

Florida Department of Transportation

Final Report

August 2013

**Assessment of Potential Concerns Associated with the
Use of Cement Kiln Baghouse Dust in FDOT Concrete Mixes**

FDOT Contract Number: BDK75 977-50

The Hinkley Center for Solid and Hazardous Waste Management

And

University of Florida Department of Environmental Engineering

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Disclaimer

“The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the State of Florida Department of Transportation.”

SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	Inches	25.4	millimeters	mm
ft	Feet	0.305	meters	m
yd	Yards	0.914	meters	m
mi	Miles	1.61	kilometers	km

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
AREA				
in²	Square inches	645.2	square millimeters	mm ²
ft²	Square feet	0.093	square meters	m ²
yd²	Square yard	0.836	square meters	m ²
ac	Acres	0.405	hectares	ha
mi²	Square miles	2.59	square kilometers	km ²

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
VOLUME				
fl oz	Fluid ounces	29.57	milliliters	mL
gal	Gallons	3.785	liters	L
ft³	Cubic feet	0.028	cubic meters	m ³
yd³	Cubic yards	0.765	cubic meters	m ³

NOTE: volumes greater than 1000 L shall be shown in m³

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
MASS				
oz	Ounces	28.35	grams	g
lb	Pounds	0.454	kilograms	kg
T	Short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ILLUMINATION				
fc	Foot-candles	10.76	lux	lx
fl	Foot-Lamberts	3.426	candela/m ²	cd/m ²

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
FORCE and PRESSURE or STRESS				
lbf	Pound force	4.45	Newtons	N
lbf/in²	Pound force per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS TO SI UNITS

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
mm	Millimeters	0.039	inches	in
m	Meters	3.28	feet	ft
m	Meters	1.09	yards	yd
km	Kilometers	0.621	miles	mi

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
AREA				
mm²	Square millimeters	0.0016	square inches	in ²
m²	Square meters	10.764	square feet	ft ²
m²	Square meters	1.195	square yards	yd ²
ha	Hectares	2.47	acres	ac
km²	Square kilometers	0.386	square miles	mi ²

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
VOLUME				
mL	Milliliters	0.034	fluid ounces	fl oz
L	Liters	0.264	gallons	gal
m³	Cubic meters	35.314	cubic feet	ft ³
m³	Cubic meters	1.307	cubic yards	yd ³

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
MASS				
g	Grams	0.035	ounces	oz
kg	Kilograms	2.202	pounds	lb
Mg (or "t")	Megagrams (or "metric ton")	1.103	short tons (2000 lb)	T

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
TEMPERATURE (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ILLUMINATION				
lx	Lux	0.0929	foot-candles	fc
cd/m ²	Candela/m ²	0.2919	foot-Lamberts	fl

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
FORCE and PRESSURE or STRESS				
N	Newtons	0.225	Pound force	lbf
kPa	Kilopascals	0.145	Pound force per square inch	lbf/in ²

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

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16. Abstract As a means of controlling mercury (Hg) stack emissions at cement kiln operations, some facilities have proposed or have instituted a practice known as dust shuttling, where baghouse filter dust (BFD) is routed to be blended with the final cement product, as an inorganic processing addition (nominally at levels up to 5% by mass) instead of returning it to the kiln. Research was conducted to provide guidance to the Florida Department of Transportation (FDOT) with regard to possible human exposure and environmental emissions associated with making and using concrete manufactured with BFD. Potential mercury releases to air and water during the storage and handling of BFD as well as the potential releases from the concrete product were assessed using laboratory experiments. Based on the compositional measurements of the samples collected in this study, along with an estimated final concrete composition based on individual measurements, the final concrete product made from similar materials is not expected to differ dramatically in overall composition from that of concrete made without BFD. In tests where concrete made with BFD was prepared and cured, less than 0.5% of Hg measured in the BFD that was released in the vapor phase. This release is expected to result in worker exposure conditions that are lower than allowable limits for worker safety. In batch leaching tests, leachate from BFD did exceed risk-based thresholds for several metal elements other than Hg, but leachate from the concrete product resulted in no concentrations above such thresholds. Furthermore, when leaching of monolithic concrete forms was examined over time in submerged conditions, the elemental metals of concern were rarely detectable and no potential concentrations of risk were noted. The results of these assays do not suggest that release of inorganic elements from concrete products manufactured with BFD of similar composition as those tested in this study and at similar mix designs will pose risk beyond any normal (made without BFD) concrete production use.			
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Executive Summary

As a means of reducing mercury (Hg) stack emissions at cement kiln operations, some facilities have proposed or have instituted a practice known as “dust shuttling,” where baghouse filter dust (BFD) is routed to be blended with the final cement product (nominally at levels up to approximately 5%) instead of returning the BFD to the kiln. This technique reduces mercury emissions to the atmosphere and allows some portion of the mercury to leave the facility with the final cement product rather than through stack emissions. Research was conducted to provide guidance to the Florida Department of Transportation (FDOT) with regard to possible human exposure and environmental emissions associated with making and using concrete manufactured with BFD.

Potential mercury releases to air and water during the storage and handling of BFD as well as the potential releases from the concrete product made using BFD were assessed using laboratory experiments. Facility operators utilizing appropriate storage and handling procedures for BFD can minimize potential release. In tests where concrete made with BFD was prepared and cured, less than 0.5% of Hg measured in the BFD that was released in the vapor phase. This release is expected to result in worker exposure conditions that are less than allowable limits for worker safety.

The total (measured in mg/kg) and leachable (measured in mg/L) concentration of trace inorganic chemicals in concrete manufactured with BFD were evaluated to assess the potential for increased environmental risk associated with the use of the BFD. Based on the measurements of the samples collected in this study, along with an estimated final concrete composition based on individual measurements, the final concrete product made from similar materials is not expected to differ dramatically in overall composition from that of concrete made without BFD. The

potential of chemical mobility (i.e. leaching when in contact with water) from a concrete product manufactured with BFD was examined using different testing procedures. In batch leaching tests, leachate from BFD did exceed risk-based thresholds for several metal elements other than Hg; however, leachate from the concrete product made using BFD resulted in no concentrations above such thresholds. Furthermore, when leaching of monolithic concrete forms was examined over time in submerged conditions, the elemental metals of concern were rarely detectable in the water that the concrete was submerged in and no potential concentrations of risk were noted. The results of these different assays suggest that leaching of inorganic elements from concrete products manufactured with BFD of similar composition as those tested in this study and at similar mix designs will not pose risk greater than any “normal” concrete that has not been amended with BFD.

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GLOSSARY OF ACRONYMS

AASHTO – American Association of State Highway and Transportation Officials

ASTM – American Society for Testing and Materials

BFD – Baghouse Filter Dust

CKD – Cement Kiln Dust

EP – Extraction Procedure (U.S. EPA)

EPA – Environmental Protection Agency (United States)

ESP – Electrostatic Precipitator

FR – Federal Register (United States)

F.A.C. – Florida Administrative Code

FDEP – Florida Department of Environmental Protection

FDOT – Florida Department of Transportation

GCTL – Groundwater Cleanup Target Level

HDPE – High Density Polyethylene

HG - AFS – Hydride Generation - Atomic Fluorescence Spectrometer

ICP - AES – Inductively Coupled Plasma – Atomic Emission Spectroscopy

IPA – Inorganic Process Addition

L/S – Liquid to Solid Ratio

LOI – Loss on Ignition

LSa – Liquid to Surface Area Ratio

LSP – Liquid-Solid Partitioning

MAIC – Major Analytical Instrumentation Center (UF)

MEP – Multiple Extraction Procedure

NCHRP – National Cooperative Highway Research Program

NIOSH – National Institute for Occupational Safety and Health

NO_x – Nitrous Oxides

NODA – Notice of Data Availability

NSI-Hg – Non-Soluble Inorganic Mercury

OH – Ontario Hydro

OSHA – Occupational Safety and Health Administration

PAH – Polycyclic Aromatic Hydrocarbons

PCC – Portland Cement Concrete

PCA – Portland Cement Association

PEL – Permissible Exposure Limit

PTFE – Polytetrafluoroethylene

RCRA – Resource Conservation and Recovery Act

SCTL – Soil Cleanup Target Level

SEM-EDS – Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy

SI-Hg – Soluble Inorganic Mercury

SPLP – Synthetic Precipitation Leaching Procedure

TC – Toxicity Characteristic

TCLP – Toxicity Characteristic Leaching Procedure

TPY – Tons per Year

UF – University of Florida

VOC – Volatile Organic Compound

XRD – X-ray Diffraction Spectroscopy

1. Introduction

Cement manufacturers produce a variety of Portland cement products at large industrial facilities often referred to by their major operational unit, a cement kiln. Inputs to the cement kiln include the raw mineral ingredients (supplying the necessary calcium, silica, iron, and aluminum) as well as fuels (coal, liquid fuel, combustible wastes) to provide the necessary heat for the formation of clinker, which is ground and blended with other minor constituents to make cement. Typical mineral ingredients include those mined from a location near the cement kiln (e.g., limestone, sand, clay, bauxite, gypsum), as well as byproducts from other industries (e.g., coal fly ash and bottom ash from coal-fired power plants, and iron mill scale from steel production facilities).

Cement kiln operators employ a variety of air pollution control techniques to limit emissions from the facility and to capture particulate materials for return to the manufacturing process. Baghouse, or other particulate control devices, such as electrostatic precipitators (ESPs), are used at various locations in the manufacturing train to collect dust particles produced in the process. In some cases, these materials, referred to herein as baghouse filter dust (BFD), are “wasted,” and that wasted material is then referred to as cement kiln dust (CKD) and removed from the system as a means of removing chemicals unfavorable to the final product (e.g., alkali salts). More often than not, however, these materials are recycled back into the cement production process. These materials are usually simply recirculated into the cement kiln feed. In order to reduce mercury emissions to the environment, some cement kiln operators have begun to add the BFD to the final cement product. This technique is commonly referred to as “dust shuttling.” Additions of BFD to the final cement product are considered to be Inorganic Process Additions

(IPA) and are allowed in accordance with the applicable ASTM and AASHTO standards, based on the final cement product. It should be stressed that BFD is not a waste material, and is not commonly removed from the recirculation process in Florida due to the low alkali salts found in raw materials as well as the process employed.

Dust shuttling has been proposed as a strategy for reducing the atmospheric emissions of mercury from the cement calcining process. Concerns over mercury in cement manufacturing have been raised because coal combustion facilities have in recent years been required to remove more mercury from their emissions, and thus mercury levels have become elevated in the byproducts such as coal fly ash, which in turn is increasingly used as a feed mineral in cement kilns. Under normal operation at Florida cement kilns, the BFD is recirculated as feed material to the kiln. This can result in a buildup of mercury in the system over time, and eventually leads to increased mercury emissions to the atmosphere through the stack. The process of dust shuttling allows mercury to be removed from the system by transferring the dust (BFD) to the final cement product, thus reducing mercury emissions to the atmosphere. Dust shuttling of BFD at levels up to 5% by mass of the cement has been demonstrated as an acceptable practice from a materials performance perspective of the final product. Both ASTM and AASHTO methods specify criteria related to performance of the concrete or cement, and thus provide the manufacturer and FDOT an ability to provide specifications for appropriate dust shuttling practices. Given that a major intent of dust shuttling is to decrease mercury emissions from the stack, this practice increases mercury output with the product. Questions have been raised regarding the potential implication of the increased mercury in the concrete used in FDOT construction projects. Additionally, given that the dust may contain elevated concentrations of other trace metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se, V, and Zn) of environmental concern, research on possible impacts to cement products containing BFD merits evaluation.

This report reflects the results of research assessing potential environmental issues associated with the use of products containing cement amended with BFD. Research project objectives included: 1) quantifying the amount of mercury and other trace metals in BFD, 2) identifying the form of mercury occurring in the BFD, 3) through laboratory experiments, assessing the potential release of mercury during various phases of handling and use of BFD, and 4) through laboratory experiments, assessing whether mercury and other trace metals will leach from the final concrete product at levels beyond regulatory limits. The overarching objective of the research is to provide FDOT with an assessment of potential human health and environmental issues from amending cement with BFD generated by dust shuttling practices.

2. Literature and Regulatory Review

2.1. Generation and Management of Cement Kiln Dust and Baghouse Filter Dust

The Florida Department of Environmental Protection (FDEP) defines BFD as dust returned to the pyro-process (i.e., production process) and is not associated with the dust that is discarded from the baghouse or ESP or the dust collected from an alkali bypass duct; this discarded dust is typically referred to as CKD. CKD is removed from the pyro-process due to its higher content of chloride and sulfate salts. This removal of CKD from the cement manufacturing process improves the quality of the final product cement and avoids unwanted buildup of alkali salts in the preheater or precalciner. BFD does not have these high salt characteristics and can be considered part of the raw feed if returned to the pyro-process (FDEP, 2009). It should be further stressed that earlier documents, e.g., Kramer and Haynes, 1982; PCA, 1992, refer to all filter dust as CKD; however, in this report CKD will be considered filter dust that does not meet compositional specifications listed in ASTM C465-10. Since older documents referred to all filter dust as CKD, this characterization will be kept when citing these studies but otherwise filter dust meeting ASTM C465 will be referred to as BFD. Furthermore, all filter dust collected in the state of Florida is done so without the use of an alkali bypass; therefore, by the above definition of CKD and BFD, only BFD is produced in Florida. No CKD is currently being produced in Florida.

Cement kiln dust (CKD) is the fine-grained, solid, highly alkaline waste removed from cement kiln exhaust gas by air pollution control devices and disposed of. Because much of the BFD is actually unreacted raw materials, large amounts of BFD can be recycled back into the production process. Some BFD is reused directly, while some requires treatment prior to reuse, e.g., alkali bypass, addition of other raw materials, intergrinding.

