prior to reaching a decomposition temperature. At present, it is unknown which species may be transported in this manner, or if this type of transport occurs at all. Addressing these speciation-specific transport questions represents a major research goal for the industry.

The above explanation neglects mercury outputs of dust removal and exhaust, illustrated in Figure 2.8. Although many facilities recycle dust, there are cases where dust detrimentally alters feedstock chemical composition. To prevent manufacture of poor-quality cement, the dust must be wasted, removing sorbed mercury from the system. A more problematic removal occurs when mercury leaves in exhaust gases. The concentration loop that provides internal mercury control only functions while the raw mill is operating. However, operation of a cement facility requires weekly mill maintenance, an 8 to 10 hour shutdown, while the kiln continues to operate. As raw meal and baghouse dust (with loop-concentrated mercury) is fed into the kiln, mercury is revolatilized and flows towards the raw mill. Instead of then flowing into the mill, exhaust flows directly to the baghouse. Mercury no longer has an opportunity to intermix and condense on cool particles and the hot gases raise dust temperatures in the baghouse, desorbing additional mercury. These factors cause an emissions spike that works against internal control. While an emissions spike has been observed, data is not available to correlate internal mercury concentration to the level of mercury emissions.

Cement Manufacturing Facility Mercury Emissions Models

Compared to the sophisticated level of mercury fate and transport modeling for the coal-fired power plant industry, the state-of-the-art mercury modeling for cement facilities is decidedly far less mature (Pavlish, et al., 2003). In fact, the present cement facility emissions models neither use actual measurements of mercury concentration within specific processing components (e.g., raw mill, preheater tower, baghouse, etc.) of the facility nor do they feature data on mercury sorption and desorption that might determine the involved exchange rates between these zones (Schreiber, et al., 2009b; Senior, et al., 2010). Although the actual modeling methods used within Schreiber's model are not described, it does appear that this approach measured mercury concentrations within the kiln inputs (i.e., raw meal and fuel), and then predicts the level of mercury outputs in exhaust gases. Therefore, while this model may be effective for Schreiber's original goal (i.e., determining if dust wastage could significantly reduce mercury emissions), this model has relatively limited utility, particularly given that it treats the entire facility as a single box with no consideration of the complex internal mercury transport mechanisms.

A more useful model is found in the work of Senior et al., 2010. Senior's model reproduces key features of mercury behavior including exhaust gas spikes upon raw mill shutdown. The model assumes five modes in which mercury can exist: "adsorbed on raw meal, adsorbed on dust, gas phase, chemically bound on raw meal, and chemically bound on dust" (Senior, et al., 2010). Senior's model reduces a facility into nodes with specific mass inflow and outflow rates, which then allows the model to be applied to any facility configuration. As a test of accuracy, the model was benchmarked against and closely matched with data sets from two German precalciner facilities. Senior's model represents a considerable improvement in cement facility mercury modeling. However, the model also highlights current gaps in mercury fate and transport knowledge. While the model does separate the facility into nodes, the model is based on measurement of mercury inputs (feedstocks and fuel) and outputs (exhaust gas and baghouse dust), not on measurements from components within the facility. In addition, Senior's model assumes that the sorption processes that occur in the baghouse and raw mill "could be given by Langmuir or Freundlich isotherm relationships" because "there are no experimental measurements of Hg sorption on cement kiln dust or raw meal" (Senior, et al., 2010). The model also does not distinguish between different species of mercury, which do have different boiling points and sorption/desorption properties.

Current and Proposed Mercury Control Strategies

Strategies for controlling mercury emissions include technologies applied in other industries, technologies already installed to control different air pollutants, and technologies developed specifically for cement facilities. Listed from lowest to highest anticipated mercury removal, control technologies include: purge of baghouse dust or raw meal, changes in feedstocks and fuels, wet scrubbing, cleaning of mercury enriched dust, dry sorbent injection, and dry and semi-dry scrubbing (Paone, 2010). These options can be applied with varying degrees of removal efficiency to cement facilities; however, without additional research, no strategy will be able to optimize removal due to a limited understanding of sorption, desorption, and compounds involved in internal loop mercury control.

Purge of Baghouse Dust or Raw Meal

The internal mercury loop between the kiln, raw mill, and baghouse concentrates mercury in both the raw meal and baghouse dust. Mercury will concentrate at higher levels on baghouse dust than raw meal due to smaller particulate size (Mlakar, et al., 2010). Therefore, removing dust from the system will reduce stack emissions. This strategy has a number of drawbacks. Dust removal necessarily removes the finest particulates from the system, reducing the effectiveness of sorption in the control loop. To remedy this concern, a purge of raw meal is proposed, but a larger mass of material, as compared to baghouse dust, must be removed due to lower concentration on raw meal (Clark, 2009). Once removed, disposal of the material presents a challenge. One option is to intermix the dust or meal with the cement product, however this practice is limited by cement standards (AASHTO, 2009; ASTM, 2009). Alternative disposal means can be expensive due to the management practices required by the material's "special waste" status.

Changes in Feedstocks and Fuels

A second low-capital option to reduce mercury emissions is to minimize mercury inputs from fuel and feedstocks. Coal represents the primary fuel source for cement kilns. It may be possible, but not likely feasible, to obtain coals with lower mercury concentrations. Many facilities also use low-cost alternative fuels that contain higher levels of mercury than coal (PCA, 2009b). Reducing the firing rate of these fuels reduces mercury emissions. In cases where feedstocks are the primary source of mercury input, facility options are more limited. In some cases additives, such is iron ore and fly ash, can contain high mercury concentrations (Hills, 2006). Substitution of these additives may be possible because they typically make up less than 1% of feedstock input. If mercury input is attributed to limestone or shale, selective quarrying in areas of low mercury materials could be instituted. In each case, reducing mercury inputs requires knowledge and monitoring of the mercury concentration in fuels and feedstocks. In addition, feedstock substitution may be cost-prohibitive because transportation costs normally force facilities to be constructed next to quarries with expected useful lives of up to 100 years.

Wet Scrubbing

Wet scrubbers are already utilized by the power industry and in a few US cement facilities to control sulfur dioxide (SO_2) and can be applied for mercury control. Within a reactor vessel, the scrubber passes flue gas through a counter-current spray of lime, limestone, or baghouse dust slurry. SO_2 in the gas reacts with lime in the slurry to form calcium sulfite, which is oxidized to calcium sulfate (gypsum). This gypsum slurry collects at the vessel's bottom and is removed. While designed for removal of SO_2 and other acid gases, the scrubber's slurry also controls mercury. The reactor vessel operates near the dewpoint of moisture in the exhaust, allowing condensation of mercury compounds. In addition, the slurry also captures water-soluble oxidized forms of mercury. While scrubbers present an opportunity for high levels of mercury control, they will not function without sufficient levels of SO_2 already present in the flue gas and require careful monitoring to ensure that pH changes and particulate interference do not hinder gypsum formation. The technology also requires large quantities of water, an impediment for facilities in arid climates. Scrubbers are also sensitive to mercury species. While high capture is achieved for oxidized mercury, little removal of elemental mercury has been observed (Paone, 2010).

Cleaning of Mercury Enriched Dust

At present, a baghouse dust cleaning technology termed the Mercury Roaster is being tested on a pilot scale by FLSmidth (Bethlehem, Pensylvania). The process steps of this approach begins with removal of baghouse dust to disrupt the internal mercury loop. This step is similar to the purge of baghouse dust (section 7.1); however, instead of being wasted, the dust is shuttled to a roaster where mercury is released to the gas phase by raising the dust's temperature above mercury compound boiling points. While maintaining this temperature, dust is separated from gaseous mercury and returned to the kiln. Gaseous mercury in the roaster is quenched and condenses on a sorbent stream (Jepsen, et al., 2009). The roaster addresses drawbacks of other strategies. Fine dust, which is an effective mercury sorbent, is not lost from the system and can continue to provide internal mercury control. The inventors predict that the roasting system will have lower operating and capital costs than methods installed to treat the primary exhaust gas stream. However, stack measurements indicate that the internal loop controls approximately 90% of emissions only when the raw mill is on (Schreiber, et al., 2005). The roaster does not control exhaust emissions downstream of the baghouse raising the possibility of high mercury emissions when the mill is shutdown.

Dry Sorbent Injection

Following the primary baghouse, a sorbent (typically powdered activated carbon optimized for mercury control) is injected into the facility's flue gas and a high percentage of mercury binds to active sites by chemisorption. A secondary baghouse then collects the sorbent, removing it from the gas stream. This sorbent is most effective for oxidized forms of mercury; however, bromine can enhance removal by oxidizing elemental mercury (Pavlish, et al., 2003). While effective for capturing both mercury and many other volatile compounds, this technology is expensive. PCA estimated a capital investment of $20 million and annual operating costs of $4 million per 1 million tons of capacity (Sullivan, 2009). Disposal is also challenging because unlike lime-based sorbents only 1% organic processing additions are permitted in the cement product (AASHTO, 2009; ASTM, 2009).

Dry and Semi-Dry Scrubbing

This system also sees wide use in the power industry and is similar to the wet scrubber in that both mercury and acid gases are controlled and similar absorbents are used. However, these sorbents are injected with little or no water. A common type of dry scrubbing, the Gas Suspension Absorber (GSA), treats flue gas with a sorbent then drafts it upwards into a reactor vessel. A limited amount of water is sprayed into the system to both control residence time and keep the exit temperature near the adiabatic dew point. Following the reactor, the sorbent is separated from gases with a cyclone similar to those in a cement facility's preheater tower. Following the cyclone, the sorbent is either wasted or recycled in the reactor to capture additional levels of mercury. Mercury capture in dry and semi-dry scrubbers is less dependent on mercury speciation than in wet scrubbers. In wet scrubbers a vapor-liquid equilibrium can develop, hindering mercury control and dry sorbent injection is hindered by high temperatures. Both of these issues are not present in a dry or semi-dry scrubber (Paone, 2010).

Comparison of Mercury Removal Efficiency

Each control strategy varies significantly in their mercury removal ability (see Figure 2.11). In addition, some strategies show significant differences between highest and lowest control estimates due in particular to mercury species sensitivity. Removal efficiency will be one of a number of considerations made by cement facilities. A secondary consideration of particular importance is the interaction of a chosen mercury control strategy with controls for other hazardous air pollutants. Although removal efficiencies are available for various control technologies, the impact of operating conditions and modes, mercury species, and mercury inputs in feedstocks and fuels on the mechanisms of removal for these technologies have not been well researched. Building a body of knowledge that considers these factors will allow cement production companies to better decide on an appropriate control strategy.