By definition, CKD is wasted BFD that is not returned to the production process and is typically disposed of in land-based disposal units (i.e., landfills, waste piles, or surface impoundments). Some CKD is sold for beneficial reuse (EPA, 2013). CKD is removed from the production process when high alkali, chloride or sulfate concentrations build up over time within the CKD. These alkali concentrations can reduce the strength and workability of cement, making it unsuitable for most construction applications; therefore, CKD is removed from the production process. At some facilities an alkali bypass is installed at the back end of the kiln, see Figure 1, to remove volatilized alkali salts. Historically, a majority of CKD generated was stockpiled or landfilled at great expense to the manufacturer. CKD has beneficial uses as a soil amendment, as media for wastewater treatment, and as landfill cover soil or backfill (Adaska, 2008). Some newly retrofitted plants that are not in Florida are currently utilizing CKD which had been landfilled or stockpiled and are reintroducing it back into the kiln. However, CKD storage has not been in practice for many years and there are no known CKD storage piles at Florida cement plants. (Adaska, 2008).

It is common in scientific research and literature to identify CKD as the material that is caught in the baghouses or electrostatic precipitators (ESPs) and recycled into the kiln to produce more cement. Some would argue that the waste dust disposed of or removed from the production process differs from the dust reused in the production process as a raw material or as an IPA in the finished product. The two materials discussed in this report are referred to respectively as Cement Kiln Dust (CKD) and Baghouse Filter Dust (BFD), with the latter reused as a raw material in the production process or as an IPA, in accordance with specification set forth in ASTM 465-10 (ASTM, 2013).

2.2. EPA Regulatory Status and History of CKD

CKD is categorized by EPA as a "special waste" and was "temporarily exempted" from federal hazardous waste regulations under Subtitle C of the Resource Conservation and Recovery Act (RCRA) by Congress in 1980 as a result of the "Bevill Amendment" (2013). The Bevill Amendment exempted CKD from being categorized as a hazardous waste for purposes of RCRA regulations. As required by RCRA, EPA studied the adverse effects on human health and the environment from the disposal of CKD. EPA found that some environmental harm results from the disposal of CKD, and in 1993, reported these and other findings to Congress. Subsequently, Congress required EPA to determine the appropriate regulatory framework for managing CKD. In 1995, EPA determined that some additional control of CKD was needed. Although current CKD disposal practices do result in some environmental damage, the EPA found that regulating CKD as a hazardous waste under RCRA was not appropriate. For the past 10 years, no cement plants in Florida have produced CKD. Furthermore, there are no plans by Florida plants to produce CKD.

In 1999, EPA published "Standards for the Management of Cement Kiln Dust; Proposed Rule" (64 FR 45632). EPA's proposed approach would allow CKD to remain classified as a non-hazardous waste provided that the specific management standards are met. CKD not managed in compliance with the standards was proposed to be a "listed waste" and would need to comply with tailored RCRA Subtitle C management standards (2013).

In 2002, EPA published a notice of data availability (NODA) in the Federal Register (67 FR 48648) that it was considering a new approach to CKD management as RCRA Subtitle D (non-hazardous, solid waste) and temporarily suspended the proposed RCRA Subtitle C (hazardous waste) portion of the 1999 rule (64 FR 45632) for 3 to 5 years to assess how CKD management practices and state regulatory programs would evolve (2013). Based upon its assessment EPA will

either formally withdraw or will promulgate that portion of the 1999 proposed rule. As to date, no further ruling has been proposed by the EPA with regard to decision making on CKD regulated as a hazardous (Subtitle C) or non-hazardous waste (Subtitle D).

2.3. Trace Metals in CKD, Cement, and Concrete

Concentrations of trace metals in CKD ranged widely from $\mu\text{g}/\text{kg}$ to a few hundred mg/kg , depending on the chemical and location of the mine that was the source of the raw material (Haynes and Kramer, 1982). A study completed by the Institute of Energy in Norway attempted to determine the distribution and fate of mercury in cement kilns and cement plants. This was done by injecting ^{203}Hg , a radioactive isotope tracer, into three different injection sites and then measuring the mercury tracer's residence time and concentration in flue gases as well as the concentration adsorbed to the filter dust. Of the three injections, one was injected into the raw milled limestone, one was injected into the precalciner or preheater, and the final injection site was directly into the rotary kiln, see Figure 1 below. The amount of the ^{203}Hg tracer was then measured in exhaust gas at the kiln and clinker cooler stacks. When the ^{203}Hg was injected into the raw milled limestone there was an immediate peak in concentration out of the stack (5% of total ^{203}Hg) and then a much lower release rate for many hours afterwards; only after two days had all the ^{203}Hg left the system. A similar result was seen from the two other injections but at different concentrations. Similarly, the measurements in the filter dust follow this same curve. These results indicate that the injected ^{203}Hg adsorbed onto the limestone and other raw materials in the raw mill and then was slowly released as a gas over time. Additionally, the ^{203}Hg was completely distributed through the system and setup a sort of internal cycling of the mercury. Adsorption of ^{203}Hg onto raw materials, especially limestone, is a function of temperature, i.e., higher temperature adsorbing less ^{203}Hg onto the raw materials due to the volatile nature of mercury (Eriksen et al., 2006). Note

that the bypass shown in Figure 1 is not adopted in Florida cement plants due to the materials characteristics and production process employed in Florida.

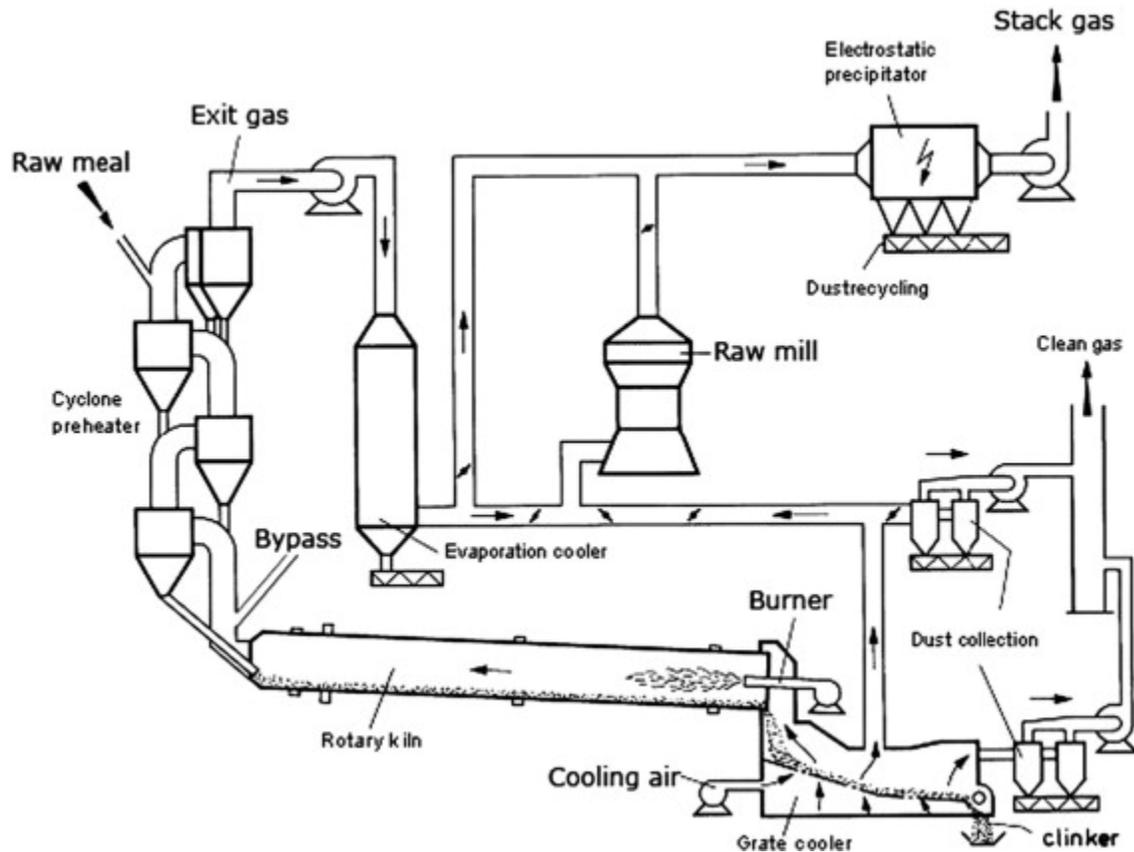


Figure 1: Diagram of a Cement Kiln with an Alkali Bypass (Karstensen et al., 2010)

The results from the Norwegian report are further echoed in a set of FDEP comments in Docket No. OAR-2002-0051 (FDEP, 2009). Mercury will be trapped in an internal cycle within the kiln process, and when the raw mill is stopped, this mercury will be captured in the baghouse and diverted to the finish mills where it will be incorporated in the final product. This process will also control heavy metal emissions by capturing them and returning them to the kiln. The control technology is to manage operating temperatures, remove the dust collected in the baghouse, and introduce the collected dust into the cement as an amendment (FDEP, 2009).

These comments cite the earlier statements by Eriksen et al. (2006) and introduce the concept of filter dust shuttling which will be discussed in greater detail in a later section of this report. The FDEP comments went further to cite a paper by the Portland Cement Association (PCA, 1992). Concentrations of mercury in the stack are sensitive to the temperature of the particulate control device and whether the raw mill is on line, i.e., whether or not the flue gases pass through the raw mill before exiting.

While a large portion of the mercury and other trace metals are introduced to the kiln via raw materials, it should be realized that the materials in the raw mill have intimate contact with the exhaust gases from the kiln which results in adsorption of volatile species onto the raw materials. Due to this, the fuel combusted can increase the concentration of these species in the raw materials being introduced to the kiln (Linero and Read, 2010). This increase will continue until the concentration entering the process via the raw materials and fuel is equal to that emitted from the stack on a long term basis (e.g., annual average). It should be noted, the concentration of Hg and other trace metals entering the system in the raw materials and/or the fuel cycle vary with resource location.

The observation that volatile and semi-volatile metals adsorb to filter dust has been referred to for nearly two decades by the cement industry. For example, in a 1992 study by the PCA, it was concluded that the volatile trace metals released from the stack at a particular cement plant can be reduced by 50% by discarding twice as much CKD (PCA, 1992). The report went further to say that the single most important factor influencing heavy metal concentration in CKD is the extent to which CKD is recirculated into the pyro-process. The report also indicated that the level of heavy metals in the fuels and raw materials is largely unimportant in determining CKD metal content on a short term basis (e.g., time less than several cycles of the raw mill).

2.4. Baghouse Filter Dust Shuttling

Baghouse filter dust (BFD) shuttling is the practice of removing a certain percentage of the dust collected in the final pyro-processing filter (usually a baghouse) prior to exhaust and adding this material as an inorganic process addition (IPA) to the finishing mill. As previously mentioned, this process is done to reduce atmospheric emissions of mercury and other trace metals, as well as reducing alkali salts build up within process equipment, by incorporating those metals and salts adsorbed to the baghouse filter dust into the final product (FDEP, 2009; Linero and Read, 2010).

In the FDEP comments mentioned earlier, it was stated that it is acceptable to shuttle filter dust into the finishing mill to a maximum of 5% as long as the filter dust meets the ASTM composition specifications, i.e., ASTM C465. Additionally, in the state of Florida, with generally low levels of alkali in the final product, the shuttling of filter dust may actually enhance the performance of the cement, especially at early ages of curing. Therefore, it is now possible to implement the practice of dust shuttling without necessarily disqualifying the cement product from Type I classification. This same phenomenon of volatile or semi-volatile metals being adsorbed to raw materials, lime, or commercial adsorbents, has been documented in studies in Germany, Canada, Oregon, Maryland, Norway, and Switzerland where filter dust shuttling has been practiced (FDEP, 2009).

The dust shuttling process is expected to significantly reduce the air emissions of mercury by incorporating and stabilizing mercury and other trace metals in the cement and concrete being amended with BFD. One facility in Maryland has seen reductions of mercury emissions up to 40% from former levels (FDEP, 2009). It is assumed that most of these reductions in air emissions are due to Hg being shuttled into the final product. It is important to consider the fate of the mercury

and other trace metals transferred from the air emissions into the cement and concrete via the dust shuttling process and its potential exposure to the public and environment (FDEP, 2009).

The FDEP conclusions, with respect to the material property effects from inorganic process additions, were similarly stated in a brief from the Portland Cement Association (PCA, 1992) announcing the harmonization of AASHTO M85 and ASTM C150. The PCA states that provisions are to be included for use of up to 5% by mass of inorganic process additions, based on information published in the National Cooperative Highway Research Program (NCHRP) Report 607. Qualification testing is required for amounts over 1% via a revised ASTM C465 or the new AASHTO specification, M327 (equivalent to the revised ASTM C465). Related changes to potential Bogue phase calculations are required to account for the use of process additions and limestone additions in the cement (PCA, 2013). The Bogue calculation is used to calculate the approximate proportions of the four main minerals in Portland cement clinker (tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite).

Additionally, the NCHRP study states that processing additions are materials interground to aid in the manufacture or handling, or both, of a Portland cement. Previously, processing additions were limited to 1% by mass in AASHTO M85 and both ASTM C150, and AASHTO M85 required qualification of processing additions by ASTM C465. None of these specifications distinguished between requirements for organic and inorganic processing additions. While the first processing additions used in Portland cement were organic grinding aids, inorganic processing additions, such as granulated blast furnace slag and fly ash, have since been used in the manufacture of Portland cements to improve efficiency of manufacturing. Within the NCHRP study, laboratory tests were conducted on inorganic process addition dosages up to and just above maximum limits imposed by existing cement specification limitations on loss-on-ignition and

insoluble residue. These would appear to limit maximum dosages of the materials tested to be between 3 and 8%, except for slag, which was not limited by this approach. A maximum dosage of any processing addition of 5% by mass of cement has been selected based on global practice (Taylor, 2008).