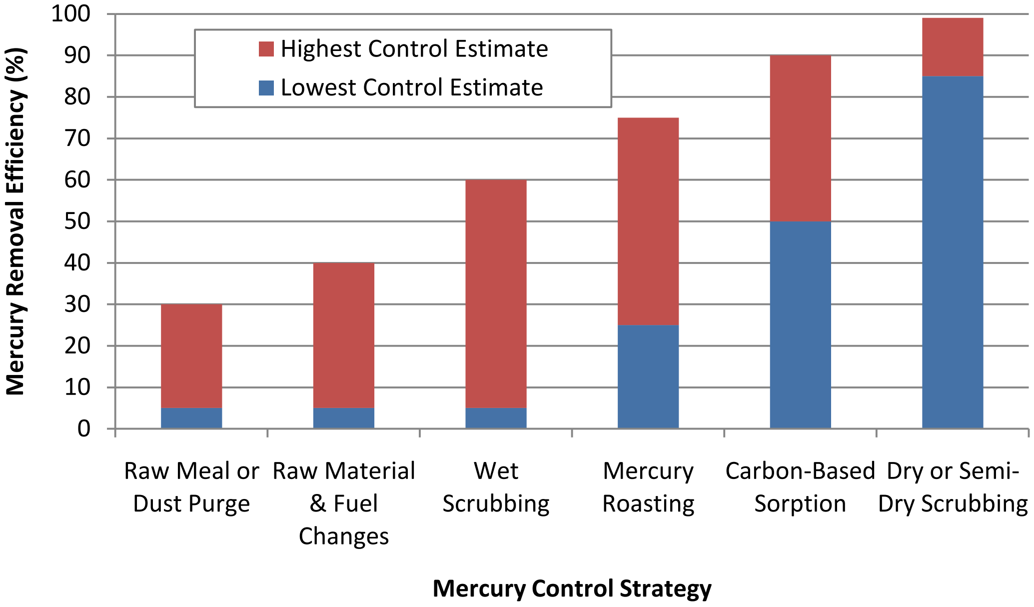

Figure 2.11. Comparison of Mercury Removal Efficiency for Proposed and Available Control Strategies (Removal Efficiency Data from Paone, 2010)

Summary

USEPA's mercury rule for cement manufacturing facilities represents a valuable public service by reducing the risk of negative health effects from anthropogenic mercury emissions. However, the rule's aggressive nature, both in the level of emissions reductions and in the short three-year compliance period, is estimated to force closure of a minimum of 10, and possibly as many as 18, of the 113 existing US cement facilities (USEPA, 2010e; Sullivan, 2010). In contrast to the expected domestic production loss, cement demand is predicted to grow. To meet this demand, imports are estimated to rise from 2008 levels by 12% (PCA, 2010b). Unfortunately, a significant portion of these imports come from countries with less stringent or non-existent mercury regulations (Lofstedt, 2010). To comply with the mercury rule and to further advance and improve current control technologies and practices, several data and information gaps need to be addressed and researched. Some of these data gaps and research needs include:

1. Identify and quantify mercury accumulation in the concentrating loop,
2. Track the dynamics of this accumulation phenomenon over time relative to facility operation,

3. Evaluate the dynamics of mercury sorption and desorption on raw meal and baghouse dust within cement facilities,
4. Develop a predictive dynamic model for mercury sorption in relation to the internal concentration loop phenomenon,
5. Develop a predictive dynamic model for mercury desorption from facility raw meal and baghouse dust during critical facility periods when the internal concentrating loop is not functioning (i.e., during raw mill shutdown periods)
6. Develop a predictive dynamic model for mercury desorption as might be applied to prospective internal mercury control processes
7. Characterize the mercury species in various materials within the cement facility and in the feedstocks and their formation under typical operating conditions, and
8. Specify chemical reactions of elemental mercury or mercury compounds with various surfaces and the mechanism of volatilization from various materials within the cement facility.

USEPA's mercury rule, while aggressive and potentially detrimental to the US cement industry provides a unique opportunity for rapid innovation in mercury control technology and development of a superior understanding of mercury fate, transport, transformation, and abatement within cement manufacturing facilities. Knowledge gained from this effort will be applicable to other volatile compounds (e.g., ammonia salts and organic material) and other manufacturing processes (e.g., taconite production) (Schwab, et al., 2007; Berndt, 2003). In addition, the fundamental knowledge gained regarding mercury sorption and desorption dynamics will be broadly applicable and aid in development of future mercury sorbents and control technologies.

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Chapter 3. Optimization of a Wet Digestion Procedure for the Determination of Mercury in Baghouse Dust and Kiln Feed Samples from a Cement Manufacturing Facility by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)

A paper to be submitted to *Analytica Chimica Acta*

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Abstract

A wet digestion sample preparation method for determination of mercury by cold vapor atomic fluorescence spectrometry was optimized for baghouse dust and kiln feed materials from a cement manufacturing facility. After an initial paired *t*-test found that the United States Environmental Protection Agency's (USEPA's) Appendix to Method 1631 cold aqua regia (wet digestion) procedure was statistically different from a thermal decomposition procedure, various modifications to the wet digestion method were tested to address the probable sources of incomplete mercury digestion and mercury volatilization. The optimized digestion procedure modified the USEPA's method by adding 15 mL of blank solution prior to acid addition, reducing hydrochloric acid (HCl) addition to 1 mL instead of 8 mL, and digesting samples overnight at 90°C. Quite similar results were obtained by optimized wet digestion in comparison to thermal decomposition and linear regression did have an r-squared value of 0.998; however, a paired *t*-test rejected the null hypothesis of 0 average difference at any significance level greater than 0.013. The disagreement between results was attributed to mercury volatilization during the digestion procedure. Although wet digestion results averaged 13% lower than thermal decomposition, the optimized wet digestion permits mercury analysis of cement manufacturing facility baghouse dust and kiln feed if a thermal decomposition based analyzer is not available.

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Introduction

Cement manufacturers in the United States release an estimated 8 tons per year (tpy) of mercury through stack emissions (USEPA, 2010a). The residence time of emitted mercury in the atmosphere ranges from several days (for mercury emitted in an oxidized or particle-bound form) to an estimate of between 6 months and 2 years (for elemental emissions), resulting in deposition of emissions both locally and globally (Durnford, et al., 2010). These emissions, although considerably less than the 50 tpy emitted by utility coal power plants, represent a health risk to humans who are primarily exposed to this neurotoxin through consumption of fish containing methylmercury (USEPA, 2010b; USEPA, 2009). In an effort to reduce human exposure to mercury, the USEPA implemented a rule that limits the emission of mercury from cement manufacturing facilities that do not burn hazardous wastes. This rule is estimated to reduce mercury emissions from existing facilities by 7.5 tpy or by about 94% of current emissions (USEPA, 2010a).

To manufacture cement, a kiln (typically fueled by coal) heats a mixture of 85% limestone, 13% clay or shale, and less than 1% each of corrective materials such as silica, alumina, and iron ore to an temperature of approximately 1,400°C (Alsop, et al., 2007; Bhatty, et al., 2004). The high temperature volatilizes mercury, causing it to leave the facility with exhaust gases. While volatilization of mercury is relatively constant and occurs in either the kiln or preheater portion of the facility, emission through the exhaust stack to the atmosphere is highly variable. Mercury emissions variability is due to a unique mechanism termed *'internal loop control'*. In many facilities, hot exhaust gases containing mercury, travel through a raw mill (to dry incoming feedstocks) and through a baghouse (to capture exhaust dust). The relatively cool temperature and high surface area of materials in each of these facility components captures mercury. Baghouse dust and kiln feed (which is produced by the raw mill) are both inputs to the kiln, creating a mercury loop that can concentrate the element by "hundreds of times" (Clark, 2009). However, this internal loop is broken whenever the feedstock mill is shutdown for necessary maintenance, causing a spike in the facility's mercury emissions (Schreiber, et al., 2005). Exploitation of the internal mercury loop holds potential to reduce the control costs associated with the USEPA's mercury rule. To realize this potential, cement manufacturers must investigate the accumulation of mercury on kiln feed and baghouse dust.

The diverse approaches to trace-level mercury determination are grouped into spectroscopic, radiochemical, and electrochemical methods (Clevenger, et al., 1997). Spectroscopic methods are the most common and include, but are not limited to, cold vapor atomic fluorescence spectrometry (CVAFS), cold vapor atomic absorption spectrometry (CVAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). CVAAS and CVAFS techniques are popular for liquid and solid samples (Morita, et al., 1998; Leopold, et al., 2010). Mercury's uniquely low vapor pressure (e.g., 0.23 Pa at 25°C), permits the element to be introduced as a vapor into a spectrometer at room temperature without the use of an atomizer (OSHA, 2010). Determination of mercury in this vapor differs for each type of analyzer. The absorption technique measures the level of 253.7 nm ultraviolet light absorbed in the spectrometer, whereas the fluorescence technique measures the intensity of light emitted by mercury atoms excited from their ground state. Analysis techniques also diverge on whether the method used to extract mercury from the sample is by wet digestion or thermal decomposition. In wet digestion, mercury is released from the solid matrix by acids (e.g., nitric acid (HNO_3) and HCl), reduced to elemental form (typically by stannous chloride ($SnCl_2$) or stannous sulfate), and volatilized by an argon gas stream (USEPA, 2001a; USEPA, 2001b; Clevenger, et al., 1997). In thermal decomposition, the sample is inserted into a decomposition furnace that typically uses two stages to first desorb the mercury from the sample and then reduce mercury to an elemental state prior to atomic fluorescence or atomic absorption spectrometry (USEPA, 2007). For solid samples, these methods have various benefits and drawbacks (see Table 3.1); however, kiln feed and baghouse dust samples are best suited to thermal decomposition. These materials are fine homogeneous powders (requiring no sample preparation for thermal decomposition), are assumed to have a homogeneous mercury distribution, and are believed to have low levels of interfering elements. However, due to benefits such as lower detection limits, lower standard error, and possible remedies for interferences, many research facilities are only equipped with liquid-based wet digestion analyzers.

Table 3.1. Advantages and Disadvantages of Wet Digestion and Thermal Decomposition Methods for Solid Sample Peparation (Beister, et al., 1997; USEPA, 2007; USEPA, 2005)

Preparation Method	Benefits	Drawbacks
Wet Digestion	-Low standard error due to homogenization by digestion -Small sample volume -Lower detection limits -Interferences can be mitigated with reagents	-Incomplete digestion -Adsorption of mercury on digestion vessel -Volatilization during digestion -Interferences (e.g., background mercury, sulfides, copper, and co-absorbing gases) -Labor and time intensive
Thermal Decomposition	-Few reagents -Little sample preparation -Rapid analysis	-Higher standard error due to sample heterogeneity -Volatilization during sample preparation -Interferences (similar to wet digestion)

Available digestion procedures for solids are presented in Table 3.2. However, these procedures were developed for sediments, soils, and sludges rather than cement facility kiln feed and baghouse dust. Unlike geologic or sedimentary solids, cement materials contain loop-concentrated mercury in addition to natural mercury concentrations. The form of mercury sorption (i.e., chemisorption or physisorption) that occurs in the loop is unknown; therefore, a digestion process that may be appropriate for geological materials may not be appropriate for kiln feed and baghouse dust.

Table 3.2. Summary of USEPA Digestion Procedures to Recover Mercury from Solids (USEPA, 2001b; USEPA, 2001a)

Method	Intended Materials	Summary of Procedure
245.5 (Digestion I)	Soils, sediments, bottom deposits, and sludge-type materials	Heated aqua regia digestion and potassium permanganate oxidation followed by the addition of sodium chloride-hydroxylamine sulfate to reduce excess permanganate
245.5 (Digestion II)	Soils, sediments, bottom deposits, and sludge-type materials	Sulfuric acid and nitric acid digestion and potassium permanganate oxidation within an autoclave followed by sodium chloride-hydroxylamine sulfate to reduce excess permanganate
A1631 (Digestion I)	Biota, wood, paper, tissue, municipal sludge, and other primarily organic matrices (excluding coal)	Hot re-fluxing nitric acid and sulfuric acid digestion followed by bromine monochloride oxidation
A1631 (Digestion I)	Coals, ores, sediments, soils, and other geological media	Cold aqua regia digestion followed by bromine monochloride oxidation

Of the different digestion methods, procedures I and II in Method 245.5 and Digestion II of the Appendix to Method 1631 are appropriate for kiln feed and baghouse dust; however, the Appendix to Method 1631 digestion was chosen because it features the fewest steps and least time required.

To determine if the Appendix to Method 1631 digestion procedure required optimization, a preliminary set of 2 kiln feed and 3 baghouse dust samples was analyzed using the Appendix to Method 1631 wet digestion procedure and a Hydra AF Gold Plus mercury analyzer (Teledyne Leeman Labs, Hudson, New Hampshire). The sample supplier also analyzed the preliminary set of samples using an RA-915+ mercury analyzer and an RP-M324 thermal decomposition attachment (OhioLumex, Twinsburg, Ohio). Figure 3.1 shows that the mercury concentrations in the 5 samples analyzed by the wet digestion procedure were all lower than the mercury concentrations analyzed by the thermal decomposition procedure. A paired *t*-test of these two sets of results showed that the results were significantly different at any significance level greater than 0.008. Difference between the two sets of results could be due to error in the supplier's analysis, operation of the Leeman instrument, or the initial digestion procedure. Error on the part of the supplier was ruled out by third party analysis of one of the supplier's kiln feed samples which found a relative percent difference (RPD) between results of 10%. Diagnostics of the Leeman analyzer completed the week prior to the preliminary test and 102% recovery of the test's spiked sample established that the Leeman analyzer was functioning properly. These checks identified the digestion procedure as a probable source of difference.

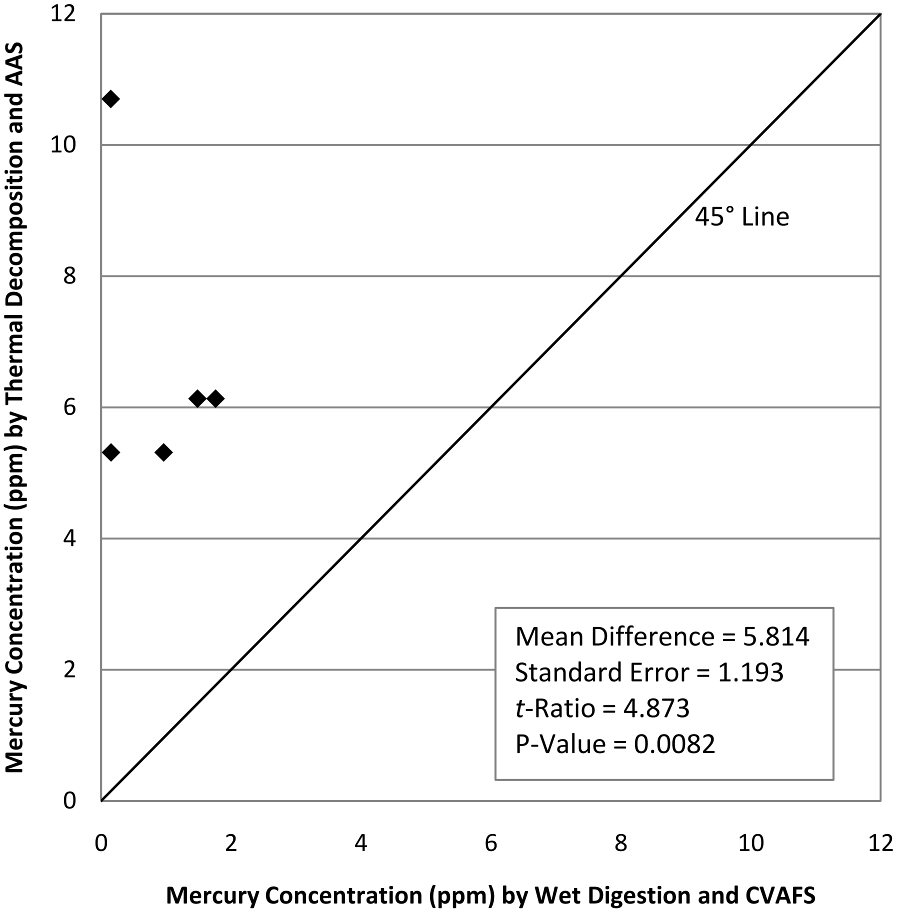

Figure 3.1. *t*-Test of Average Difference in Mercury Concentration Results by Wet Digestion Prior to Optimization and Thermal Decomposition

Based on the preliminary tests, this study's objective was to optimize the Appendix to Method 1631 digestion method for determination of mercury in kiln feed and baghouse dust from cement manufacturing facilities. Working from this digestion method, various modifications were made to optimize the procedure for kiln feed and baghouse dust. The paired *t*-test used to assess the Appendix to Method 1631 digestion requires a minimum of two matched pairs and is time consuming to test multiple digestion procedure modifications. Instead, the thermal decomposition method was assumed as an "error-free" basis point. Identified modifications were initially analyzed on the basis of RPD. Due to the low concentration results obtained by the Appendix to Method 1631 digestion, the modifications having the largest positive RPD were incorporated into an optimized digestion procedure. A large sample-set was analyzed with the optimized digestion and the mean average difference between these results and the supplier's results was assessed with a paired *t*-test.

Materials and Methods

Reagents and Standard Solutions

Concentrated HCl (trace metal grade; Fisher, Hampton, New Hampshire), concentrated nitric acid (HNO_3) (trace metal grade; Fisher, Hampton, New Hampshire), and a bromine monochloride (BrCl) solution (1.08% weight/volume (w/v) potassium bromide, 1.52% w/v potassium bromate, and 35.2% by weight HCl; Teledyne Leeman Labs, Hudson, New Hampshire) reagents were used to digest the samples. The reduction solution was trace metal grade $SnCl_2$ (2% w/v; Teledyne Leeman Labs, Hudson, New Hampshire). Prior to use in the experiments, all reagents were purged with argon (99.996% pure; Iowa State University Chemistry Stores, Ames, Iowa) for a minimum of 12 hours (Teledyne Leeman Labs, Inc., 2001). Certified stock mercury standards of 1000 parts per million (ppm) (±1%; Fisher, Hampton, New Hampshire) and 1 ppm (±2%; Teledyne Leeman Labs, Hudson, New Hampshire) were purchased. Working mercury standards of 10 ppm and 1 ppm were prepared monthly and stored in fluorinated high-density polyethylene (HDPE) bottles. Initial analyzer calibration standards (i.e., 5 or 10 ppb) were prepared on the day of sample digestion in a 500 mL HDPE bottle. Calibration standards of lower mercury concentrations were prepared by diluting samples of the initial calibration standard.

A 2% by volume HCl rinse solution, used to minimize carryover between samples, was prepared using trace metal grade HCl and Type I reagent grade water from a Barnstead Nanopure II conditioning system. In addition, a 1% by volume HCl blank solution was prepared with trace metal grade HCl and Type I water and was used to prepare working mercury standards and to dilute digested samples. These solutions were prepared monthly, purged with argon for a minimum of 12 hours, and stored in fluorinated HDPE bottles.

Glassware and plastic ware were precleaned in an overnight bath with a 1:1 by volume HCl solution. Following the bath, materials were rinsed five times with Type I water. When not in use, reagents, standard solutions, glassware, and plastic ware were stored in zippered polyethylene storage bags to prevent mercury contamination.

Kiln Feed and Baghouse Dust Sample Collection and Storage

Kiln feed and baghouse dust samples were collected from a cement manufacturing facility demonstrating internal loop control. To obtain a representative sample set, 11 baghouse dust and 12 kiln feed grab samples were taken over a 4-day period that included a raw mill shutdown event. Kiln feed is a fine powder in which 85% of material is smaller than 75 micrometers and baghouse dust represents the finest portions of this feed; therefore, sieving was not required prior to digestion. Sample homogenization was also unnecessary. The prehomogenization step prior to milling feedstocks and homogenization that occurs within feed storage silos results in a kiln feed mass ratio with standard deviation of less than 3% (Alsop, et al., 2007). Following the supplier's analysis by thermal decomposition, a three-inch by four-inch zippered polyethylene bag with a subset of the grab sample was provided for analysis by wet digestion. Samples were stored in these bags at room temperature until digestion and were opened only to permit extraction of a quantity sufficient for digestion.

Sample Analysis by Thermal Decomposition

The supplier analyzed samples using an RA-915+ mercury analyzer and an RP-M324 thermal decomposition attachment (OhioLumex, Twinsburg, Ohio). Following volatilization by thermal decompositions, the analyzer determines mercury concentration by Zeeman atomic absorption spectrometry with high frequency modulation of light polarization (ZAAS-HFM). The Zeeman effect correction employed minimizes interferences caused by the solid's matrix and is suitable for sample analysis without acid digestion (Morita, et al., 1998). The limit of detection for the samples analyzed was 0.8 parts per billion. In each sample analysis set, a spiked sample and duplicate sample were analyzed to monitor the analyzer's performance.

Initial Wet Digestion Procedure and Sample Analysis

The Appendix to Method 1631 digestion method is a procedure developed for coal, ores, sediments, soils, and other geological media. For samples that do not contain elemental carbon, this procedure calls for the following digestion steps: (1) weigh a 0.5-1.5 gram (g) aliquot of sample in 50 mL digestion vessel, (2) add 8.0 mL concentrated HCl, (3) swirl, (4) add 2.0 mL concentrated HNO_3, (5) cap the digestion vessel with clean glass marble or inverted fluoropolymer cone, (6) digest the sample at room temperature for a minimum of 4 hours but preferably overnight, (7) dilute digestate to 40 mL with reagent water, (8) shake vigorously, and (9) allow settling until the supernatant is clear. Diluted digestates were analyzed within two days of digestion; however, the procedure does permit storage for up to one year.

In this study, a centrifuge tube (50 mL, polypropylene, flat top, sterile; Fisher, Hampton, New Hampshire) was used as the digestion vessel. The tube's threaded cap served as a cap for the digestion vessel instead of a marble or cone. To analyze samples with the Leeman instrument, any solids remaining following digestion (e.g., silica) must be removed to prevent clogging of the instrument's tubing. Therefore, instead of allowing settling, each sample was filtered with a 0.45 micrometer filter (plain surface, mixed cellulose ester; Millipore, Billerica, Massachusetts) just prior to analysis. This filtration step also eliminated possible interferences due to presence of these particulates. Using this procedure as the starting point, numerous modifications were tested to optimize mercury analysis of baghouse dust and raw meal.

A Teledyne Leeman Labs Hydra AF Gold Plus instrument analyzed the digested samples for mercury. The analyzer has a working range of less than 0.05 parts per trillion to 250 parts per billion (ppb) (Teledyne Leeman Labs, Inc., 2001). The analyzer pumps a digested sample together with stannous chloride ($SnCl_2$) to reduce the divalent mercury to elemental mercury. The mixture flows into a gas-liquid separator where argon purges and transports the mercury through a counter-flow Nafion dryer. Following the dryer, the gaseous elemental mercury is excited by a collimated 253.7 nanometer light source causing florescence that is detected by two independent off-axis photomultiplier tubes (Teledyne Leeman Labs, Inc., 2010). To minimize any carryover of mercury from one sample to the next, the analyzer rinses the sample update probe and the gas-liquid separator with an HCl solution. To minimize variance in day-to-day operating conditions, the main fan of the analyzer was turned on the night before an analysis run and the analyzer's mercury lamp was turned on half an hour before analysis began.

The analyzer computer's WINHg software has preprogrammed mercury analysis protocols based on the anticipated mercury content of samples. A protocol titled "2-500 ppb AFS only" was selected (see Table 3.3 for the protocol's operational parameters). This protocol does not use the analyzer's available gold traps due to high anticipated mercury content of the samples.

Table 3.3. Protocol Operational Parameters

Variable	Setting
Argon flow rate	0.4 liters/minute
Peristaltic pump rate	4 mL/minute
Rinse time between samples	60 seconds
Sample uptake time	25 seconds
Signal integration time	45 seconds

As check of the digestion procedure and to monitor the analyzer's operation, a blank sample, a duplicate sample, a spiked sample, and a calibration standard were analyzed as part of the sample set. Two replicates of the calibration standards were analyzed and fitted to a linear curve.

Digestion Procedure Modifications

Incomplete digestion of mercury and mercury volatilization were identified as the most probable sources of disagreement between wet digestion and thermal decomposition methods (Horvat, 2005). To address the concern that the digestion procedure volatilized mercury prior to analysis, the following modifications were tested: (1) addition of blank solution prior to acid addition, (2) placing tubes in a -20°C bath prior to acid addition, and (3)modifying the quantity of HCl added. The intent of these modifications was to reduce the violent reaction between the cement facility samples and HCl.

To address the concern of incomplete digestion, modifications tested were: (1) digesting samples overnight at 90°C and (2) adding 0.07 N BrCl. Raising digestion temperature increases the favorability of mercury reduction reactions and BrCl improves mercury recovery in organic matrices. The effectiveness of these modifications are presented and discussed in Section 3.

Determination of Analyzer's Linear Range

Prior to the optimization effort, preliminary tests were completed to determine the analyzer's linear range. The preprogrammed Leeman analysis protocol was listed as appropriate up to 500 ppb. A calibration curve with 500 ppb as the highest level calibration standard is desirable because it allows larger sample masses, reducing potential error due to sample heterogeneity and digestate dilution. However, as displayed in Figure 3.2 the calibration curve was non-linear. Additional curves were tested using mercury standards of lower concentrations (Figure 3.3 and Figure 3.4). These tests established that for the mercury analyzer, linearity was not achieved until 100 ppb was used as the maximum calibration standard.