To summarize, the harmonization of AASHTO M85 and ASTM C150 has resulted in changes to the allowed mass percent of inorganic process additions allowed in Type I Portland cement, i.e., 5% by mass of cement. Cement manufacturers must ensure that the BFD they are using as an inorganic process addition meets the specifications of ASTM C465 or equivalent. According to the NCHRP study this would preclude the use of greater than 8% by mass of cement addition of BFD due to Loss-On-Ignition (LOI) and insoluble residue limitation of BFD. This conclusion is an important distinction for later development of experimental methodology described within this report.

2.5. Leaching of CKD, Cement, and Concrete

Several studies have been done in the past to characterize the concentration of constituent elements in CKD, cement, and in concrete. A 1982 study by the U. S. Bureau of Mines concluded that CKD is a large volume material and a potential resource as a substitute for lime. The study found that any environmental considerations are minor and that CKD produced in the USA is not a hazardous waste as defined by current regulations under RCRA (Haynes and Kramer, 1982).

This study was the first nationwide survey and characterization of CKD. The elemental and anion variations in U.S. CKD are presented below in Table 1. Major elements, i.e., Al, Si, K, Ca, Ti, and Fe, were measured using a fused disk x-ray spectrographic technique. All other elements were determined through acid digestion (HNO₃/HF) and analysis by flame atomic

absorption spectroscopy (AAS). It should be noted that the acid digestion method used in this study constituted a total digestion of all minerals, including siliceous minerals which are typically considered inert and do not release their bound trace constituents. The CKD from 72% of the existing U.S. cement plants was assessed using the EPA Extraction Procedure (EP) toxicity test for its hazardous waste potential, with respect to concentrations of the eight metals listed in Table 2. All but one sample was in compliance with the EP toxicity limits (see Table 2 below); the non-complying sample slightly exceeded the EP toxicity test criterion for lead. While this analysis is incomplete with respect to leachability, it does provide a bench mark of CKD composition for comparison of current samples of CKD or BFD.

Table 1: Elemental and Anion Variation in U.S. Cement Kiln Dust

Element or Anion	Range mg/kg	Mean mg/kg	Median mg/kg
Ag	< 3 – 17	5.4	4.8
Al	9900 – 50200	23200	23100
As	1.3 – 518	24	9.3
Ba	< 55	< 55	< 55
Be	< 2	< 2	< 2
Bi	< 50	< 50	< 50
Ca	106000 – 367000	295000	305000
Cd	< 1.5 – 352	21	7.3

Table 1 Continued: Elemental and Anion Variation in U.S. Cement Kiln Dust

Element or Anion	Range mg/kg	Mean mg/kg	Median mg/kg
Cr	11 – 172	41	34
Cu	7 – 206	30	24
Fe	1000 – 44400	14700	14100
Hg*	< 0.13 – 1.0	< 0.13	< 0.13
K	3400 – 232000	36600	26800
Li	< 4 – 76	18	16
Mg	1980 – 19100	7820	6820
Mn	63 – 2410	383	280
Mo	< 50	< 50	< 50
Na	495 – 27700	4700	3190
Ni	< 12 – 91	22	29
Pb	17 – 1750	253	148
Sb	< 1.6 – 70	3.2	< 1.6
Si	26900 – 111000	63500	65100
Sn	< 100	< 100	< 100
Sr	62 – 8750	670	430
Ti	500 – 2900	1193**	1100
Tl	< 60 – 185	< 60	< 60
V	< 100	< 100	< 100
Zn	32 – 8660	462	167
Br ⁻	< 200	< 200	< 200
Cl ⁻	< 100 – 123000	6900	4900
F ⁻	100 – 3600	1300	1000
NO ₃ ⁻	200 – 16700	< 200	< 200
PO ₄ ⁻	200 – 1600	< 200	< 200
SO ₄ ⁻	4100 – 316000	77800	68600

(Haynes and Kramer, 1982)

* Mercury values based on only 16 samples.

**Apparent mistake in literature; mean was recalculated.

Table 2: Maximum Concentration of Contaminants for Toxicity Characteristic Metals

EPA Hazardous Waste Number*	Contaminant	Maximum Concentration, mg/L
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

*Pursuant to 40 CFR 261.30: Lists of Hazardous Wastes

In a 1992 PCA study, the characterization, production and current composition of CKD was updated from the 1982 study (PCA, 1992). Similar to the 1982 report, approximately 70% of cement plants were surveyed and tested for both total (acid soluble) and leachable heavy metal concentration (EPA Method 1311: Toxicity Characteristic Leaching Procedure (TCLP)) in CKD and cement. The results showed no consistent correlation between total metals and leachable metals. That is, samples containing the highest total metals concentration did not necessarily produce the highest TCLP results (PCA, 1992). Moreover, samples containing the highest level of total metals leached only moderate amounts of metals. It was concluded that none of the cement samples exceeded the RCRA limits, i.e., Toxicity Characteristic (TC), for any of the metals. However, TCLP results for CKD from one facility produced samples exceeding TC limits for selenium and lead. The report stated that this result can be explained by the fact that the facility in question recycles 100% of their CKD back into the pyro-process. In the interim, between the report by Haynes and Kramer and the PCA study, changes in raw materials, fuels, processes, and test techniques occurred. Surprisingly, the PCA report states that there is no significant change in

concentrations of metals in the CKD that was tested. Additionally it was stated that lead and chromium proved to be of greater interest than other metals because they are present in CKD and cement in measureable levels. Many of the other metals, while present, are at levels that are unlikely to cause a hazardous waste classification by TC. Totals and TCLP results can be seen in Table 3 and Table 4, respectively. The cement did not leach constituent metal to the degree to which the CKD did. While constituent concentrations of elements in CKD, cement, and concrete will vary with location the average concentration listed in the 1992 and 1982 reports give a useful reference point.

Table 3: Total Concentration of Trace Metals in CKD and Cement (PCA, 1992)

Element	Total in Cement, mg/kg			Total in CKD, mg/kg		
	<u>Min.</u>	<u>Avg.</u>	<u>Max.</u>	<u>Min.</u>	<u>Avg.</u>	<u>Max.</u>
Mercury	< 0.001	0.014	0.039	0.004	0.66	25.50
Selenium	0.62	NM	2.23	2.68	28.14	307.00
Thallium	0.01	1.08	2.68	1.40	43.24	776.00
Cadmium	0.03	0.34	1.12	0.1	10.3	59.60
Lead	1.0	12.0	75.0	34.0	434.0	7390.0
Antimony	0.7	NM	4.0	0.3	NM	3.4
Silver	6.75	9.20	19.90	4.80	10.53	40.70
Arsenic	5.0	19.0	71.0	2.0	18.0	159.0
Nickel	10.0	31.0	129.0	1.0	22.0	60.0
Barium	91.0	280.0	1402.0	35.0	172.0	767.0
Beryllium	0.32	1.13	3.05	0.13	0.65	3.54
Chromium	25.0	76.0	422.0	8.0	41.0	293.0

Table 4: TCLP Results from Cement and CKD (PCA, 1992)

Element	TCLP-Cement, mg/L			TCLP-CKD, mg/L		
	Min.	Avg.	Max.	Min.	Avg.	Max.
Mercury	0.0001	0.0006	0.005	0.0002	0.0018	0.0223
Selenium	0.001	0.011	0.025	0.006	0.152	1.711
Thallium	0.002	0.01	0.028	0.01	0.38	4.50
Cadmium	0.0003	0.0019	0.0123	0.0001	0.0288	0.22
Lead	0.002	0.009	0.029	0.002	0.349	9.718
Antimony	0.003	NM	0.063	0.003	0.012	0.031
Silver	0.003	0.07	0.12	0.03	0.07	0.17
Arsenic	0.005	0.027	0.084	0.003	0.066	0.636
Nickel	0.06	NM	0.17	0.06	0.13	0.32
Barium	0.49	1.35	4.27	0.12	1.04	9.19
Beryllium	0.0001	0.0005	0.003	0.0001	0.0004	0.0029
Chromium	0.07	0.54	1.54	0.01	0.1	1.29

A complete understanding of the chemistry of hydration of cement is not available due to the complex nature of the process. However, several studies have indicated that cement and CKD leachability is influenced strongly by solubility of mineral structure containing trace metals; while concrete leachability is more controlled by diffusion of metal through the pore structure of the cement matrix (Van der Sloot, 2002; Duchesne and Reardon, 1998; Shivley et al. 1986; Hillier et al. 1999; Poon et al. 1985; Serclerat et al. 2002).

In CKD, trace element mobility is correlated to the solubility of minerals during the hydration process (Duchesne and Reardon, 1998; Serclerat et al. 1999). In the study by Duchesne and Reardon, it was stated that CKD is composed of mostly oxidized, anhydrous phases. These phases include lime (CaO), arcanite (K₂SO₄), and sylvite (KCl) and are unstable and are highly soluble in water at standard temperature and pressure (Duchesne and Reardon, 1998). When CKD

contacts water, these phases will either completely dissolve or more stable and less soluble phases will precipitate. The concentration of some constituent elements in CKD leachates is controlled by the solubility of secondary precipitates while other elements are controlled by their availability to the leachate solution and their diffusive flux into solution from the leaching of primary phases over time (Duchesne and Reardon, 1998). To differentiate between these two classes of leaching behavior, leaching procedures of several liquid to solid ratios of CKD were conducted. It was pointed out that if the liquid to solid ratio is halved and the element concentration in the leachate does not double then there must be a solid phase control on the elements mobility. The test results indicated that there are no solubility controls on Na, Cl, Cr, Mo, Se, and, in most instances, K. However, evidence for solubility control was seen for Si, Ca, SO_4^{2-} , Mg, Al, Zn, Ti, Sr and Ba concentrations (Duchesne and Reardon, 1998). These results strongly suggest the dependence of elemental mobility on the liquid to solid ratio. This is important to cement and concretes because differing water additions to mixes during hydration can affect both the mobility of trace metals and permeability of the hardened concrete.

In a different study the effects of varying pH were observed on the leachability of three trace metals, Zn, Cr, and Pb, in mortar bars. Mortar bars are made from a mixture of cement, water, and sand that is then allowed to set. The study found that most of the metals were retained when exposed to deionized water. However, metal concentrations differed for some metals as the pH was varied, i.e., Zn, Cr^{3+} and Pb (Serclerat et al. 1999). These results are significant but a more complete analysis of all trace metals should be done with varying liquid to solid ratios.

Another paper cited several sources stating that silicate mineral structures are well documented in the adsorption of amphoteric metals on to their surface (Shively et al. 1986). Additionally, amorphous iron oxy-hydroxide surfaces have been shown to provide multiple

adsorption sites for trace metals. Leaching tests with varying pH were also addressed in the study by Shively et al. Acid attacks the cement through the permeation of the pore structure and dissolution of ions back through the chemically altered surface layer into solution. This reaction is similar to the natural weathering of silica-rich minerals in the environment (Shively et al. 1986).

It has been reported that multiple extractions of leachate showed a decrease in metals concentration and lowering of the pH in the leachate (Shively et al. 1986; Poon et al. 1985). These results show a very different scenario than a single extraction technique. In the Shively et al. report it was shown that none of the samples failed the TC for heavy metals despite being doped with concentrations much higher than those seen in typical cement.

In the Poon et al. study it was stated that the interaction of many metals with the microstructure of the hydrated cement occurs in the early stage of hardening (Poon et al. 1985). However, the mechanism of fixation, i.e., chemical reaction or physical encapsulation, has still not been clearly revealed and may vary for different elements. For example, the immobilization mechanism for cesium in cement is thought to be purely physical encapsulation since cesium does not form an insoluble precipitate under the alkaline conditions of cement solutions. It should be realized that elements that do not form an insoluble precipitate or are not chemically bound to the cement matrix may be more mobile in cement or concretes with higher porosity, e.g., cement treated with higher portions of air entrainment agent (Poon et al. 1985).

Two different studies, Hillier et al. (1998) and Marion et al. (2005), looked at the long-term leachability of concrete monolithic structures. However, both studies used deionized water as their leachate in tanks without multiple extractions of leachate. This is significant because as previously stated in Shively et al., the acid-cement reaction in lower pH leachates reflects natural degradation of the cement matrix. Additionally, concrete structures in the environment are rarely

isolated and contained in the same water for an extended period. This would cause the leachate to become highly alkaline and this could significantly affect the mobility of constituent elements.

2.6. Vapor Phase Release of Mercury from BFD and Cement

Among the studies with the Hg-contained cement, most focused on the leaching characteristics of the curing concrete, while very few focused on the vapor phase Hg release. A head-space study (Hamilton and Bowers, 1997) showed that vapor phase Hg was released from the Hg-doped (0.2% wt./wt.) solidified cement monolith. The release rate of Hg was a function of time and temperature. The study also indicated that the vapor phase Hg release from the cement monolith was possibly due to moisture and temperature increase during the mixing and curing. However, the study was carried out with a very high concentration of doped Hg (0.2% wt./wt.) in cement which is not likely to happen in the industrial setting. Another study (Golightly et al., 2009) demonstrated that about 0.31% of total Hg was released from curing concrete, when 55% of the cement was replaced by coal fly ash. A study (Goodrow et al., 2005) in New Jersey revealed that the total Hg contribution to the local atmosphere from cement-stabilized waste was negligible (<4% of the total gaseous mercury concentration), although the release rate (130 kg/yr) was on par with other industrial sources.

3. Transportation Department Survey

3.1. Survey Objectives and Methodology

A component of this study was to identify concerns, practices, and recommendations which are in place at transportation departments in states other than Florida. All survey questions can be seen in Table 5 below; responses to survey inquiries can be seen in Tables 6 and 7.