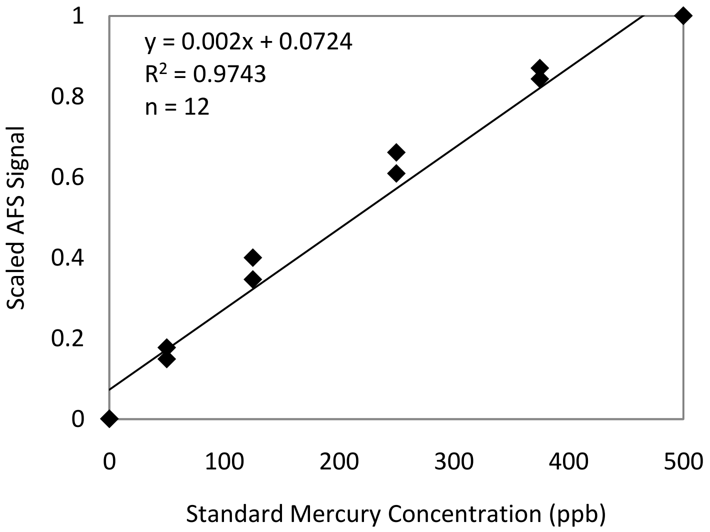

Figure 3.2. Linearity Assessment of 0 to 500 ppb Calibration Curve

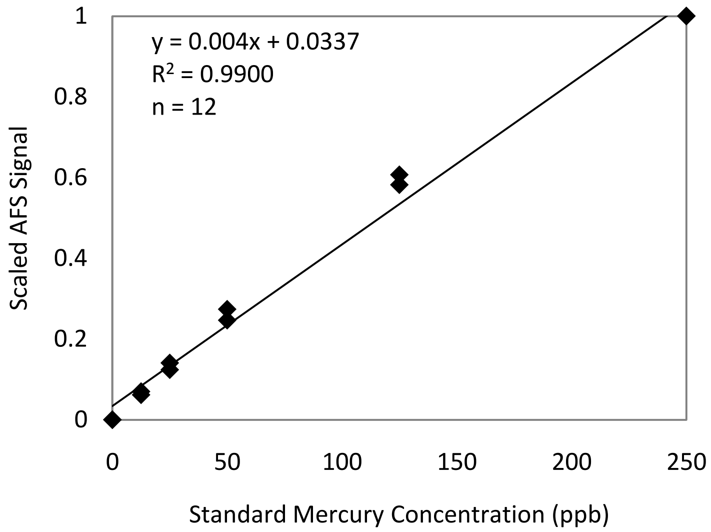

Figure 3.3. Linearity Assessment of 0 to 250 ppb Calibration Curve

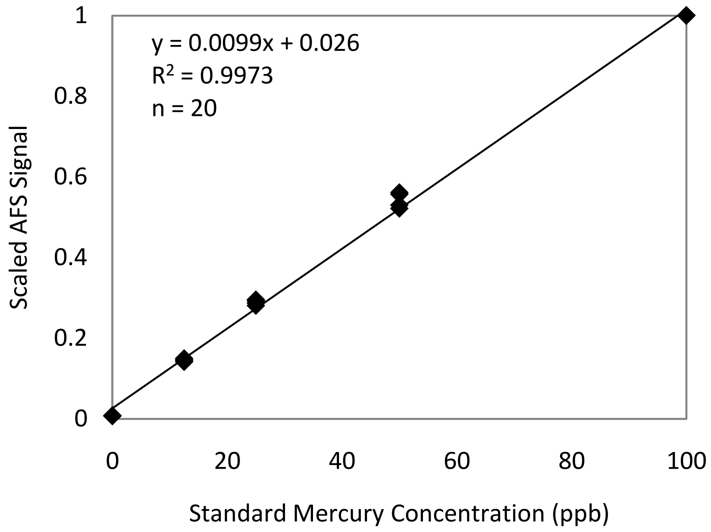

Figure 3.4. Linearity Assessment of 0 to 100 ppb Calibration Curve

Results and Discussion

Optimization of Wet Digestion Procedure for Kiln Feed and Baghouse Dust

The relative percent difference (RPD) between results obtained by wet digestion, with various modifications, and thermal decomposition was calculated. Negative RPDs indicate the wet digestion result was far less than the thermal decomposition result, near-zero RPDs indicate close agreement, and positive RPDs indicate a wet digestion result greater than the thermal decomposition result. Rather than selecting modifications nearest to zero RPD, for this study, modifications with the greatest RPD were viewed to have the greatest improvement on the digestion procedure. This view does increase the risk of selecting a modification that had erroneously high results due to sample contamination; however, evidence of contamination was not apparent in close monitoring of matrix spikes (recovery averaged 97% with a 10% standard deviation) and duplicate samples (RPD averaged 4% with a 1% standard deviation).

As displayed in Table 3.4, adding up to 20 mL of blank solution and overnight digestion at 90°C garnered increases in RPD. These two modifications were incorporated into a partially optimized digestion procedure. Reduced HCl volume, placement of tubes in a -20°C bath prior to adding HCl, and 0.07N BrCl addition also appeared to influence RPD. However, in the first experiment, up to three modifications were tested on a single sample, preventing differentiation of each modification's impact. These inconclusive modifications were tested on the partially optimized procedure in an attempt to garner further increases in RPD (see Table 3.5). BrCl addition had the lowest RPD of all modifications tested and placement of tubes in a -20°C water bath did not significantly increase RPD. While some ambiguity does exist, reducing HCl (to as little as 1 mL) did increase RPD.

Table 3.4. Analysis of Modifications to USEPA Appendix to Method 1631 Digestion Procedure

Concern Addressed	Digestion Procedure Modification(s)	N	RPD Modified Digestion and Thermal Decomposition
Volatilization	-Add 2 mL blank solution prior to adding 8 mL HCl	1	-180.4%
	-Add 5 mL blank solution prior to adding 8 mL HCl	1	-148.5%
	-Add 10 mL blank solution prior to adding 8 mL HCl	1	-151.6%
	-Add 20 mL blank solution prior to adding 8 mL HCl -Place tubes in -20°C bath prior to adding 8 mL HCl	1	-101.4%
	-Reduce HCl to 4 mL -Add 20 mL blank solution prior to adding 4 mL HCl -Place tubes in -20°C bath prior to adding 4 mL HCl	1	-88.1%
	-Reduce HCl to 2 mL -Add 20 mL blank solution prior to adding 2 mL HCl -Place tubes in -20°C bath prior to adding 2 mL HCl	1	-79.6%
	-Reduce HCl to 1 mL -Add 20 mL blank solution prior to adding 1 mL HCl -Place tubes in -20°C bath prior to adding 1 mL HCl	1	-75.1%
Volatilization, Incomplete Digestion	-Add 20 mL blank solution prior to adding 8 mL HCl -Place tubes in -20°C bath prior to adding 8 mL HCl -Digest overnight at 90°C	1	8.3%
	-Reduce HCl to 4 mL -Add 20 mL blank solution prior to adding 4 mL HCl -Place tubes in -20°C bath prior to adding 4 mL HCl -Digest overnight at 90°C	1	12.0%
	-Add 20 mL blank solution prior to adding 8 mL HCl -Digest overnight at 90°C	2[a]	-21.8%
	-Add 20 mL blank solution prior to adding 8 mL HCl -Add 0.07N BrCl prior to digesting overnight -Digest overnight at 90°C	2[a]	-38.5%

[a] Standard deviation was 9.1% or less for tests with multiple samples

Table 3.5. Analysis of Additional Modifications to Partially Optimized Digestion Procedure

Concern Addressed	Digestion Procedure Modification(s)	N	RPD Modified Digestion and Thermal Decomposition
Incomplete Digestion	-Add 0.07N BrCl prior to digesting overnight	4[a]	-36.8%
Volatilization, Incomplete Digestion	-Reduce HCl to 4 mL	1	28.5%
	-Reduce HCl to 2 mL	1	13.6%
	-Reduce HCl to 1 mL	1	22.8%
	-Place tubes in -20°C bath prior to adding HCl	1	1.4%
	-Reduce HCl to 4 mL -Place tubes in -20°C bath prior to adding HCl	1	11.6%
	-Reduce HCl to 2 mL -Place of tubes in -20°C bath prior to adding HCl	1	11.6%
	-Reduce HCl to 1 mL -Place tubes in -20°C bath prior to adding HCl	1	17.0%

[a] Standard deviation was 5.3% for the test with multiple samples

Due to ambiguity in HCl reduction tests, the level of reduction was decided based on observations made during the experiments. Significant bubbling occurs during the exothermic reaction between HCl and sample material. The carbon dioxide release from calcium carbonate, indicated by the bubbling, could also carry volatilized mercury out of the tube. The greatest decrease in bubbling occurred when HCl addition was reduced to 1 mL; therefore this modification was included in the optimized procedure. Two additional untested modifications were considered appropriate on the basis of observation. The exothermic reaction upon HCl addition also visibly expelled particulate and blank solution from the centrifuge tube. To reduce the quantity of mercury-containing material expelled, the first modification reduced blank solution from 20 to 15 mL, increasing the travelling distance between the liquid level and the top of the 40 mL centrifuge tube. Bubbling produced by this reaction continues following acid addition; therefore, the second modification tightly capped the tube between procedure steps. Risk of pressure buildup and digestion vessel fracture was considered negligible because the cap's seal was not hermetic. The optimized digestion procedure featured the following steps: (1) weigh a 0.2-0.6 g aliquot of sample into centrifuge tube; (2) add 15 mL of blank solution and cap; (3) remove cap, add 1.0 mL concentrated HCl, tightly recap; (4) swirl; (5) remove cap, add 2.0 mL concentrated HNO_3, tightly recap; (6) digest samples at 90°C overnight;

(7) filter with 0.45 micrometer filter; (8) dilute digestate to 100 mL with blank solution; and (9) shake vigorously.

Optimized Wet Digestion Procedure Results for a Large Sample Set

Using the optimized digestion procedure, the full set of 11 baghouse dust and 12 kiln feed samples were analyzed. As displayed in Figure 3.5, the results from this sample set showed a strong linear relationship with the results obtained by the thermal decomposition method (i.e., the r-squared value was 0.998); however, a *t*-test rejects the null hypothesis of zero average difference at any significance level greater than 0.013. In fact, even following optimization, the wet digestion results were on average 13% lower than the thermal decomposition method. However, the optimized procedure showed substantial improvement over the original Appendix to Method 1631 digestion method for samples with high calcium carbonate fractions such as cement kiln feed and baghouse dust. Sources for the result disagreement include mercury contamination of samples, sample heterogeneity, incomplete mercury digestion, and mercury volatilization.

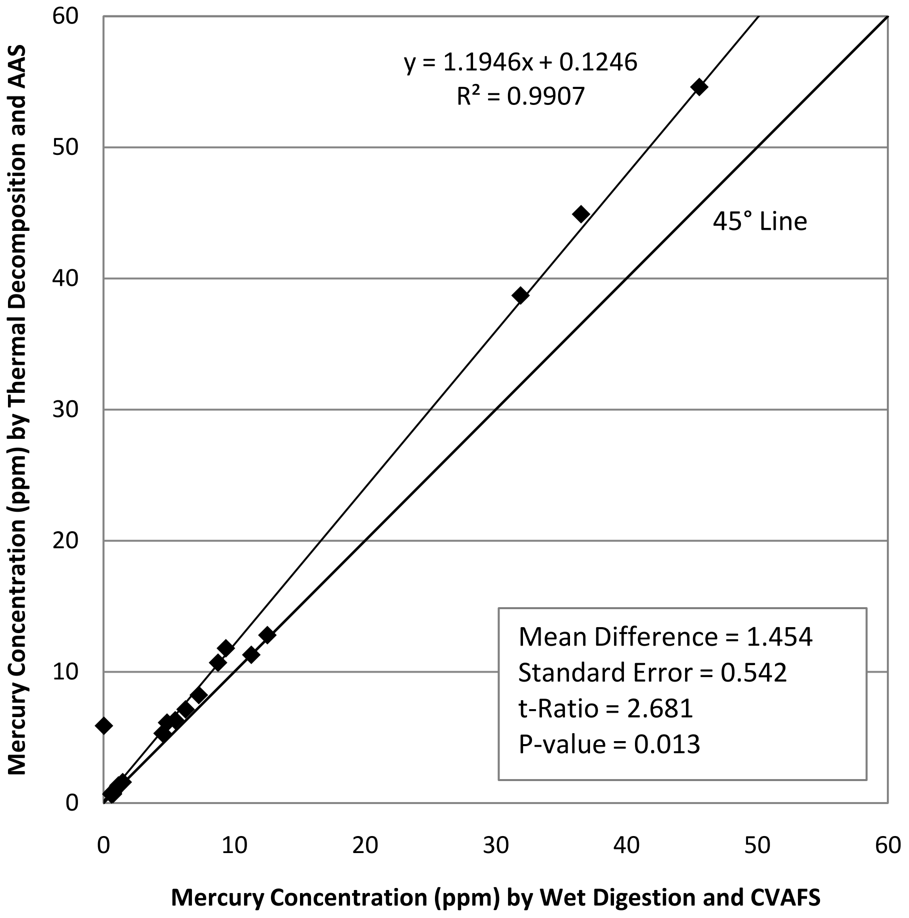

Figure 3.5. *t*-Test of Average Difference in Mercury Concentration Results by Wet Digestion Following Optimization and Thermal Decomposition

Recoveries obtained on matrix spikes and low RPD of duplicates indicate that the *t*-test result cannot be attributed to either sample contamination or heterogeneity. Heterogeneity concerns are further subdued by the high r-squared value observed. Incomplete digestion is also improbable. Acids used in this effort were stronger and the time the sample was held at high temperature was longer than previous similar studies (Van Delft, et al., 1988; Horvat, et al., 1991; Jones, et al., 1997).