3.2. Results of Survey

Responses to the survey of transportation departments were received from 18 states. No respondent reported complaints or issues with regard to mercury or other heavy metals related to cement. Only two of the eighteen reported an awareness of the concern for mercury emissions at cement plants. The state of Washington Department of Transportation cited a study by the National Transportation Board (NCHRP Reports 443 and 448), which investigated leaching from common DOT construction materials, including Portland Cement Concrete (PCC). The experimental methods of the study included batch, flat plate (monolithic), and column leaching tests on PCC. The study focused on aquatic toxicity due to leaching, quantified by algal toxicity tests. The study concluded, from an overall perspective, the project methodology as applied to numerous tested materials indicates mostly benign impacts on the near-highway aquatic environment. Almost all tested Construction and Repair (C&R) materials exhibit minimal toxicological effects when used in their highway assemblage form (e.g., when integrated into a pavement or fill). Impacts are further reduced and eliminated by sorption in soils. This is not to say that there will never be negative impacts from use of these materials, but the overwhelming weight of evidence indicates that there are no significant environmental problems.

Several state DOTs allowed for the use of baghouse dust as an inorganic process addition at industries' discretion up to 5%, as long as the final cement product meets AASHTO M85, ASTM C150, and ASTM C465 specifications. However, these specifications do not take into consideration environmental regulation and are primarily concerned with finished product material properties. Additionally, the study cited by Washington State DOT did not use EPA standard leaching method and did not compare leachate metal concentration to regulatory limits.

Table 5: List of Survey Questions

Question Number	Question
1	Have you had complaints, issues, or questions about mercury and other heavy metals as it relates to cement? (Yes/No/Unknown) If so, from what industries, or sources?
2	Is baghouse dust recycled in the cement production process in your state? (Yes/No/Unknown) If yes, is there any regulation regarding how much baghouse dust is allowable? For example, up to 5% is allowable in Florida.
3	Is the release of mercury and other heavy metals from cement and concrete a concern in your state?
4	Does your agency enforce or recommend any specifications regarding mercury or other trace metals in cements? (Yes/No/Unknown) If yes, could you give some brief information or code citation?
5	What actions (research, regulations, monitoring, etc.) have been taken in your state to address the issue of mercury and other metals in cement?
6	We would greatly appreciate the contact information of someone in your state who is experienced with these issues. Please list their information below.

Table 6: Survey Question Responses

State	Question Response				
	1	2	3	4	5
Alabama	None	Unknown	Unknown	No	None
Georgia	None	Yes	Unknown	No	None
Illinois	None	No response	Unknown	No	None
Indiana	None	Yes, allowable limit set by cement industry with respect to ASTM C150 or equivalent	Not at this time	No	None
Iowa	None	Unknown	Not at this time	No	None
Louisiana	None	N/A, no cement kiln in LA.	No	No, unless specified in AASHTO M85/ASTM C150	None
Mississippi	None	No	Not at this time	No	None
Missouri	Concerns expressed by industry with respect to cost of compliance to NESHAP standards	Allowed in the state at industry's discretion with compliance to AASHTO M85, up to 5% baghouse dust allowed	No, any metals would remain immobilized in concrete	No	Compliance with NESHAP
Montana	None	Allowed by state so long as cement meets AASHTO M85 or ASTM C150, no plants currently practicing	No	No	None

Table 6 Continued: Survey Question Responses

State	Question Response				
	1	2	3	4	5
New York	None	Yes, NYDOT not involved in regulating additions	Yes	No, regulated by NY Dept. of Environmental Conservation	No, regulated by NY Dept. of Environmental Conservation
Oregon	None	Unknown	No	No	None
Pennsylvania	None	Allowed by state so long as cement meets AASHTO M85 or ASTM C150, up to 5% allowed	Yes	No	None
South Carolina	None	Unknown if practiced but not prohibited or limited	Not at this time	No, unless specified in AASHTO M85/ASTM C150	None
Utah	None	Not recycled, citing high alkali content of baghouse dust	No	No	None
Vermont	None	No response	No	No	None
Washington	None	Allowed in the state at industry's discretion with compliance to AASHTO M85/ASTM C150, up to 4% baghouse dust allowed	No, refer to NCHRP Reports 443 and 448	No, unless specified in AASHTO M85/ASTM C150	No, refer to NCHRP Reports 443 and 448
West Virginia	None	Unknown	No	No	None
Wyoming	None	Unknown but allowed so long as in accordance with ASTM C150	Unknown	No	No response

Table 7: Contact Person for State DOT Survey Responses

State	Contact
Alabama	Shannon Golden AL DOT
Georgia	Myron Banks GA DOT
Illinois	Douglas A. Dirks Illinois DOT, Bureau of Materials and Physical Research
Indiana	Anthony Zander Indiana DOT
Iowa	Chengsheng Ouyang Materials Office, Iowa DOT
Louisiana	Bert Wintz LA DOT
Mississippi	James A. Williams, III, P.E. Mississippi DOT
Missouri	Sam Marshall Missouri DOT
Montana	Matt Needham Montana DOT
New York	Karen L. Groff NY DOT
Oregon	Keith Johnston, PE Oregon DOT
Pennsylvania	Patricia Miller Pennsylvania DOT
South Carolina	Melissa L. Campbell South Carolina DOT
Utah	Bryan Lee or Sara Carlock Utah DOT
Vermont	William Ahearn P.E. Vermont Agency of Transportation
Washington	Thomas E. Baker, P.E. Washington DOT
West Virginia	Mike Mance West Virginia DOT
Wyoming	Rick Harvey Wyoming DOT

4. Florida Portland Cement Manufacturing Industry Assessment

A current list of Portland cement plants operating in Florida is provided in Table 8. The participating facilities in this study were the CEMEX Brooksville South cement plant facility (Brooksville) and the Titan-Pennsuco facility (Titan); however, samples of baghouse filter dust and cement have not been received from the Titan facility. Participating facilities provided material samples (Brooksville), facility tours, and interviews. Other facilities which were invited to participate and declined include the Suwannee American Cement facility and the Vulcan Materials Company facility. Figure 2 shows the locations of these cement facilities.

The CEMEX facility, located in Brooksville, FL, is an integrated facility that includes a Portland cement manufacturing plant having one preheater dry-process kiln system (emission unit 018; initial operation in the mid-1980s), one precalciner dry-process kiln (emission unit 044) (initial operation in 2009) system, and a power plant. The power plant boiler is a coal fired unit that is currently under construction to be converted to a biomass-fired unit capable of generating 77 MW. Kiln 1, along with the in-line kiln/raw mill and clinker cooler 1 share a baghouse fabric filter system and exhaust stack with the power plant. However, Kiln 2, the related in-line kiln/raw mill, and clinker cooler 2, share a common baghouse fabric filter system and stack not connected to either kiln 1 or the power plant boiler. All baghouse filter dust which was collected from this facility for the study came from the Kiln 2 baghouse.

The Brooksville facility is the only facility in the state of Florida currently practicing baghouse filter dust shuttling. Other facilities in Florida will likely be using this technique within less than two years given the upcoming revised NESHAP, subpart LLL (40 CFR 63) requirements to limit Hg emissions to 55 lb/million ton of clinker on a 30-day average for existing kilns. All kilns in Florida are defined as existing kilns for purposes of the recently revised NESHAP.

Under current guidance from ASTM, the FDOT is restricting the Brooksville facility to adding up to 5% BFD by mass of the cement to protect the final product material properties. It should be noted, as can be seen in Figure 3, the facility does not add the BFD in a predictable fashion daily. The average transfer/addition of BFD to the finish mill from the sample data provided for the month of December 2012 is $3.16 \pm 0.64\%$, this is well below the specification. One conclusion that can be drawn from this data is that all cement produced at the Brooksville facility will contain some percentage of BFD; however, it is difficult to predict additions made on a batch basis. This fact will influence experimental methodology outlined within this report. Four samples of BFD and one sample of cement were provided from this facility for analysis.

Table 8: List of Current Cement Plants in Florida

Company	Location	No. of Kilns
Suwannee American Cement LLC.	5117 U.S. 27 Branford, FL 32008 Phone: (386) 935-2444	1
Vulcan Materials Company	4000 NW County Road 235, Newberry, FL 32669 Phone: (352) 472-4722	2
American Cement Company	4750 County Road 470, Sumterville, FL 33585 Phone:(352) 569-5393	1
CEMEX	10311 Cement Plant Rd, Brooksville, FL 34601 Phone: (352) 799-7881 and 1200 NW 137th Ave, Miami, FL 33182 Phone: (305) 221-7645	2 (Brooksville) and 1 (Miami)
Titan-Pennsuco	11000 Northwest 121 Way, Medley, FL 33166 Phone: (800)-588-3939	1

The Titan-Pennsuco facility, located in Medley, FL, consists of a Portland cement plant, an aggregate plant, two batch ready-mix concrete plants, and a cement block plant. The Portland cement plant has an allowable production rate of 2,190,000 tons per year (TPY) of clinker and 2,400,000 TPY of cement. It includes fuel and raw material storage, feed bins, a coal mill, a dry

process pyro-processing line, transfer equipment, finish mills, clinker and cement silos, product packaging, and load out facilities. Pollution control equipment for the cement plant consists of a common baghouse system designed for capturing particulate emissions from the kiln, raw mill, coal mill and cooler; absorption of sulfur compounds and metals into the product; combustion controls for volatile organic compounds (VOC) and carbon monoxide (CO); indirect firing, multiple burn points, and a Low NO_x calciner for NO_x; and baghouses for particulate emissions from other process emission units. Based on the Title V air operation permit, this facility is a major source of hazardous air pollutants.

Florida's Cement Kilns



Figure 2: Location of Cement Kilns in the State of Florida (FDEP, 2007)

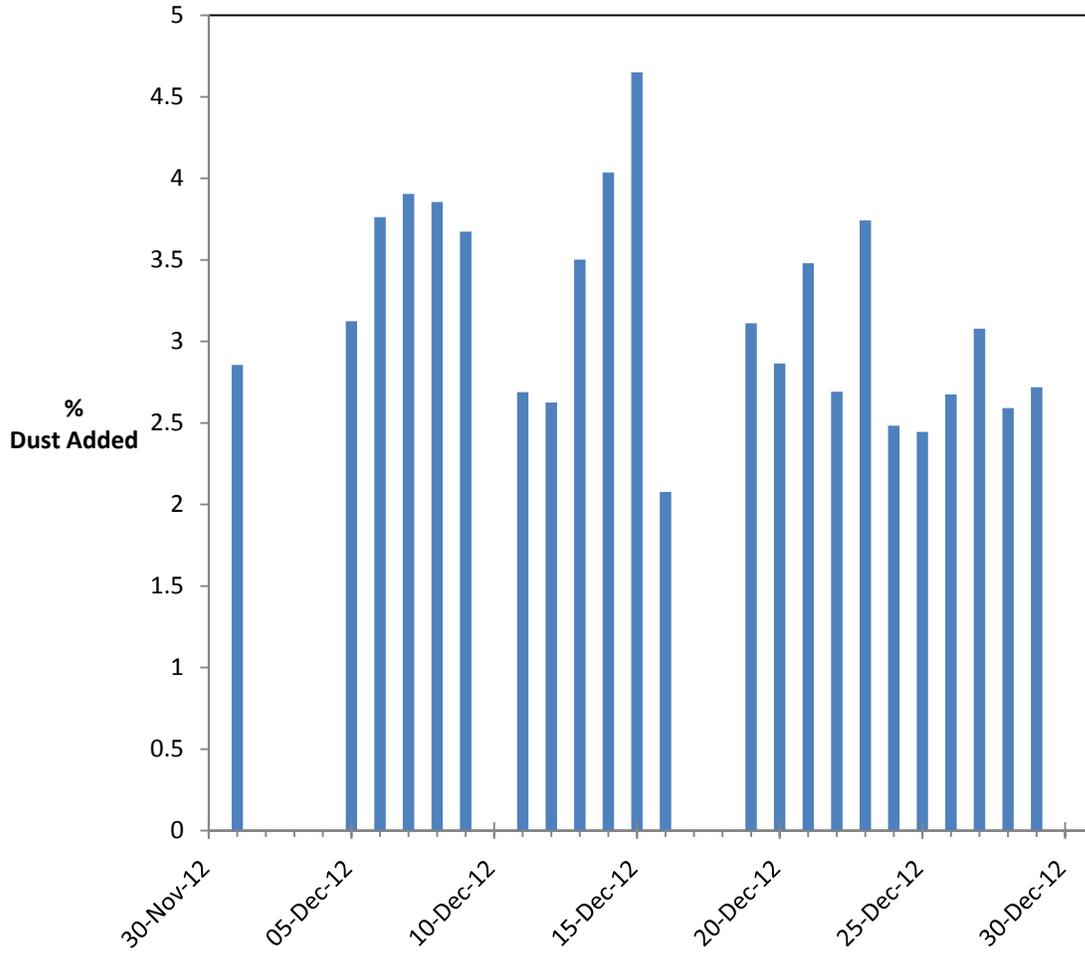


Figure 3: Daily Percent Additions of BFD at Brooksville South Cement Plant for 12/2012

5. Characterization of Baghouse Dust (BFD)

After BFD was collected from the participating facilities, it was subjected to various characterizations. The two predominant oxidation states of mercury, Hg^{2+} or Hg^0 , greatly affect its solubility and volatility. Since the form of mercury is a key parameter in determining its fate and its potential risk during handling, it is critically important to first characterize its form and corresponding concentration in the dust. In addition to mercury, other trace elements contained in BFD may also impact potential BFD use in concrete and cement. The physical and chemical characteristics of BFD play a role in the fate of mercury and trace metals. Hence, the BFD samples were characterized for a comprehensive suite of physical and chemical properties, including gross elemental composition, mineralogical composition, and trace metal concentrations (As, Ba, Cd, Cr, Hg, Pb, Se, V, and Zn). To provide baseline data regarding BFD aqueous leachability as a function of key environmental conditions, the BFD samples were also assessed for trace metals leachability using standardized leaching protocols: Synthetic Precipitation Leaching Procedure (SPLP), a pH dependence leaching procedure (EPA Method 1313), and a Multiple Extraction Procedure (MEP).

5.1. BFD Characterization Methodology

The following methodology describes laboratory techniques and procedures utilized for the completion of Task 4 pursuant to the initially submitted proposal to the FDOT. Sample collection and storage, leaching protocol, and other laboratory analytical techniques will be described in this section.

5.1.1. Sample Collection and Storage

Samples of BFD or cement collected from the participating facility were stored in five-gallon High Density Polyethylene (HDPE) buckets, see Table 9. Prior to use of any BFD or cement sample in experiments the material was homogenized by rotating the storage vessels in an end-over-end fashion for approximately 2 hours. Additionally, attempts were made, when removing a sample from the sample storage vessel for use in experiments, to mix the bulk sample and select the aliquot randomly.

Table 9: Sample Inventory and Collection Date

Sample Identification	Participating Facility	Volume / Date Collected
BFD A	CEMEX Brooksville	15 gal. / 10-28-2011
BFD B	CEMEX Brooksville	10 gal. / 12-15-2011
BFD C	CEMEX Brooksville	10 gal. / 02-28-2012
BFD D	CEMEX Brooksville	10 gal. / 08-24-2012
Cement A	CEMEX Brooksville	10 gal. / 08-24-2012

Concern was raised that during storage of the samples some loss of mercury could occur due to volatilization. To determine the possibility of total mercury loss and the conversion of Hg^{2+} species to elemental mercury during sample storage, an experiment was initiated. After collecting samples on 02/07/2012, the samples were immediately stored in glass jars with HDPE (High Density Polyethylene) screw caps. One of these samples was placed in a desiccator to lower the initial moisture content. The samples of desiccated BFD and “as received” BFD were analyzed for mercury content and mercury speciation. Other samples were placed in a sealed chamber with a controlled relative humidity of 40%. Periodically, these stored samples were tested for mercury content and speciation.

5.1.2. Bulk Elemental Analysis and Mineralogical Composition of BFD

An initial analysis of cement and BFD samples collected from the Brooksville facility was performed via Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and X-Ray Diffraction Spectroscopy (XRD). The bulk elemental analysis was performed via SEM-EDS at the UF Major Analytical Instrumentation Center (MAIC) on the UF campus. SEM-EDS is a semi-nondestructive technique for determining the major elements present within a dry powdered material, e.g., cement or BFD. Samples need to only be carbon coated, to allow sufficient current to pass through the sample to ground, and can be quickly and directly analyzed. Similarly, the samples were prepared for mineralogical compositional analysis via XRD at the MAIC lab.

5.1.3. Total Trace Metals Analysis (EPA Method 3050b)

Total trace metals analysis was performed on all BFD and cement samples collected from participating facilities in accordance with EPA Method 3050b - Acid Digestion of Sediments, Sludges, and Soils. It should be noted that this method is not a total digestion technique for most materials. It is a strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure; however, this should not be a concern since silicate bound compounds are not considered mobile in the environment. The method consists of weighing out 1-2 grams of representative solid sample and exposing the solid sample to numerous additions of nitric acid, hydrogen peroxide, and hydrochloric acid under refluxing conditions for up to 5 hours. The sample is then diluted and stored for later analysis via Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Cement and BFD samples were analyzed for total mercury

concentration and speciation in accordance with EPA Method 1631 by Cold Vapor – Atomic Fluorescence Spectroscopy (CV-AFS).

5.1.4. Characterization of Mercury Species

The digestion procedure to determine mercury speciation was derived based on the sequential extraction procedure described in EPA Method 3200 (US EPA, 2005), while the analysis of total mercury concentration was based on EPA Method 7474 (US EPA, 2007). For each type of material, i.e., cement, BFD, fine aggregate, or coarse aggregate, five replicates of 0.5 grams each were weighed using an analytical scale (Sartorius MC210S, Goettingen, German) with a precision of 0.01 mg. The solid samples were then placed in thread capped Polytetrafluoroethylene (PTFE) tubes; 10 mL of the appropriate extraction solution for different mercury species (listed in Table 10) was added to the PTFE tube. The PTFE tubes were heated up to about 100 °C for 30 minutes in a microwave digestion system (CEM MDS 81D, Matthews, NC). The digests were diluted with deionized water to a pre-determined level, to accommodate the linear dynamic range of the analytical instruments. The diluted solution was transferred into a 50 mL centrifuge tube and analyzed by a hydride generation - atomic fluorescence spectrometer (HG-AFS) (Aurora Biomed 3300, Vancouver, BC, Canada). The detection limit of the HG-AFS was around 1 ng/mL. The mercury concentration in each type of samples was averaged from the five replicates.

In addition to the characterization, a 7-day time-series study was carried out on two batches of the BFD (Oct, 2011; Dec, 2011) to evaluate the Hg loss from the BFD, by exposing them to natural weather (~30 °C, 60~70% relative humidity). The BFD was spread out on a flat surface as a thin layer and left outdoors. A small portion of the sample was collected on a daily basis during the 7-day period. The retrieved sample was dried in the desiccator to remove excessive water absorbed

on the BFD, digested and analyzed by HG-AFS. The condition was used to simulate storing the BFD in an open area with unlimited head-space.

Table 10: Classification and Extraction Method for Mercury Species

Hg Phase	Hg Species	Environmental Mobility	Toxicity	Extraction Solution
Soluble inorganic Hg (SI-Hg)	Hg ²⁺ (HgCl ₂ , HgSO ₄ , HgO, Hg(NO ₃) ₂ , Hg(OH) ₂)	Mobile	Toxic	10% HCl
Alkyl Hg	Methyl Hg, Ethyl Hg	Mobile	Highly toxic	Toluene
Non-soluble inorganic Hg (NSI-Hg)	Hg ⁰	Semi-mobile	Less toxic	Calculated from mass balance
	HgS, Hg ₂ Cl ₂	Non-mobile	Less toxic	
Total Hg	All of the above			Aqua regia (HNO ₃ : HCl, 1:3 v/v)

* Digestion procedure followed EPA Method 3200 (US EPA, 2005); analysis of mercury concentration followed EPA Method 7474 (US EPA, 2007)

5.1.5. Synthetic Precipitation Leaching Procedure (EPA Method 1312)

Leaching is one way of characterizing the mobility of constituents of a solid material and their potential release into the surrounding environment. The EPA has determined a set of tests to aid in determining the potential leachability of solid materials; these tests are defined in the EPA's SW-846 (Test Methods for Evaluating Solid Waste, Chemical/Physical Methods).

One of these leaching tests is the widely utilized Synthetic Precipitation Leaching Procedure (SPLP). The SPLP is an EPA SW-846 method for determining the mobility of contaminants in a liquid, soil or waste under weathering conditions, i.e., acid rain precipitation. For solid phase materials, e.g., BFD or concrete, the solid material is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is deionized water adjusted to a pH of 4.22 ± 0.05 with a mixture of 60/40 by mass of sulfuric acid

and nitric acid, respectively. The solid phase and solution were sealed and mixed in an end-over-end fashion for approximately 18 hours. Following extraction, the liquid extract was separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. This liquid extract was then stored at pH 2, by nitric acid addition, for later analysis with ICP – AES and CV-AFS.

5.1.6. pH Dependence Leaching Test (EPA Method 1313)

Two important parameters of nearly all leaching procedures are pH and liquid to solid ratio. Both parameters are of crucial importance in determining the long term leaching behavior of cements and concretes. This can be further elucidated by considering the effect of a large water body on the leachability of concrete. In leaching tests using small liquid to solid ratios, the pH can be driven by the dissolved species from the solid phase. In the case of cement or concrete, these species are basic in nature and therefore produce a leachate that has a high pH. In this situation, the concrete or cement sample would never be exposed to a lower pH. This does not simulate the real world event of submerging concrete structures in large water bodies. Due to this consideration some of the leaching test traditionally used for determining leachability may not fully characterize the risk due to mobility of constituents, e.g., TCLP and SPLP. However, it should be noted that this does not exclude the utility and importance of these tests and the need to execute them.

To address these concerns, a pH dependent leaching test was utilized, namely, EPA Method 1313 - Liquid-Solid Partitioning as a Function of Extract pH in Solid Materials Using a Parallel Batch Procedure. This method is designed to provide aqueous extracts representing the liquid-solid partitioning (LSP) curve, that is, the extent to which an analyte leaves the solid phase and partitions to the liquid extract, as a function of pH for inorganic constituents (e.g., metals and radionuclides), semi-volatile organic constituents (e.g., polycyclic aromatic hydrocarbons or PAHs) and non-volatile organic constituents (e.g., dissolved organic carbon) in solid materials. The LSP curve is

evaluated as a function of final extract pH at a liquid-to-solid ratio (L/S) of 10 mL extractant to 1 g dry sample (g-dry) and conditions that approach liquid-solid chemical equilibrium. The pH of sample leaching batches is controlled with additions of nitric acid or sodium hydroxide to attain a range of eluate pHs between 2 and 13. This method also yields the acid/base titration and buffering capacity of the tested material at an L/S of 10 mL extractant/g-dry sample. The maximum mass of constituent released over the range of method pH conditions, i.e., $2 \leq \text{pH} \leq 13$, may be considered an estimate of the maximum mass of the constituent leachable under field leaching conditions for intermediate time frames and the domain of the laboratory test pHs. Although, it should be noted that, the relationships between eluate concentrations observed from this method and field leachate must be considered in the context of the material being tested and the field scenario being evaluated. This method provides solutions considered indicative of eluate under field conditions, only where the field leaching pH is the same as the final laboratory extract pH and the LSP is controlled by aqueous phase saturation of the constituent of interest. Following extraction, the liquid extract was separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. This liquid extract was then stored at pH 2 for later analysis with ICP – AES and CV-AFS.

5.1.7. Multiple Extraction Procedure (EPA Method 1320)

The Multiple Extraction Procedure (MEP) is designed to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions reveal the highest concentration of each constituent that is likely to leach in a natural environment. The MEP is applicable to liquid, solid, and multiphase samples.

Waste samples are extracted with deionized water which is maintained at a pH of 5 ± 0.2 , with acetic acid. Following extraction, the liquid extract was separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. This liquid extract was then stored at pH 2 for later analysis with ICP – AES and CV-AFS. Then the solid portions of the samples that remain after application of the first extraction are re-extracted nine times using synthetic acid rain extraction fluid, see SPLP methodology above. If the concentration of any constituent of concern increases from the 7th or 8th extraction to the 9th extraction, additional extractions are repeated until these concentrations decrease. Following each extraction, the liquid extract was separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. This liquid extract was then stored at pH 2 for later analysis with ICP – AES and CV-AFS.

5.2. Results of BFD Characterization

5.2.1. Bulk Elemental Analysis and Mineralogical Composition of BFD

The initial characterization of the BFD included a gross elemental composition and mineralogical composition. The elemental composition of the BFD was determined using a Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) system. The results of this analysis can be seen in Table 11.

Table 11: Energy Dispersive Spectroscopy of BFD and Cement Samples

Element	Element Concentration (%wt.)				
	BFD A	BFD B	BFD C	BFD D	Cement A
Al	1.56	1.75	1.12	1.31	2.20
C	7.38	14.70	22.57	21.80	15.30
Ca	56.76	27.55	24.35	24.18	35.74
Cl	0.28	N.D.*	0.09	0.10	N.D.*

*Non-detectable

Table 11 Continued: Energy Dispersive Spectroscopy of BFD and Cement Samples

Element	Element Concentration (%wt.)				
	BFD A	BFD B	BFD C	BFD D	Cement A
Fe	1.65	0.73	0.41	0.60	2.71
K	0.77	0.35	0.23	0.25	0.36
Mg	0.17	0.23	0.19	0.20	0.28
O	27.65	52.10	48.59	48.96	37.55
S	0.16	N.D.*	0.07	N.D.*	0.63
Si	3.68	2.57	2.37	2.44	5.23
Ti	0.27	N.D.*	N.D.*	0.17	N.D.*

*Non-detectable

A semi-quantitative mineralogical analysis of the BFD was conducted with X-ray Diffraction (XRD). The minerals present in the samples initially collected at the Brooksville facility include: calcium carbonate, titanium oxide, titanium hydride, carbon sulfide, silicon sulfide, graphite, silicon dioxide, ferric oxide, and calcium oxide. Based on the relative abundance of each element and the peak intensity of the XRD analysis, it was determined that the major crystalline phase in the baghouse filter dust is calcium carbonate, likely from the raw materials, i.e., limestone. As can be seen in Table 12, other mineral forms are minor or trace constituents. As expected, the three aliquots were mineralogically identical as can be seen in the diffractogram of the XRD analysis of the three aliquots in Figure 4 below.