The consistent pattern by which wet digestion results fell below thermal decomposition measurements implies that volatilization losses occurred. Throughout the digestion procedure, there are many opportunities for these losses. The most obvious are at times when the digestion vessel is uncapped. However, because the tube's capped seal is not hermetic, volatilization losses also may have occurred during the overnight 90°C digestion. In other efforts, researchers were able to improve results by digesting samples in sealed vessels (Van Delft, et al., 1988; Horvat, et al., 1991; Jones, et al., 1997). However, for this work, the benefits from use of a sealed digestion vessel (e.g., a Pyrex ampoule) were viewed as unnecessary. In future work, if greater accuracy is desired, hermetically sealed digestion vessels are recommended.

Conclusion

The USEPA Appendix to Method 1631 wet digestion procedure was optimized for CVAFS mercury analysis of cement manufacturing facility kiln feed and baghouse dust. While wet digestion is well suited for liquid samples and for heterogeneous materials, baghouse dust and kiln feed are typically analyzed using a thermal decomposition approach. This study's optimization effort substantially improved the wet digestion procedure and addressed incomplete digestion and volatilization concerns by adding 15 mL of blank solution to the digestion vessel prior to acid addition, reducing HCl addition from 8 mL to 1 mL, and digesting the sample overnight at 90°C. Although a paired *t*-test rejected the null hypothesis of zero average difference, between the optimized wet digestion and a thermal decomposition approach at any significance level greater than 0.013, digestion measurements were on average only 13% lower. The modifications made do permit optimized digestion procedure use for mercury analysis when a thermal decomposition based mercury analyzer is not available.

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Chapter 4. Observations of Cement Manufacturing Facility Mercury Fate, Transport, and Internal Concentration

A paper to be submitted to *Fuel*

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Abstract

Cement manufacturing facilities with in-line raw mills that use mercury containing kiln exhaust to dry incoming feedstocks demonstrate *'internal loop control'* of mercury that could be exploited to achieve mercury emissions reductions. To determine whether this exploit is practical, observations were used to identify and track mercury desorption, sorption, and internal concentration at specific points within a facility. At the facility observed, emissions averaged 207 pounds mercury per million metric tons clinker; however, silica (a feedstock representing 13% of kiln feed) represented 60% of mercury input, indicating fuel substitution and a dust or raw meal purge may be effective control strategies. Significant levels of internal mercury concentration were observed on baghouse dust and raw meal. In addition, baghouse dust concentration of mercury was significantly higher during periods when the raw mill was operating, indicating that the loop's sorption processes occur primarily within the raw mill on the finest particulates. Desorption occurred primarily in Preheater 1; mercuric chloride was hypothesized to be the primary specie within the facility. Observations in relation to operating conditions found increases in mercury emissions, baghouse dust concentration, and kiln feed concentration upon mill shutdown. Mercury inputs did not balance mercury outputs at any point during the study period, but the loop did appear to provide control of mercury emissions when the mill was operating. Stack emissions data was compared to a second kiln with an in-line raw mill to determine whether conclusions from a single facility can be broadly applied. Although the response was different from expectations, similarities did exist. Additional

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research must evaluate the dynamics of mercury sorption and desorption from raw meal and baghouse dust and develop predictive dynamic models for the internal mercury loop.

Introduction

Globally and within the United States, cement manufacture represents 6% of the annual anthropogenic mercury emissions (Pirrone, et al., 2009; USEPA, 2009a; USEPA, 2010a). The human health risk of the neurotoxicant requires the United States Environmental Protection Agency (USEPA) to regulate these emissions under the Clean Air Act (USEPA, 2010b). The USEPA 2010 final rule for mercury emissions from cement manufacturing facilities is estimated to result in a 7.5 ton per year reduction (approximately 94% of the total cement facilities emission) by limiting existing facilities to 55 pounds mercury per million metric tons clinker (lb Hg/10^6 metric tons clinker) and new facilities to 21 lb Hg/10^6 metric tons clinker (USEPA, 2009b; USEPA, 2010b; USEPA, 2010c). In order to develop the mercury control technologies required to meet USEPA's rule, the industry requires aggressive research to understand mercury fate and transport within cement manufacturing facilities.

Mercury emission from a cement manufacturing facility results from the clinker production stage of the manufacturing process (the stage's components and mercury inputs are displayed in Figure 4.1). This stage entails both the chemical reactions to produce clinker (i.e., 3 to 25 millimeter calcium silicate nodules) and the majority of the facility's energy expenditure. Although wet and dry clinker production processes are practiced, mercury research is focused on the dry process. Mercury enters this stage within a homogenized mixture of feedstocks (85% limestone, 13% clay or shale, and less than 1% each of corrective materials such as silica, alumina, and iron ore) that is fed into the raw mill (Alsop, et al., 2007). The mercury content of these feedstocks is typically at trace levels (e.g., for 89 facilities limestone mercury concentration averaged 43 parts per billion (ppb)); however, wide variance does occur (e.g., 1 of the 89 facilities reported a limestone mercury concentration of 1,121 ppb) (USEPA, 2009b). The raw mill creates a fine powder (so-called 'raw meal') that is transferred to a homogenizing silo. The material leaves the silo as so-called 'kiln feed' which is shuttled into a preheater and precalciner tower, marking the beginning of the meal's chemical transformation into clinker. A series of cyclone separators (called 'preheaters') intermix the meal with high temperature (i.e., initially at 1,050°C) exhaust gases to recover energy, preheat the feed and begin the chemical reactions for the production of clinker (Alsop, et al., 2007). Preheating the feed strips mercury from the feed and transfers the element into the exhaust gases (Senior, et al., 2010). Within the kiln, the reactions to produce clinker are completed at near 1,400°C (Bhatty, et al., 2004).

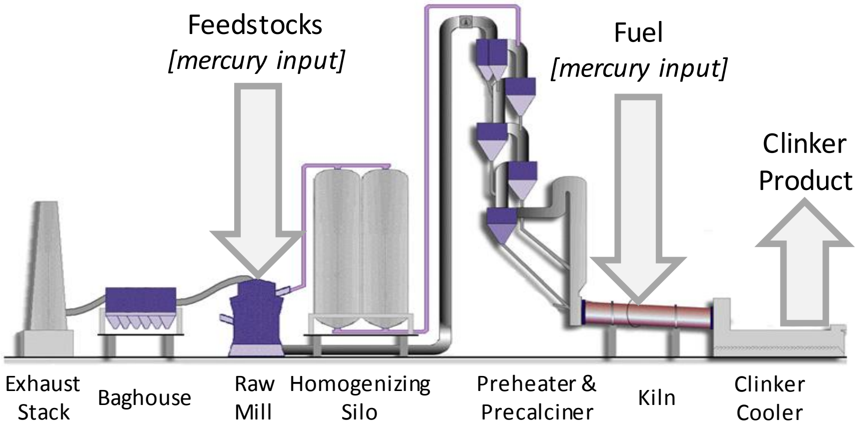

Figure 4.1. Overview of the Clinker Production Stage in the Dry cement Manufacturing Process

To minimize energy loss, exhaust gas (containing volatilized mercury) from the preheater and precalciner tower is often routed to the raw mill, assisting in drying the incoming feedstocks. The mill operates between 90 and 120°C allowing condensation and sorption of gaseous mercury onto the cool feedstock particulates (Schreiber, et al., 2005). Particle-bound mercury in the raw meal flows to the homogenizing silo, capturing the element within the clinker production stage. A second mass of mercury bound onto fine particulates and gaseous mercury flows into the baghouse. The dust cake on the baghouse fabric represents another material that sorbs gas-phase mercury. Typically, dust is recycled and serves as a feedstock for the kiln. This recycling also captures mercury within the clinker production stage.

Capture of mercury within the clinker production stage completes an ‘internal mercury loop’ that captures mercury within the facility. As long as the facility is operated with the mill on, mercury is volatilized and sorbed within the facility, creating a loop that can increase mercury concentration on the raw meal by “hundreds of times” (Clark, 2009). This internal loop can remove in excess of 90% of mercury from the exhaust gases.

However, operation of a cement facility requires weekly raw mill maintenance (an 8 to 10 hour mill shutdown) while the kiln continues to operate (Schreiber, et al., 2005). As raw meal and baghouse dust (with loop-concentrated mercury) is fed into the kiln, mercury is re-volatilized and flows towards the raw mill. However, instead of flowing into the mill, the exhaust gases flow directly to the baghouse. Mercury no longer has an opportunity to intermix with and sorb on the cool particles and hot gases raise the dust temperatures in the baghouse, desorbing additional mercury. These factors cause an emissions spike during the mill shutdown periods that works against loop control.

The internal mercury loop holds potential as a cement facility mercury control and removal mechanism. With knowledge of mercury's sorption and desorption behavior from raw meal and baghouse dust it may be possible to develop novel control strategies that exploit this mechanism (e.g., purging raw meal or baghouse dust or cleaning mercury enriched dust) to achieve USEPA's emissions limit without use of comparatively expensive and inefficient 'tail-pipe' technologies (e.g, dry sorbent injection, dry scrubbing, or wet scrubbing)(Paone, 2010). However, with one known exception that reports mercury concentration at specific points within a Slovenian facility (Mlakar, et al., 2010), published literature only reports stack emissions measurements or continuous emissions monitoring data (Schreiber, et al., 2005; Schreiber, et al., 2009a; Schreiber, et al., 2009b; Senior, et al., 2010). To determine whether the internal loop can be beneficially used, the industry will require a model that can accurately predict sorption and desorption of various mercury species from raw meal and baghouse dust. Prior to this development, facility observations are required to develop an understanding of mercury fate, transport, and internal concentration within a representative facility.

By using facility observations, this study addressed the following objectives: (1) determine facility mercury inputs; (2) identify points of desorption, sorption, and concentration of mercury; (3) track concentration of mercury within the loop over a raw mill shutdown period; (4) compare stack mercury emissions over a raw mill shutdown period with a second representative kiln; and (5) complete a mass balance of mercury inputs and outputs over multiple time periods.

Materials and Methods

Description of Facilities

This study featured data collected from two facilities. Data from the second facility were for the sole purpose of emissions comparison and did not address the study's remaining objectives. Table 4.1 presents a summary of each facility's operating characteristics during the data collection periods.

Table 4.1. Characteristics of Facilities

Characteristic	Facility 1	Facility 2
Manufacturing process	Dry 5-stage preheater In-line calciner In-line raw mill	Dry Two 4-stage preheater strings Separate-line calciner In-line raw mill
Production capacity (metric ton/year)	~700,000	~800,000
Estimated mercury emissions* (lb/10^6 metric ton clinker)	80	3,300
Baghouse dust recycling (%)	100	100
Raw mill feed rate (metric ton/hour)	180	240
Kiln feed rate (metric ton/hour)	90	200
Primary fuel	Coal	Coal
Exhaust temperature (°C)		
Kiln outlet	1050	1050
Preheater 1 outlet	350	200
Baghouse outlet, raw mill on (°C)	100	100
Baghouse outlet, raw mill off (°C)	200	160

* USEPA, 2009c

Sampling and Analytical Methods

Periods, Materials, and Points

The facility owner collected data over five separate sampling periods from specific materials and points to address study objectives (see Table 4.2). Sampling began with a 10-month period in which all input materials were sampled. A 2-day sampling period, limited to the materials with the greatest amount of change in mercury concentration due to raw mill shutdown and restart, occurred during month 9 of the 10-month period. The third period, a 4-day sampling effort addressing mercury desorption, sorption, and concentration, occurred in the final 2 days of month 9 and continued into month 10. Additional sorption analysis was completed with collection of baghouse dust samples throughout the 10-months of observation. To compare stack emissions, 11.5 hours of data for a raw mill shutdown-restart event was selected from measurements obtained at the second facility in a previous study by the Energy and Environment Research Center (Jones, et al., 2007).