Table 12: Mineral Composition of Brooksville BFD

Crystalline Phase Identified	Chemical Formula	Crystalline Phase Relative Amount (%wt.)
Calcium Carbonate	CaCO ₃	≥ 55%
Titanium Oxide	TiO ₂	≤ 0.3%
Carbon Sulfide	C _x S ₂	≤ 0.2%
Silicon Sulfide	SiS ₂	≤ 0.2%
Graphite	C	≤ 7.5%
Silicon Dioxide	SiO ₂	≤ 4%
Ferric Oxide	Fe ₂ O ₃	≤ 2%

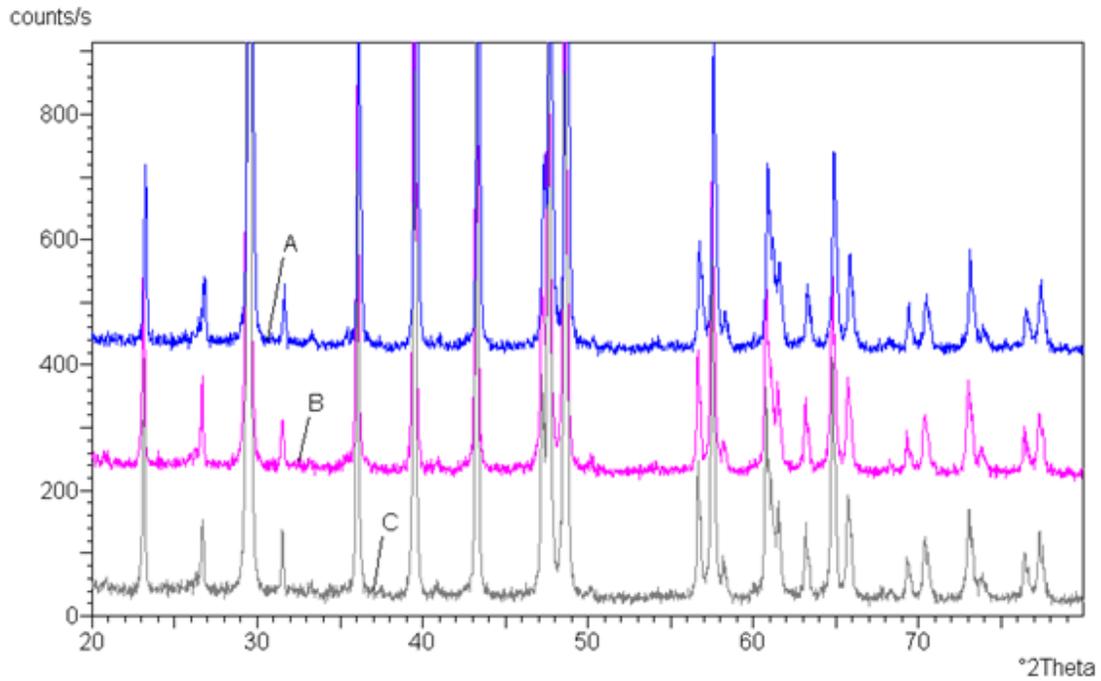


Figure 4: Diffractogram of Brooksville BFD Demonstrating Homogeneity

5.2.2. Total Trace Metals Analysis and Mercury Speciation

Table 13 lists the Hg concentration and speciation in the BFD, cement, and other constituents in the concrete samples. Alkyl-Hg was below the detection limit in all the samples, and therefore was eliminated from following studies. The high temperature and combustion condition in the cement kiln likely decomposes any organic phase compounds.

The total Hg concentration in the BFD samples ranged from 0.91~1.52 mg/kg (ppm). It was higher than the average value of 0.66 mg/kg (mean) in CKD previously determined by Portland Cement Association (PCA, 1992). It should be noted that Hg concentration in the BFD measured by PCA had a large standard error with some samples having up to 25.50 mg/kg total Hg, and some as low as 0.004 mg/kg. The BFD from different cement kiln plants does not have the same characteristics. The variance of Hg in the coal fly ash utilized, raw materials, wastes, and fuels could contribute to the difference among different operating regimes of the same cement plant. More mobile and toxic SI-Hg (soluble inorganic mercury) accounted for 61.54~73.43% of total Hg in the samples, while the rest was in NSI-Hg (nonsoluble inorganic mercury) phase.

The total Hg concentration in the Brooksville cement was 74.51 $\mu\text{g}/\text{kg}$. It was approximately one order of magnitude lower than the BFD. When mixing 5% of BFD with 95% of cement, the significance of Hg contributed from BFD diminished due to the small proportion. The concentration in the cement was also higher than the available studies (PCA, 1992; Pistilli and Majko, 1984) in past decades; the latter showed Hg in the cement was averaging below 14 $\mu\text{g}/\text{kg}$ with the highest to be 39 $\mu\text{g}/\text{kg}$.

Figure 5 shows the change of Hg in the 7-day time-series study in the open area using the BFD. The vaporization of NSI-Hg was significant on the first day, from 0.36 mg/kg to 0.27 mg/kg for Oct, 2011 sample of BFD, and from 0.25 mg/kg to 0.15 mg/kg for Dec, 2011 sample. The concentration of NSI-Hg stayed relatively unchanged afterward. The SI-Hg remained constant during the 7-day period. The total Hg loss was 13.83~17.52% on the first day, and totaled 20.21~21.16% during the 7-day period, mostly contributed from NSI-Hg vaporization.

Table 13: Mercury Concentration and Speciation of BFD, Cement and Concrete Components

Material	Collection Date	Total Hg (µg/kg)	Soluble Inorganic-Hg (µg/kg)	Percentage of Soluble Inorganic-Hg (%)
BFD A	Oct 2011	910 ± 60	560 ± 20	61.5
BFD B	Dec 2011	1430 ± 70	1050 ± 40	73.4
BFD C	Feb 2012	1520 ± 90	990 ± 100	65.4
BFD D	Aug 2012	1440 ± 23	1030 ± 100	71.5
Cement A	Aug 2012	74.51 ± 6.24	47.02 ± 8.94	63.1
Coarse aggregate	Jun 2011	4.32 ± 1.52	2.63 ± 1.16	60.8
Fine aggregate	Jun 2011	0.44 ± 0.06	0.33 ± 0.04	73.2

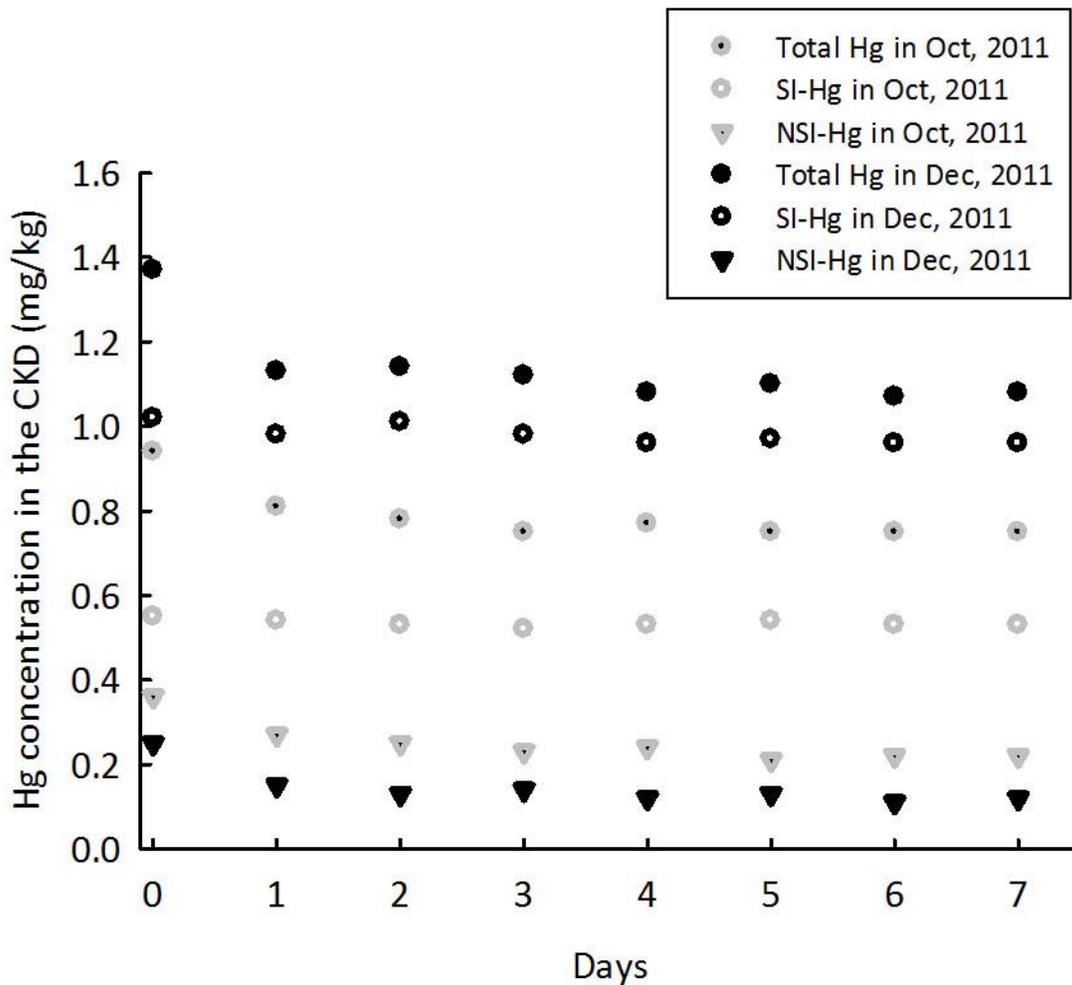


Figure 5: BFD Open Air Storage Experimental Results

The total trace metals concentration for the BFD and cement collected from the participating facilities can be seen in Table 14 and concrete constituents trace metals concentrations can be seen in Table 15; the total concentrations are compared to Florida Soil Cleanup Target Levels (SCTL). Florida SCTLs were developed based on direct human contact (i.e., direct exposure), and based on soil acting as a source of groundwater or surface water contamination (i.e., leachability). The calculation of default SCTLs can be seen in Equation 1; all pertinent default values used in Equation 1 can be found in Table 16 (FDEP, 2005). The SCTLs

for metals are used in this study as a bench mark to compare concentration levels to. It should be stressed that it is not the intention to imply that the BFD is to be used in a manner where workers or the public would be in direct contact with the material, i.e., direct application to soils.

$$SCTL = \frac{THI \times BW \times AT \times RBA}{EF \times ED \times FC \times \left[\left(\frac{1}{RfD_0} \times IR_0 \times 10^{-6} \frac{kg}{mg} \right) + \left(\frac{1}{RfD_d} \times SA \times AF \times 10^{-6} \frac{kg}{mg} \right) + \left(\frac{1}{RfD_i} \times IR_i \times \left(\frac{1}{VF} + \frac{1}{PEF} \right) \right) \right]}$$

Equation 1: Calculation of Default SCTLs

Table 14: Total Trace Metals Concentration in BFD and Cement

Element	Brooksville Cement (mg/kg)	Baghouse Filter Dust Oct. 2011 (mg/kg)	Baghouse Filter Dust Dec. 2011 (mg/kg)	Baghouse Filter Dust Feb. 2012 (mg/kg)	Baghouse Filter Dust Aug. 2012 (mg/kg)	SCTL (mg/kg) Residential / Industrial
Ag	0.149 ± 0.0190	0.411 ± 0.061	0.360± 0.012	0.216± 0.013	0.299± 0.013	410/1200
As	50.24 ± 2.02	18.57 ± 0.793	27.58 ±0.940	17.52 ±0.803	19.58 ±0.466	2.1 / 12
Ba	190.38 ± 6.68	74.93 ± 3.00	71.33 ± 2.34	49.29 ± 1.55	75.57 ± 1.28	120 / 130000
Cd	4.847 ± 0.184	1.68 ± 0.078	1.62 ± 0.047	1.51 ± 0.081	1.43 ± 0.014	82 / 1700
Cr	53.37 ± 1.80	19.88 ± 0.676	18.83 ± 0.428	16.90 ± 0.415	23.61 ± 0.671	210 / 470
Pb	90.37 ± 3.19	18.44 ± 0.912	25.72 ± 0.675	17.07 ± 0.646	52.70 ± 0.569	400 / 1400
Se	N.D.	5.63 ± 0.134	3.96 ± 0.198	3.22 ± 0.141	4.61 ± 0.05	440 / 11000
V	136.4 ± 5.13	49.79 ± 1.99	59.86 ± 2.08	50.72 ± 2.45	41.04 ± 0.692	69 / 10000
Zn	635.4 ± 20.23	51.15 ± 1.73	68.75 ± 2.15	64.29 ± 2.07	99.55 ± 1.22	26000 / 630000

*All values are replicate average ± replicate standard deviation

Table 15: Total Trace Metals Concentration in Concrete Aggregate

Element	Commercial Coarse Aggregate (mg/kg)	Commercial Fine Aggregate (mg/kg)	SCTL (mg/kg) Residential / Industrial
Ag	0.0416 ± 0.00790	N.D.	410 / 1200
As	0.647 ± 0.168	0.113 ± 0.0440	2.1 / 12
Ba	5.07 ± 0.108	1.17 ± 0.0629	120 / 130000
Cd	0.135 ± 0.022	0.121 ± 0.007	82 / 1700
Cr	4.84 ± 0.195	0.954 ± 0.0903	210 / 470
Pb	0.823 ± 0.0545	1.35 ± 0.0244	400 / 1400
Se	N.D.	N.D.	440 / 11000
V	3.00 ± 0.315	1.26 ± 0.105	69 / 10000
Zn	4.46 ± 1.36	14.95 ± 3.84	26000 / 630000

*All values are replicate average ± replicate standard deviation

Table 126: Default Parameters for the Calculation of Florida CTLs

Symbol	Definition	Receptor	Default
BW	body weight (kg)	Aggregate resident	51.9
		Child	16.8
		Adult/Worker	76.1
IR _o	ingestion rate, oral (mg/day)	Aggregate resident	120
		Child	200
		Adult/Worker	50
EF	exposure frequency (days/yr)	Aggregate resident	350
		Child	350
		Adult/Worker	250

Table 16 Continued: Default Parameters for the Calculation of Florida CTLs

Symbol	Definition	Receptor	Default
ED	exposure duration (years)	Aggregate resident	30
		Child	6
		Adult/Worker	25
SA	surface area exposed (cm ² /day)	Aggregate resident	4810
		Child	2960
		Adult/Worker	3500
AF	adherence factor (mg/cm ²)	Aggregate resident	0.1
		Child	0.2
		Adult/Worker	0.2
AT	averaging time (days) (carcinogens)	Aggregate resident	25550 (70 years)
	averaging time (days) (non-carcinogens)	Aggregate resident	10950 (30 years)
		Child	2190 (6 years)
		Adult/Worker	9125 (25 years)
IR _i	inhalation rate (m ³ /day)	Aggregate resident	12.2
		Child	8.1
		Adult/Worker	20
DA	dermal absorption (unitless) (organics)	-	0.01
	dermal absorption (unitless) (inorganics)	-	0.001
VF	volatilization factor (m ³ /kg)	-	chemical-specific
PEF	particulate emission factor (m ³ /kg)	-	1.24 x 10 ⁹
TR	target cancer risk (unitless)	-	10 ⁻⁶
THI	target hazard index (unitless)	-	1

Comparing the total trace metals concentration in the BFD, cement and aggregates shows that the BFD is in excess of SCTL (industrial and residential levels) with respect to arsenic alone. However, as can be seen, the cement collected from the Brooksville facility is in excess of SCTLs for vanadium (residential level), barium (residential level), and arsenic (residential and industrial levels). However, if one compares the total trace metals concentrations in the coarse and fine aggregate used in experiments to the concentrations seen in the BFD and cement, a mass balance calculation can be done for a concrete mix, see Figure 6 below. The mass balance for a concrete mix can be calculated using Equation 2 below.

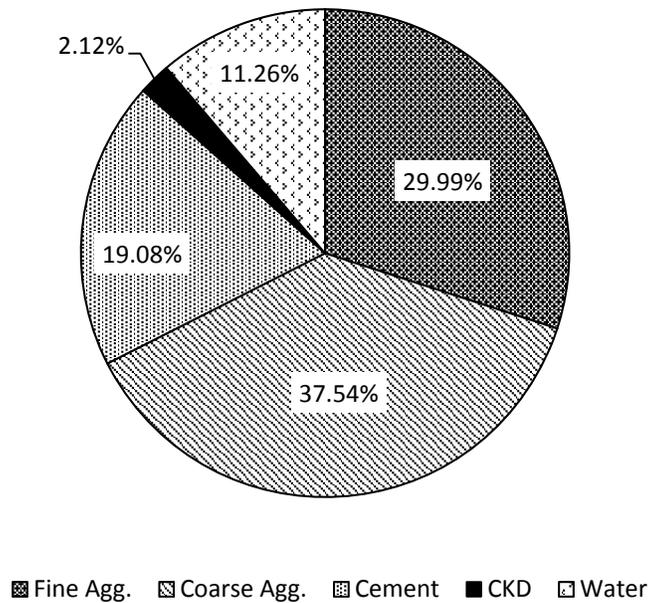


Figure 6: Experimental Concrete Mix with 10% Addition of BFD

$$C_{mix} = C_{CA}R_{CA} + C_{FA}R_{FA} + C_{CEM}R_{CEM} + C_{BFD}R_{BFD}$$

Equation 2: Mass Balance Equation for Concrete Mix

From this relationship, a set of mass balance calculations can be done to estimate total metals concentration in concrete mix designs that are typical. In general, coarse and fine aggregates constitute 70-85% of concrete with the remaining 30-15 % consisting of water and cementitious materials (Kosmatka et al, 2002). This guideline was used in determining the concrete mix design used in experiments for this study. The results of the mass balance calculations can be seen in Table 17.

**Table 137: Mass Balance of Trace Metals Associated with 70% Aggregate Design Mix
(Dry Weight Basis)**

Element	1% BFD Addition (mg/kg)	5% BFD Addition (mg/kg)	10% BFD Addition (mg/kg)	20% BFD Addition (mg/kg)	SCTL (mg/kg) Residential / Industrial
Ag	0.048	0.049	0.050	0.054	410 / 1200
As	10.86	10.60	10.28	9.63	2.1 / 12
Ba	42.37	41.40	40.18	37.75	120 / 130000
Cd	1.107	1.078	1.042	0.970	82 / 1700
Cr	13.35	13.10	12.79	12.16	210 / 470
Hg	0.020	0.032	0.046	0.075	3 / 17
Pb	19.79	19.47	19.07	18.28	400 / 1400
Se	0.010	0.049	0.098	0.195	440 / 11000
V	30.22	29.41	28.40	26.38	69 / 10000
Zn	139.73	135.18	129.50	118.14	26000 / 630000

*Brooksville cement and BFD collected in August 2012 used in calculations

As can be seen in Table 17, on a mass balance calculation basis it is unlikely that the concrete mix design would exceed SCTL for all metals except arsenic which still exceeds the residential SCTL. Another point of interest from the mass balance assessment is that as more BFD is added the concentrations of mercury and selenium increase since the BFD has much higher initial concentrations of mercury and selenium. Comparison of cement and BFD samples collected for this study, with those from the national surveys conducted in 1982 and 1992, shows that the total metals concentrations fall close to the expected ranges from these surveys, with the one exception being silver. For both the cement and BFD collected, the total silver measured was significantly lower than the 1982 and 1992 surveys.

5.2.3. Synthetic Precipitation Procedure

It should be stressed that the total metals analysis is not necessarily correlated with the leaching of metals. As previously mentioned in the literature review section, a 1992 PCA study showed that the TCLP leaching results showed no consistent correlation between total metals and

leachable metals. That is, samples containing the highest total metals concentration did not necessarily produce the highest TCLP results (PCA, 1992). The results of SPLP analysis can be seen in Table 18 for BFD and the cement collected at the participating facilities. The following elements were below the detection limit of the analytical instrument used; Ag, As, Cd, and Pb. Note that measurements for mercury are in units of ng/L. As can be seen in Table 18, the cement collected from the Brooksville facility was in excess of the Groundwater Cleanup Target Level (GCTL) for chromium, while the BFD collected was in excess of the GCTLs for selenium and vanadium.

Table 148: SPLP Results for BFD and Cement Samples

Element	Brooksville Cement (mg/L)	Baghouse Filter Dust Oct. 2011 (mg/L)	Baghouse Filter Dust Dec. 2011 (mg/L)	Baghouse Filter Dust Feb. 2012 (mg/L)	Baghouse Filter Dust Aug. 2012 (mg/L)	GCTL (mg/L)
Ag	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	0.1
As	< 0.0096*	< 0.0096*	< 0.0096*	< 0.0096*	< 0.0096*	0.01
Ba	1.22 ± 0.043	0.350 ± 0.009	0.630 ± 0.016	0.560 ± 0.031	0.219 ± 0.0068	2
Cd	< 0.0006*	< 0.0006*	< 0.0006*	< 0.0006*	< 0.0006*	0.005
Cr	0.278 ± 0.008	0.0348 ± 0.0005	0.0261 ± 0.0007	0.012 ± 0.0004	0.0286 ± 0.0004	0.1
Hg** (ng/L)	7.06 ± 0.778	677.0 ± 28.4	854.0 ± 10.1	1575.0 ± 7.03	1174.0 ± 4.37	2000
Pb	< 0.0085*	< 0.0085*	< 0.0085*	< 0.0085*	< 0.0085*	0.015
Se	< 0.0155*	0.0777 ± 0.0002	0.0859 ± 0.0022	0.0251 ± 0.0017	0.0666 ± 0.0012	0.05
V	< 0.0014	0.0832 ± 0.0017	0.215 ± 0.0047	0.146 ± 0.0023	0.145 ± 0.0042	0.049
Zn	0.057 ± 0.0025	0.0779 ± 0.0066	0.346 ± 0.1	0.5 ± 0.333	0.0356 ± 0.0037	5

* Below detection limit; **Note all mercury concentrations are in ng/L (ppt)

Groundwater Cleanup Target Levels (GCTLs) are standards set by the FDEP to protect human health from contaminants in groundwater. The GCTLs are either primary or secondary standards, based on the Florida Drinking Water Standards (Chapter 62-550 F.A.C.), or minimum criteria concerning health considerations and aesthetic factors but are not listed in Chapter 62-550

F.A.C. It is appropriate to compare SPLP results to Florida GCTLs and this is the motivation for the comparison made in Table 18. The default GCTLs can be calculated using the relationship seen in Equation 3 and default values found in Table 16.

$$GCTL(\mu g/L) = \frac{RfD_0 \times BW \times RSC \times CF}{WC}$$

Equation 3: Calculation for Default GCTLs

5.2.4. pH Dependent Leaching Procedure

As previously mentioned, it is important to go beyond the commonly utilized leaching protocols, i.e., TCLP or SPLP, and investigate leaching under pH dependent scenarios and weathering conditions. These conditions can be simulated by the pH dependence leaching test (EPA Method 1313) and MEP (EPA Method 1320) utilized in this study. The homogeneity of the BFD samples was recognized early on and full characterization under pH dependence and sequential extraction was only performed on BFD D sample. The results of the pH dependence test on BFD D can be seen in Figure 7.

As can be seen in Figure 7, metals leached in varying concentrations at different eluate pHs. However, only barium, vanadium, and selenium leached above GCTLs; barium leached above GCTL at a pH of 4 while selenium leached above its GCTL at pHs of 4 and 11 (natural pH) and vanadium leached above GCTL at all pH values. Silver, arsenic, cadmium, and lead were below detection limits of the instrument.

While it is unlikely that field conditions will persist at a pH of 4, the BFD did show that it leached above GCTL for selenium at the BFD's natural pH, and vanadium leached above GCTLs in all cases, both of which are realistic leaching scenarios. Additionally, it should be noted that the

BFD is not a product that is directly used by FDOT and is only used in its incorporated form in cement products; however, this analysis does provide baseline leachability under key environmental parameters. A final note should be made to the fact that for Method 1313 the L/S ratio decreased from 20 for the SPLP to 10 for the Method 1313 leaching protocol. This fact could help explain the differences in the magnitude of release of analytes.

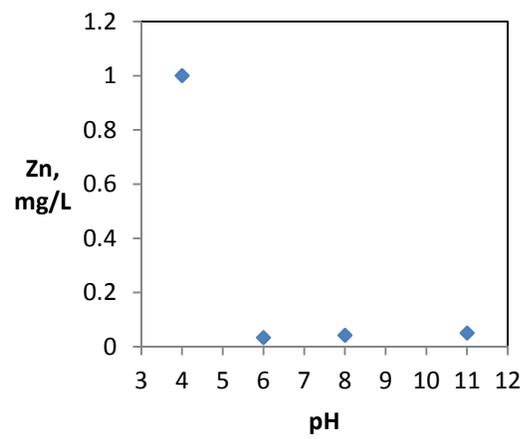
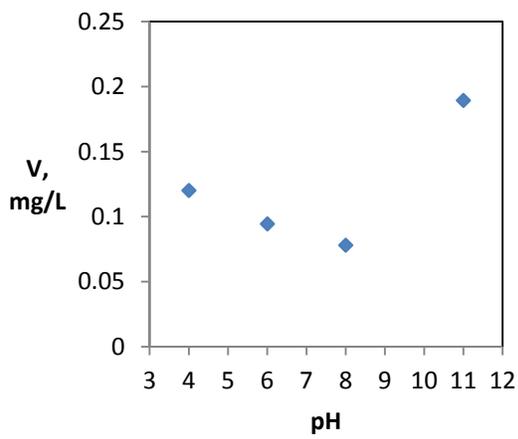
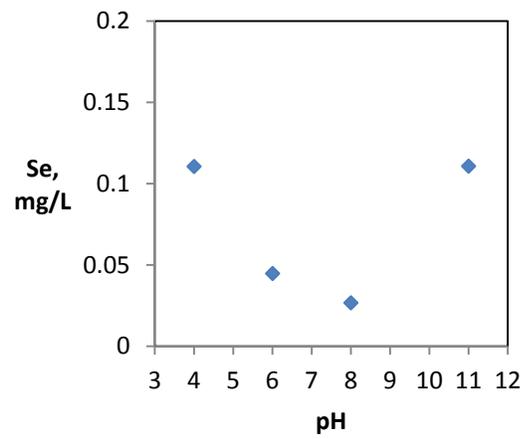
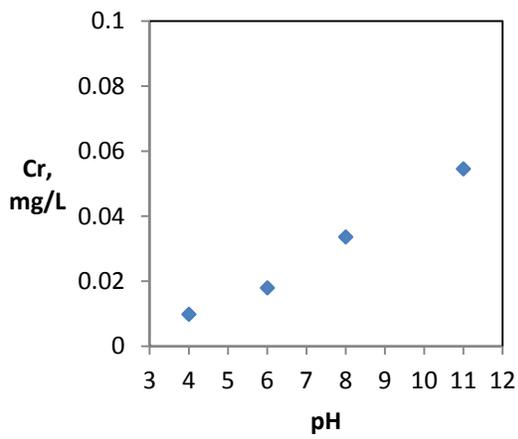
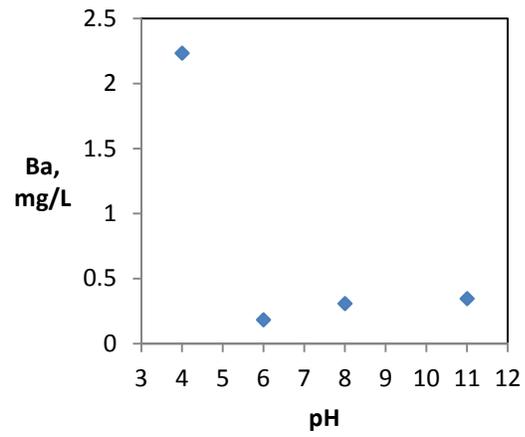
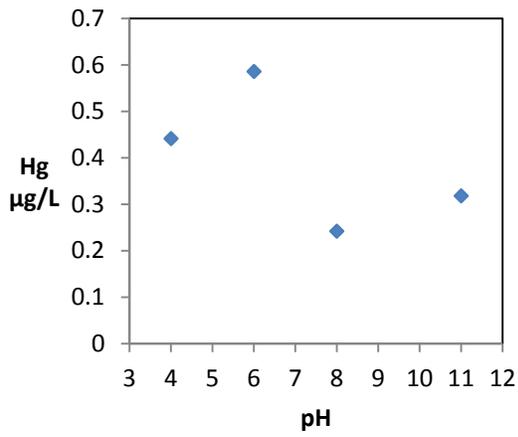


Figure 7: pH Dependent Leaching Test Results on BFD

5.2.5. Results of the Multiple Extraction Procedure

The MEP can account for solid-liquid phase equilibrium (if it exists) and weathering of solid samples from exposure to multiple extractions of acidic leachate. The results of the MEP on the BFD D can be seen in Figure 8. As can be seen, arsenic, selenium, and vanadium exceed GCTLs; with silver, cadmium, chromium, and lead below the detection limit of the instrument. After each sequential extraction, concentrations in the extraction fluid decreased with the exception of arsenic; which was initially below the detection limit but after two sequential extractions the concentration of arsenic was recorded above the detection limit and the GCTL. This result can be explained by the weathering of the solid phase by acid attack from the extraction fluid allowing additional bound arsenic to be released.