Table 4.2. Sampling Periods, Frequency, Materials, Points, and Types

Facility	Objective(s) Addressed*	Sampling Period Length	Sampling Frequency	Materials and Points Sampled	Sampling Method
1	1, 5	10 months	Monthly	Limestone Silica Bottom Ash Slag Fuel	Composite
	2	4 days	Daily	Exhaust	Sorbent trap
				Raw meal Kiln feed** Baghouse dust Clinker	Composite & Grab
				Fuel Preheater 1 Preheater 2 Preheater 3	Grab
	2	10 months	Monthly	Baghouse dust	Composite
	3, 4, 5	2 days	Between 2.0 and 3.5 hours	Exhaust	Sorbent trap
				Baghouse dust Kiln feed**	Composite
2	4	2 days	2.5 minutes	Exhaust	Continuous mercury monitor

* 1 - determine facility mercury inputs; 2 - identify points of desorption, sorption, and concentration of mercury; 3 - track accumulation of mercury within the loop over time; 4 - compare stack mercury emissions over a raw mill shutdown period with a second representative kiln; 5 - complete a mass balance of mercury inputs and outputs over multiple time periods.

** Kiln feed represents a mixture of raw meal and baghouse dust that is fed from the homogenizing silo into Preheater 1

Sampling and Analysis

The type of sampling was selected to provide representative measurements throughout each monitoring period (see Table 4.2, column 6). Monthly composites of daily 0.5-kilogram (kg) grab samples were made of each feedstock and fuel input during the 10-month period. Following collection, grab samples were immediately stored in zippered polyethylene bags. At the end of each month, the grab samples were intermixed and ground into a homogenous powder. A 50-gram aliquot was then removed from the larger composite sample mass and stored in a polyethylene bag until analysis.

Emissions monitoring, during the 2-day and 4-day sampling periods at Facility 1, was completed with dual sorbent traps (Method 30B Unspiked, OhioLumex, Twinsburg, Ohio). These traps were considered valid if the mass of mercury captured by the second section of the trap was less than or equal to 5% of the mercury mass collected in the first section and if relative percent difference between traps was less than 10%.

During the 4-day period, the traps were held in place for approximately 1 day. In most cases, a daily composite sample of raw meal, kiln feed, baghouse dust, and clinker was made from 0.5 kg grab samples (taken at 2-hour or 4-hour intervals) that fell within the traps start and end time. However, on day 1 of the 4-day period grab samples were used to observe kiln feed (5 samples at 4-hour intervals), raw meal (2 samples at a 2-hour interval), and clinker (8 samples at 2-hour intervals). Materials difficult to obtain (i.e., fuel and preheater stages 1 through 3) were limited to grab samples. In the 2-day period, the sorbent traps were held in place for intervals that ranged from 2.0 to 3.5 hours. Baghouse dust and kiln feed composite samples were made from grab samples that fell within each sorbent trap emissions monitoring interval. To provide additional information on mercury flows during the 2-day effort, baghouse outlet temperature, raw mill feed rate, and kiln feed rate were recorded at 10-minute intervals.

Unlike the feedstock and fuel inputs, samples obtained during the 2-day and 4-day periods were homogeneous. To prevent contamination, following collection, cool grab samples (i.e., raw meal, kiln feed, baghouse dust, clinker, and fuel) were immediately placed in zippered polyethylene storage bags. At the end of the sampling period, these grab samples were intermixed and homogenized to create composite samples. Hot preheater samples were obtained with a sampling cup inserted into the outlet stream. Once obtained, these samples were immediately placed in an ice bath to minimize mercury loss by volatilization. After cooling to ambient temperature these samples were placed in polyethylene storage bags.

All samples from Facility 1 were analyzed with an RA-915+ mercury analyzer with an RP-M324 sorbent trap attachment (OhioLumex, Twinsburg, Ohio). While designed for direct analysis of sorbent traps, this analyzer also includes a sample boat for dry materials analysis. This analyzer uses Zeeman atomic absorption spectrometry using high frequency modulation of light polarization (ZAAS-HFM) and a thermal decomposition approach to analyze solids. The Zeeman effect correction employed by the analyzer minimizes interferences caused by the solid's matrix and is suitable for sample analysis without acid digestion (Morita, et al., 1998). The limit of detection for the samples analyzed was 0.8 parts per billion. In each sample analysis set, a spiked sample, duplicate sample, and sample of a certified reference material were analyzed to monitor the analyzer's performance.

Mercury emissions at Facility 2 were measured using a Tekran Model 3300 atomic fluorescence-based mercury vapor analyzer (Tekran Instruments Corporation, Knoxville, Tennessee) at 2.5 minute intervals. This instrument has a limit of detection of 0.05 micrograms per cubic meter (Tekran, 2006). Just prior to the data collection effort, a quality control standard of a known analyte concentration was analyzed and the result fell within 5% of the certified concentration.

Results and Discussion

Facility Mercury Inputs

Mercury input to Facility 1 (see Figure 4.2) over the 10-month period averaged 207 lb Hg/10^6 metric tons clinker, with a standard deviation of 81 lb Hg/10^6 metric tons clinker. This input level is far greater than the 80 lb Hg/10^6 metric tons clinker estimated (USEPA, 2009b). Unlike 70% of United States cement facilities, of which limestone contributes at least one-third of mercury inputs, only 29% of Facility 1 emissions were from limestone (USEPA, 2009b). Instead, silica contributed 60% of mercury input. Typically, the input mass of silica, an additive used to correct the feedstock mixture chemical composition, is less than 1% of kiln feed. This percentage holds true if a pure substance (i.e., sand) is used. At Facility 1, the silica input is in the form of sandstone. This sandstone also supplies chemical constituents typically derived from clay or shale and represents approximately 13% of kiln feed at the facility.

It may be feasible for the facility to source silica with low mercury concentration. If the facility were able to reduce silica mercury input to zero, average mercury input would drop to about 71 lb Hg/10^6 metric tons clinker. With inputs reduced to this level, a purge of baghouse dust or raw meal could be a feasible strategy to meet the emissions limit. These strategies have an estimated emissions reduction effectiveness of between 5 and 30% and mitigate mercury emissions by purging a portion of the material with loop-concentrated mercury from the system (Paone, 2010). However, the substantial variability of inputs does raise doubts that these strategies will allow the facility to meet the 55 lb Hg/10^6 metric tons clinker emissions limit on a 30-day rolling average as required by the USEPA. As displayed in Figure 4.3, if silica mercury input is reduced to zero and a baghouse dust or raw meal purge had an emissions reduction effectiveness of 30% (an optimistic value), stack emissions would be below the emissions limit in 7 of the 10 months. However, due to input variability, in three of the months, the emissions limit would not be achieved.

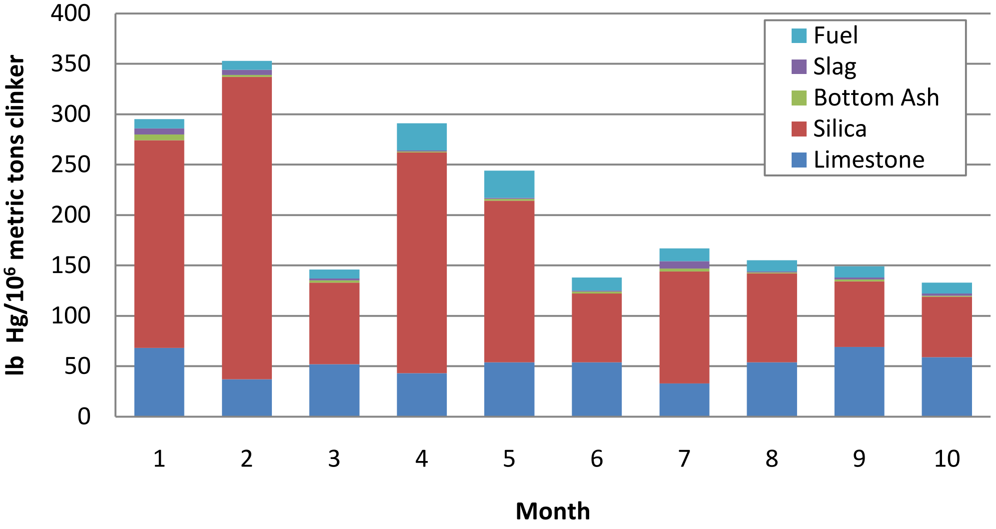

Figure 4.2. Facility 1 Monthly Average Mercury Inputs

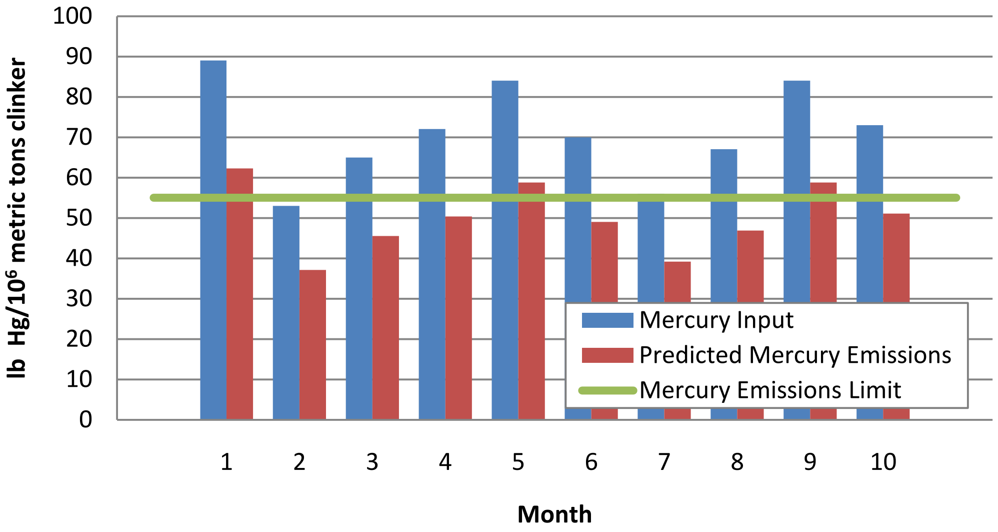

Figure 4.3. Facility 1 Monthly Average Mercury Input of all Constituents Except Silica and Predicted Emissions Assuming a Baghouse Dust or Raw Meal Purge With an Emissions Reduction Effectiveness of 30%

Input mercury concentration variability at a particular facility can be determined with feedstock and fuel observations. While these observations do allow prediction of mercury emissions, they only allow an estimation of baghouse dust or raw meal purge effectiveness. A better estimate of these control strategies requires internal observations of mercury loop concentration and evaluation of the dynamics of mercury sorption on raw meal and baghouse dust.

Identification of Mercury Desorption, Sorption, and Concentration Points

Observations made during the 4-day sampling effort are presented in Figure 4.4. Feedstock concentration (the average of month 9 and 10 composite samples) and emissions (based on sorbent traps with a sampling period of 1 day) are also presented. In 7 of the 11 samples analyzed mercury concentration was below the detection limit of the OhioLumex analyzer. The four detectable samples had recorded mercury concentrations of 1 ppb. Although these results were used to develop the figure, based on the explanation above, they should be viewed with skepticism. Almost all mercury compounds will volatilize in 1,400°C temperatures of the kiln. However, it is possible that mercury silicates (e.g., $HgSiO_3$ or $Hg_6Si_2O_7$), a set of stable mercury compounds with unknown decomposition temperatures, may be able to travel through the kiln (Schreiber, et al., 2005).

Detection of mercury silicates is unlikely because the OhioLumex analyzer uses a thermal decomposition method that raises matrix temperature to 700°C. This temperature is less than the highest temperature that occurs within the kiln. If mercury silicates did exist within clinker at 1 ppb, clinker would represent a mercury outlet of 2.2 lb Hg/10^6 metric tons clinker. If clinker mercury concentration were instead 10 ppb, the outlet increases to 22 lb Hg/10^6 metric tons clinker, a value greater than the emissions limit for new facilities.

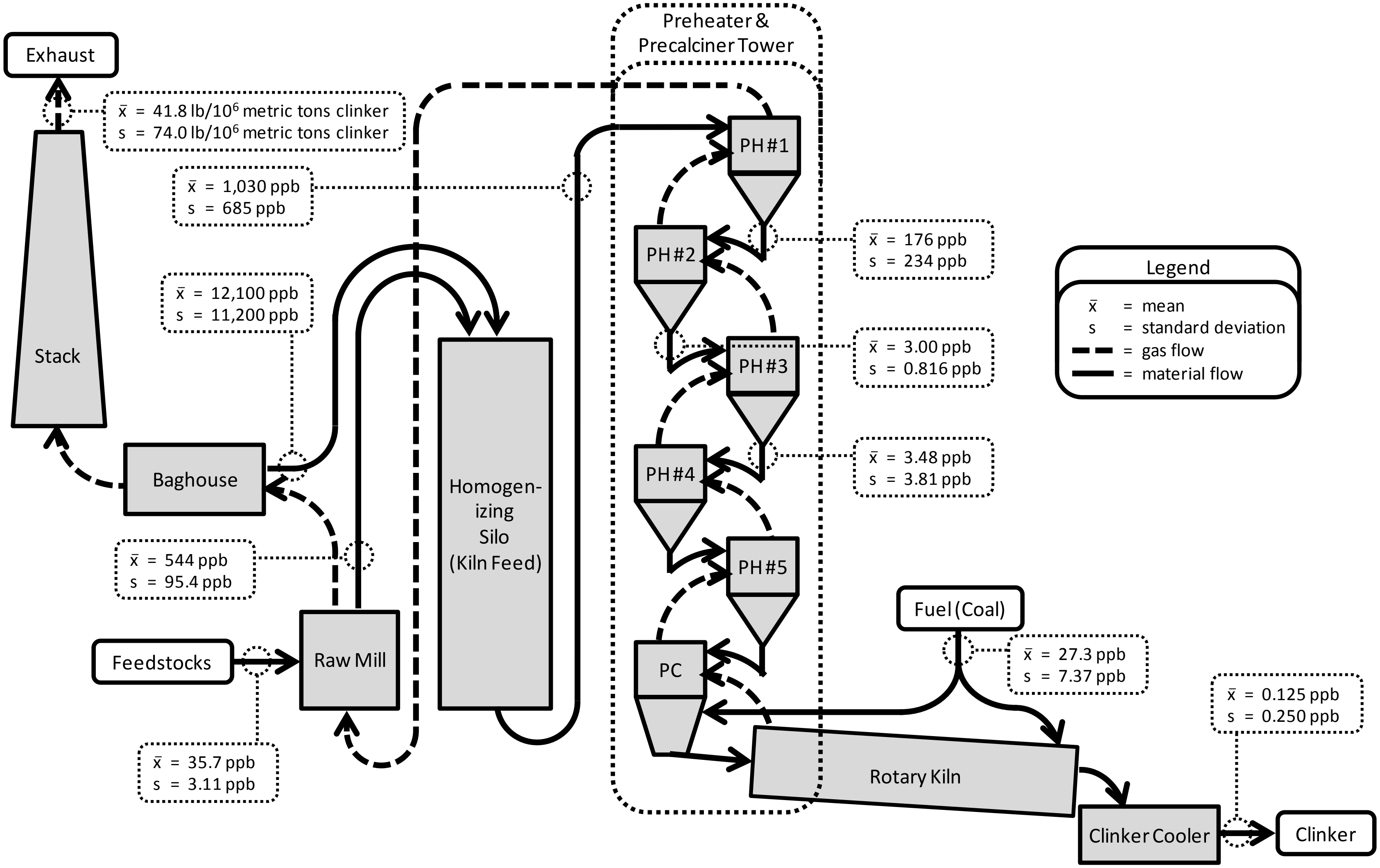

Figure 4.4. Diagram of Facility 1 Gas and Material Flow and Observed Mercury Concentration (All Observations are Based on Four Samples Except Feedstocks, Which are Based on Two Monthly Composite Samples)

The concentrations presented in Figure 4.4 do provide evidence of loop concentration. Relative concentration over feedstock concentration was 339 times for baghouse dust, 29 times for kiln feed (i.e., the mixture of baghouse dust and raw meal fed into Preheater 1), and 15 times for raw meal. The increase in concentration that occurs between kiln feed and raw meal is due to baghouse dust recycling. Due to the high level of loop concentration, the kiln feed requires only 4.2% of baghouse dust to increase concentration of raw meal to the observed value.

To further elucidate the sorption processes that occur within the internal mercury loop, monthly baghouse dust composite samples, representing periods of raw mill shutdown and operation, were analyzed. These samples revealed substantially higher mercury concentration in the dust when the mill was operating (see Table 4.3). The significantly larger level of mercury loop concentration on baghouse dust compared to kiln feed indicated that loop concentration occurred primarily on the finest particulates within the system (i.e., particles captured by the baghouse). The observation of higher concentration on baghouse dust when the mill is operating suggests that mercury sorbs on fine particulates within the mill rather than on the dust cake within the baghouse. If sorption instead occurred primarily on the dust cake, Table 4.3 would show higher mercury concentration when the mill was not operating because in this period the concentration of mercury in exhaust gases was higher. It is improbable that the drop in concentration can be explained by the rise in baghouse outlet temperature from 100 to 200°C that occurred upon raw mill shutdown. While this temperature increase was significant it was not above the boiling or decomposition temperature of any mercury compounds predicted to exist within a facility (see Table 4.4).

Table 4.3. Baghouse Dust Mercury Concentration during Periods of Raw Mill Shutdown and Operation

	Raw Mill Status	
	Operating	Shutdown
Month	Baghouse Dust Mercury Concentration (ppm)	
1	21.1	5.0
3	57.9	9.5
4	53.2	10.7
5	81.3	10.3
6	69.6	10.2
7	81.4	9.5
8	39.0	8.6
9	29.5	7.9
10	20.8	5.7
Average	50.4	8.6

Table 4.4. Properties of Mercury Compounds (Paone, 2010)

	Hg^0	$HgCl_2$	$HgSO_4$	HgS	HgS	HgO
Name	Elemental Mercury	Mercuric Chloride	Mercuric Sulfate	Mercury Sulfide (Red)	Mercuric Sulfide (Black)	Mercuric Oxide
Melting Temperature (°C)	-38.9	277		344		
Boiling Temperature (°C)	357	304		583	446	
Decomposition Temperature (°C)			450			476

Desorption of mercury occurs in the initial stages of the preheater series. Eighty-three percent desorption was observed following Preheater 1 and near 100% desorption was observed after Preheater 2. Following Preheater 3, mercury concentration averaged 3.48 ppb, a level much lower than the 1,030 ppb of the kiln feed entering Preheater 1.

The level of desorption that occurs within the preheaters allows speculation of the mercury species within the system based on the melting and decomposition temperature of specific mercury compounds. Melting, boiling, and decomposition temperatures of compounds predicted to exist within the kiln are presented in Table 4.4. A temperature profile of a 5-stage preheater tower with an in-line calciner indicated that at the outlet of Preheater 1, kiln feed temperature was 300°C and that at the outlet Preheater 2, kiln feed temperature wass 470°C (Alsop, et al., 2007). The stage 1 outlet temperature was near mercuric chloride's boiling point; observed desorption could be due to loss of this compound. At the stage 2 outlet, it appeared that elemental mercury, mercuric sulfate and mercuric sulfide (black) could be desorbed. The relatively stable mercury sulfide (red) and mercuric oxide compounds could explain the small levels of mercury that observed following this stage. The observations agreed with equilibrium calculations predicting mercuric chloride as the dominant mercury species within the facility (Schreiber, et al., 2009a). However, the hypotheses made regarding the mercury species present are purely on a boiling and decomposition temperature basis. Actual desorption may be substantially influenced by factors such as meal-gas intermixing and pressure within the vessel. Further research should be completed to determine the dynamics of mercury desorption within the preheater tower and identify mercury species that exist within the kiln. This data may provide insight to both enhance the 'internal mercury loop' and develop novel control technologies that use thermal desorption to clean baghouse dust and kiln feed.

Tracking of Mercury Stack Emissions and Concentration within the Loop over a Raw Mill Shutdown and Restart Period

Figure 4.5 plots the stack mercury emissions, baghouse dust mercury concentration, and kiln feed mercury concentration for a raw mill shutdown-restart event (note, to permit use of the same scale for baghouse dust and kiln feed mercury concentration, kiln feed mercury concentration was multiplied by 10). Stack emissions from the facility exponentially increased through the duration of mill shutdown. Upon mill restart, stack emissions dropped to near-zero levels. As plotted, emissions dropped prior to mill restart. In reality, it is probable that emissions continued to increase exponentially until mill restart.

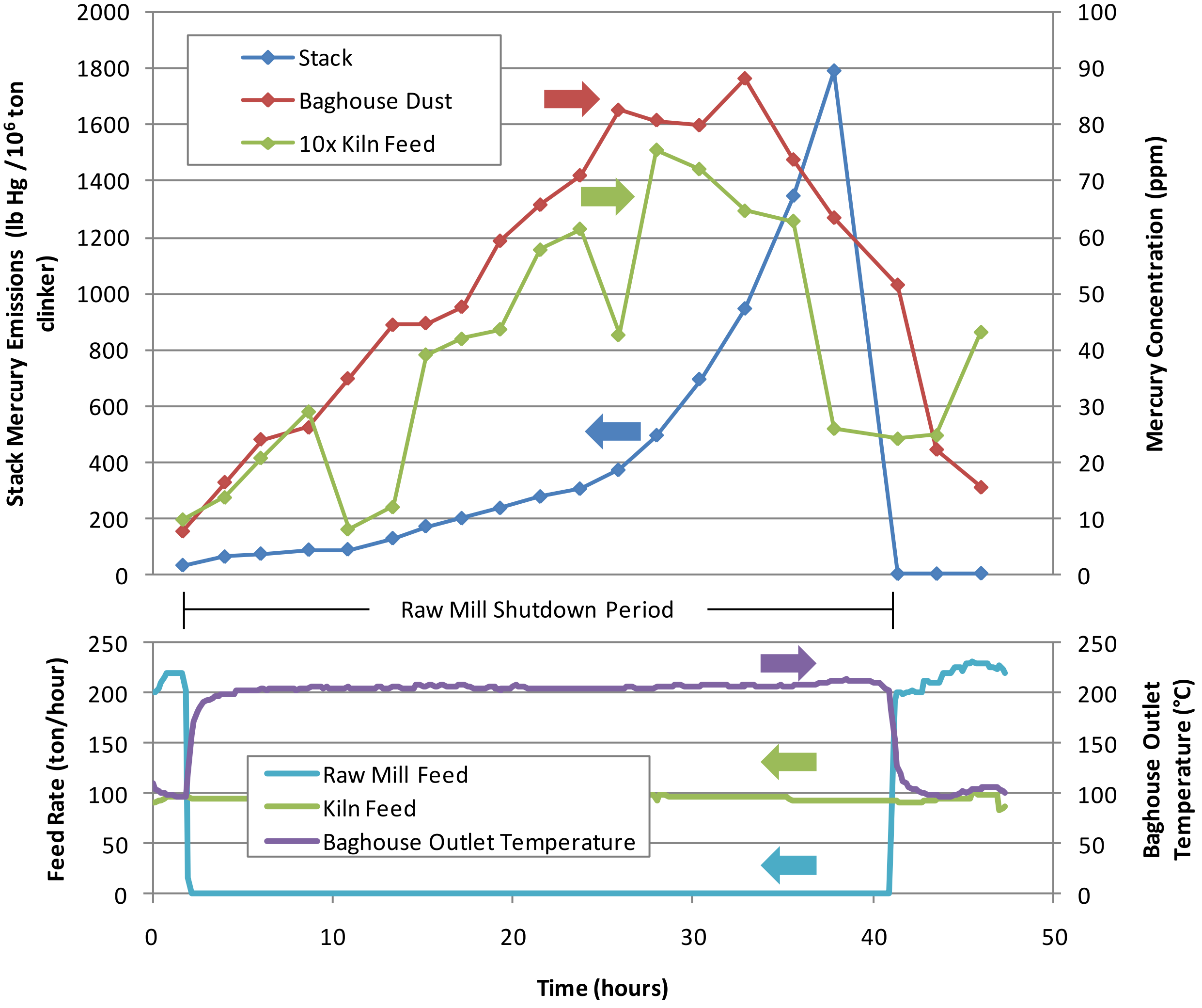

Figure 4.5. Mercury Concentration Response of Exhaust, Baghouse Dust, and Kiln Feed to Raw Mill Shutdown (Note: Kiln Feed Mercury Concentration was Multiplied by 10)

Mercury concentration on baghouse dust and kiln feed also increased as stack mercury emissions increased. These results were unexpected. Due to the effect of the loop, mercury concentrations on these materials should be at their highest level upon mill shutdown. As internal loop-concentrated mercury was lost to the atmosphere, material concentration should decrease. The deviation from expectations can be explained as follows. Baghouse dust has an unknown maimum capacity for mercury sorption. As stack mercury emissions increased, baghouse dust sorbed increasing amounts of mercury. Kiln feed observations may have resulted from loop concentrated material stored within the silo during previous periods. Over this period, mercury had been desorbed and sorbed multiple times and this cycling gradually increased the concentration of mercury in the kiln feed. However, concentration had not reached equilibrium within the silo. Initial observations showed less exposure to loop-concentrated mercury than feed entering the kiln at later points of observation. This reasoning would hold if the facility's homogenizing silos had nearly emptied at the end of the shutdown event. Therefore, at the same time of raw mill restart, all loop-concentrated mercury had exited the silos, resulting in a drop in kiln feed concentration. At present, the dynamics of mercury sorption on raw meal and baghouse dust are unknown. Research that identifies these dynamics for specific mercury species will aid both facility operators and developers of novel control technologies for the cement industry.

Comparison of Raw Mill Shutdown Stack Mercury Emissions with a Second Representative Facility

The concentrating loop cannot be beneficially used if knowledge from one facility cannot be applied to another facility. To determine whether future research may be broadly applicable, Figure 4.6 compares stack emissions, from the initial raw mill shutdown event at Facility 1 with emissions from a similar event at Facility 2. This plot does have striking differences; however, it does appear that knowledge gained from one facility is applicable to another. The most dramatic difference between emissions measurements of the two facilities was the exhaust gas concentration. The maximum mercury concentration of Facility 1was approximately 500 micrograms per cubic meter (µg/m^3) whereas the maximum exhaust concentration of Facility 2 reached nearly 6,000 µg/m^3. In addition, Facility 2 showed an emissions spike followed by a constant emission level upon mill shutdown whereas the mercury emission of Facility 1 continued to build until the raw mill resumed operation. One possible reason is that in the second facility, prior to mill shutdown, baghouse dust had reached its maximal sorption capacity. Upon mill shutdown, temperature in the baghouse increased by approximately 60°C. This temperature increase reduced the sorptive capacity of the dust, causing mercury desorption and a spike in emissions. Following this initial spike, the sorptive capacity of the dust reached an equilibrium point. It is also probable that mercury sorption of kiln feed at Facility 2 had also reached the maximal sorption level; therefore, as feed continued to enter the kiln during the shutdown event, mercury emissions remained constant. In addition, due to the relatively shorter duration of the shutdown event, no change in kiln feed mercury concentration occurred. Additional research must be completed to determine the factors that influence sorption of mercury on raw meal and baghouse dust. In addition, the maximal levels of sorption and time to reach this point must be investigated to develop understanding of the loop.

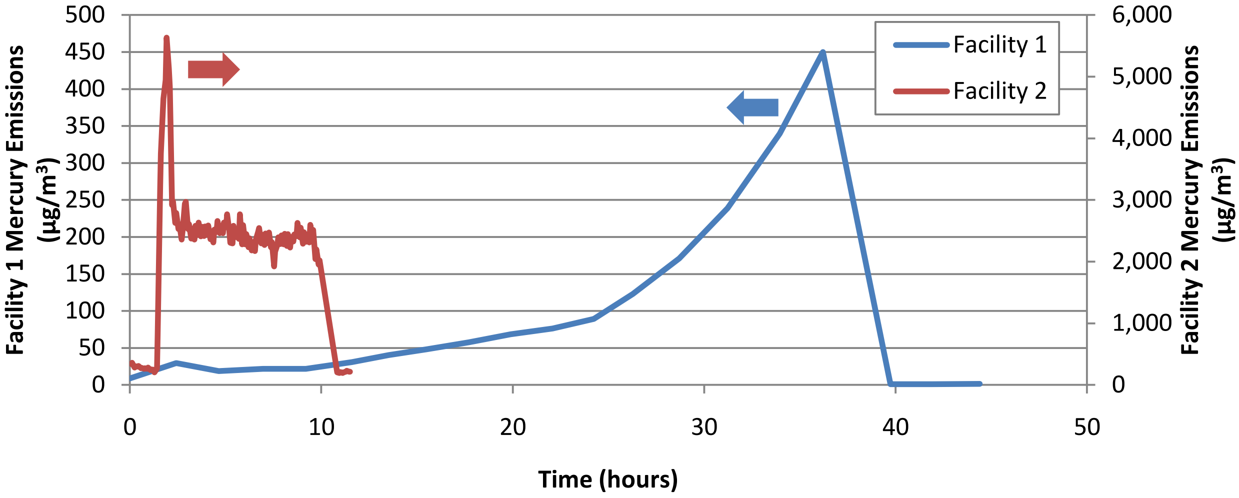

Figure 4.6. Comparison of Facility 1 and Facility 2 Mercury Emissions

Mercury mass balance for the 2-day observation period

Due to internal loop concentration of mercury prior to the raw mill shutdown-restart that occurred during the 2-day observation period, mercury inputs and outputs should not balance. Figure 4.7 displays the mass balance inputs and outputs (note, for the initial balance accumulation within the facility was assumed to be zero).

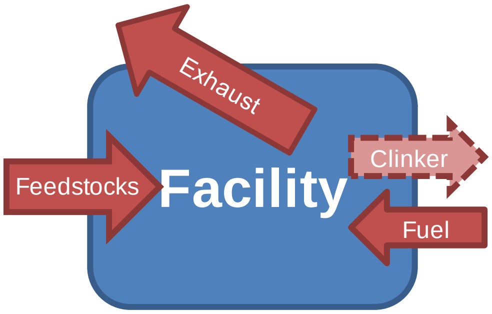

Figure 4.7. Facility 1 Mass Balance

Fuel, clinker, and feedstock mercury concentration data was not collected during the 2-day observation period; therefore, fuel and clinker concentration were assumed to equal the values reported in Figure 4.4 and feedstock concentration was assumed to equal the value reported in Figure 4.2. Feedstock and fuel concentrations were multiplied by feed rates and operating time and clinker concentration was multiplied by kiln production rate and operating time to determine the pounds of mercury input to and output from the system. Stack mercury emissions were determined by multiplying each sorbent trap emissions observation in Figure 4.5 by the average clinker production while the trap was sampling exhaust gas and by the time the trap sampled exhaust gas. These individual observations were summed over the 2-day period to determine total mercury output.

Table 4.5 displays the mass balance results. Over the 2-day period, mercury inputs were 9% of mercury outputs. This imbalance indicates that substantial loop concentration occurred prior to the raw mill shutdown event. Balancing of inputs and outputs would occur if the raw mill was operating continuously prior to the observed shutdown event. At the data point prior to mill shutdown stack mercury emissions were 0.003 lb/hour. If it is assumed that prior to the 2-day observation, stack emissions were constant at this rate and feedstock, fuel, and clinker input and output rates were also constant, mercury inputs would balance mercury outputs if the raw mill had operated continuously for 100 hours (4.2 days) prior to the 2-day sampling period. These operating conditions do fit within typical raw mill maintenance schedules and provide a plausible explanation of the imbalance observed.

Table 4.5. Mercury mass balance for the 2-day observation period

Mercury Inputs			Mercury Outputs		
Feedstocks			Stack Emissions		
Mercury concentration (ppb)	38		Stack mercury output (lb)		1.5
Raw mill feed rate (ton/hour)	220				
Raw mill operating time (hour)	7.1				
Feedstock mercury input (lb)		0.12			
Fuel			Clinker		
Mercury concentration (ppb)	27		Mercury concentration (ppb)	1.0	
Coal mill feed rate (ton/hr)	6.1		Kiln production rate (ton/hour)	94	
Coal mill operating time (hour)	47		Kiln operating time (hour)	47	
Fuel mercury input (lb)		0.015	Clinker mercury output (lb)		0.0088
Total mercury input (lb)		0.14	Total mercury output (lb)		1.5

Conclusions

Observations at a cement manufacturing facility demonstrating *'internal loop control'* provided new insights into fate, transport, and internal concentration. Monthly observations of inputs revealed that at the facility observed, silica mercury content was unusually high. This unique characteristic may allow successful implementation of a low-cost stack emissions mitigation strategy such as a baghouse dust or raw meal purge. Observations at points within the facility identified that over 80% of mercury was desorbed in Preheater 1, where kiln feed temperature increases from ambient to 300°C. Based on this observation, it was hypothesized that mercuric chloride is the dominant species circulated within the internal mercury loop. The study also found that mercury sorption occurs primarily on the finest particulates within the kiln, but it also appears that sorption occurs within the raw mill, rather than on the baghouse dust cake. In comparison with a second representative facility, differences were evident, but these differences do not prevent knowledge gained from one facility from being applied at others demonstrating an 'internal mercury loop'. Over a 2-day raw mill shutdown-restart event, inputs were 9% of outputs. This result was expected because the raw mill was not operating during the majority of the monitoring period. In addition, if the mill were operating continuously for 100 hours prior to the shutdown it is probable that mercury inputs and outputs would balance.

While the study observations do provide valuable insights into mercury fate and transport within cement production facilities, research must continue to advance the development of novel control technologies and provide facility operators with tools that can augment kiln operation to maximize control via the internal mercury loop. This research should:

1. evaluate the dynamics of mercury sorption and desorption on raw meal and baghouse dust within cement facilities,
2. develop a predictive dynamic model for mercury sorption in relation to the internal concentration loop phenomenon, and
3. develop a predictive dynamic model for mercury desorption from facility raw meal and baghouse dust during critical facility periods when the internal concentrating loop is not functioning (i.e., during raw mill shutdown periods).

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Chapter 5. Overall Conclusions

The aggressive cement manufacturing facility mercury emissions rule promulgated by the USEPA represent an opportunity for technological advancement in the understanding of mercury fate and transport both within cement facilities and other industrial operations. Although a substantial body of cement mercury knowledge does exist, additional objectives must be addressed for the industry to be able to comply with the rule without significant numbers of plant closures. These objectives include advancement of an understanding of the dynamics of mercury sorption and desorption from baghouse dust and raw meal that causes mercury to concentrate within a manufacturing facility. These advancements would best serve the industry if a predictive model were developed that could be applied to prospective internal mercury control processes. Sorption and desorption properties are unique to mercury species; therefore, additional work must characterize these species within facility inputs and under typical operating conditions.

With these ultimate research goals identified, this study addressed intermediate goals that provide groundwork for future cement mercury emissions research. Due to benefits such as lower detection limits, lower standard error, and possible remedies for interferences, many research entities are only equipped with liquid-based wet digestion analyzers. However, for kiln feed and baghouse dust samples from cement facilities, analysis is best suited to a thermal decomposition approach. The study's optimization effort substantially improved the USEPA digestion procedure by addressing incomplete digestion and volatilization concerns. A paired *t*-test did reject a null hypothesis of zero average difference between the optimized wet digestion and a thermal decomposition approach at any significance level greater than 0.013, but the digestion measurements were on average only 13% lower. The modifications made do permit optimized digestion procedure use for mercury analysis when a thermal decomposition based mercury analyzer is not available.

The study also used observations at a cement manufacturing facility demonstrating '*internal loop control*' to provide new insights into mercury fate, transport, and internal concentration. Concentration of mercury in the silica feedstock was abnormally high and it appeared probable that the facility could use a baghouse dust or raw meal purge to achieve the stack mercury emissions limit. The study also identified that the majority of mercury desorbed in Preheater 1. This desorption could indicate that mercuric chloride was the dominant species within the facility. At the observed facility, mercury sorption occurred primarily on the finest particulates within the kiln, but it also appeared that sorption occured within the raw mill, rather than on the baghouse dust cake.

Insights gained from these facility observations are applicable to other facilities that demonstrate *'internal loop control'* of mercury. With knowledge gained from these studies, cement facility mercury fate and transport work can continue. This work should focus on identifying specific mercury species within cement facilities and determining the dynamics of their sorption and desorption. With this information, predictive models that allow prediction of internal concentration at a facility should be developed.

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