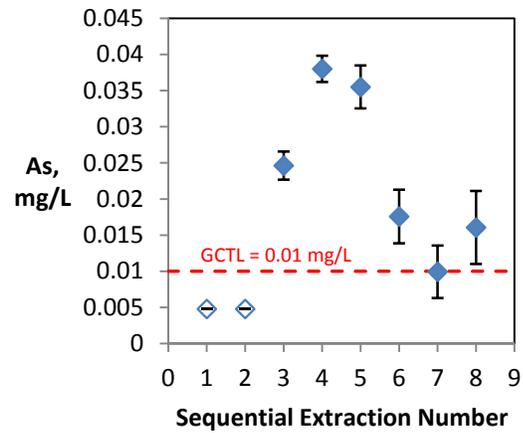
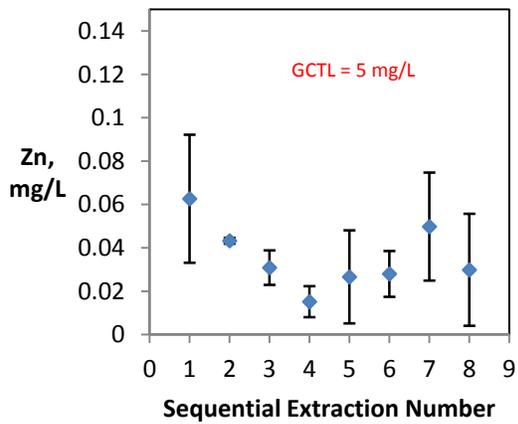
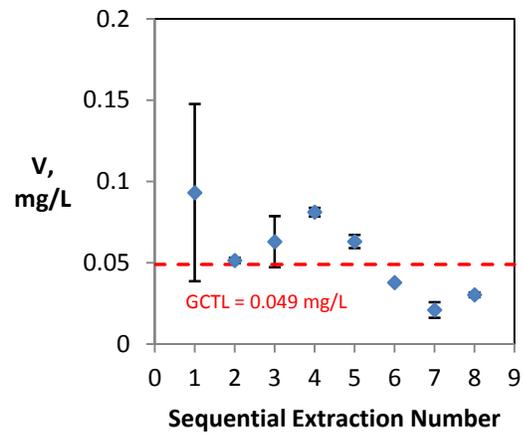
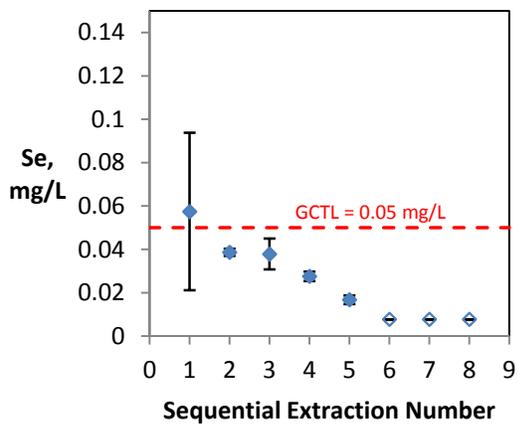
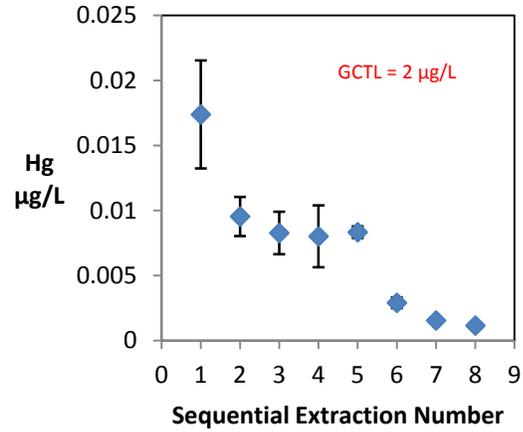
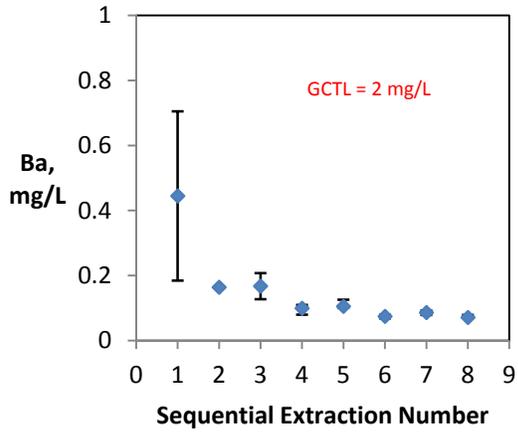


Figure 8: Multiple Extraction Procedure Results on BFD

6. Laboratory Experiments for Characterizing Release during Handling

Laboratory experiments were carried out to examine the potential impact of BFD and trace metals identified in the characterization of the BFD and cement. Airborne exposure was assessed using closed vessel head space testing while the BFD or cement was in its powder state. Cement specimens of different BFD concentrations were placed in glass vessels. The specimens were exposed to different environmental conditions such as temperature and relative humidity to emulate conditions that may be encountered during storage. Gas samples were collected and analyzed following appropriate NIOSH (National Institute of Occupational Safety and Health) standard methods. Aqueous leachability of cement specimens of different BFD concentrations were also subjected to SPLP to provide an understanding of how aqueous environmental conditions resulting from cement impacts BFD leachability.

6.1. Methodology for Laboratory Leaching Experiments

One can see from the mass balance assessment performed in Section 5.2 of this report, the contribution of trace metals from the BFD to a cement/BFD blend will be minimal due to the small mass allowed to be added as an inorganic process addition under current standards, i.e., 5% by mass. Therefore, with this data in mind, it was considered that the effect of the addition of BFD to cement's leachability would be minor and could be fully characterized by comparison of SPLP results to those of cement and BFD alone. Furthermore, it was decided to use BFD D sample since it was fully characterized in Chapter 5 of this report.

Blends of cement and BFD, collected from the Brooksville facility, were made at 5% and 10% by mass. The decision to limit the maximum addition of BFD to 10% for experiments was due to the finding from the National Cooperative Highway Research Program (NCHRP) Report

607. According to the NCHRP study, the use of greater than 8% by mass of BFD would exclude cement from use, per ASTM C-150, due to Loss-On-Ignition (LOI) and insoluble residue limitations of BFD. Please see Section 2.4 for additional details.

6.1.1. Laboratory Leaching Experiments on BFD and Cement Blends

The results from the SPLP analysis of the BFD/cement blends can be seen in Table 19 below. It can be seen that for the BFD/cement blends only chromium exceeds the GCTLs; it is also likely that the chromium released in the SPLP results is largely due to the contribution from the higher initial chromium concentration of the cement and not the BFD, see Table 18. Additionally, with the exception of selenium, mercury and barium, all concentrations of trace metals are lower for the blends than the cement. These results support the conclusion that, at the additions of BFD currently allowed by ASTM standards, the amended cement represents no increased risk to worker or environmental health as compared to cement alone.

Table 19: SPLP Results from BFD/Cement Blends at 5% and 10% by Mass

Element	Cement A (mg/L)	5% BFD Blend (mg/L)	10% BFD Blend (mg/L)	BFD D (mg/L)	GCTL (mg/L)
Ag	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	0.1
As	< 0.0096*	< 0.0096*	< 0.0096*	< 0.0096*	0.01
Ba	1.22 ± 0.043	1.47 ± 0.0159	1.60 ± 0.0428	0.219 ± 0.0068	2
Cd	< 0.0006*	< 0.0006*	< 0.0006*	< 0.0006*	0.005
Cr	0.278 ± 0.008	0.172 ± 0.047	0.149 ± 0.0213	0.0286 ± 0.0004	0.1
Hg (ng/L)	7.06 ± 0.778	7.22 ± 0.375	8.94 ± 0.368	1174.0 ± 4.37	2000
Pb	< 0.0085*	< 0.0085*	< 0.0085*	< 0.0085*	0.015
Se	< 0.0155*	0.0253 ± 0.00886	0.0232 ± 0.0032	0.0666 ± 0.0012	0.05
V	< 0.0014	< 0.0014	< 0.0014	0.145 ± 0.0042	0.049
Zn	0.057 ± 0.0025	0.0552 ± 0.00022	0.0586 ± 0.0036	0.0356 ± 0.0037	5

6.2. Laboratory Air Exposure Experiments Methodology

Real-time measurement of vapor phase Hg release from the cement and BFD in the powder phase was performed in a small enclosed cylindrical tube. The conceptual illustration of the system is shown in Figure 9. Gas flows from two air cylinders were mixed at a chamber to create a total flow of 1~2 liter per minute (Lpm). The ratio of flow rates between water saturated air and dry air was used to control the relative humidity (RH), which was monitored by a hygrometer inside the mixing chamber. The gas stream then went through the small enclosed cylindrical tube with heating tape wrapped around. It was used to test vapor phase Hg release from the BFD, cement, and BFD/Cement mixture under a given flow rate, RH, and temperature. Thermometers mounted in the cylindrical tube were used to monitor the temperature. An initial mass of 500 g of BFD, cement, and 5% BFD/95% cement was weighed and distributed on the bottom of the cylindrical tube shown in Figure 9. Two flow rates (1 and 2 Lpm) and four relative humidities (0%, 25%, 75%, 100%) were employed. The temperature in the tube was either room temperature (~23 °C) or elevated by the heating tape (~80 °C). This experiment was designed to identify the potential effect of environmental parameters on storing BFD and cement in an enclosed environment prior to handling. In addition to 500 g of BFD, 100 g of BFD was also tested, which a similar surface area had exposed to the air flow in the cylindrical tube (Figure 9).

The gas stream carrying any released vapor phase Hg was sent through a Hg transformation unit (Figure 10) developed in a previous study (Li and Wu, 2006). By switching to 10% potassium chloride (KCl) solution, the SI-Hg was absorbed in the impinger, while only NSI-Hg passed the unit. On the other channel, SI-Hg was reduced to Hg⁰ by 10% Tin (II) chloride (SnCl₂) solution. In this channel, all the vapor phase Hg passed through the unit. The measured difference of these two channels was the amount of SI-Hg. The 10% sodium hydroxide

(NaOH) solution in the unit removed any acidic gas, and a condenser reduced the moisture content in the gas stream. Both were to prevent potential damage to the Hg analyzer. A real-time Hg analyzer (Ohio Lumex RA915+, Twinsburg, OH) monitored the Hg concentration in the gas stream, with a resolution of 2 ng/m³. The Hg analyzer was calibrated using a mercury permeation device (VICI Metrics Dynacal, Poulosbo, WA) which can release Hg⁰ vapor at a constant rate. The analyzer was zeroed using ultrahigh purity nitrogen cylinder gas prior to each test.

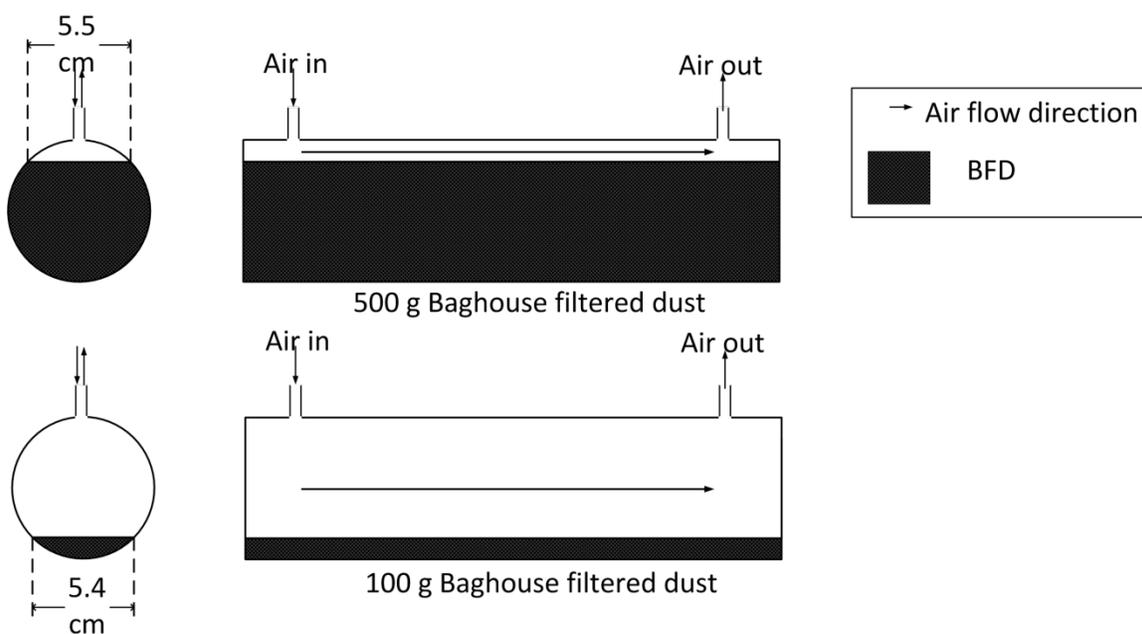


Figure 9: Cross Sectional and Lateral View of the Cylindrical Tube Loaded with BFD.

After passing the Zeeman atomic absorption spectrometer in the real-time Hg analyzer, the gas stream then entered the Ontario Hydro (OH) trap. Since SI-Hg was either removed or reduced by the Hg transformation unit, the original OH sampling train was modified to skip the 10% KCl solution impingers. Two solutions of 100 mL of hydrogen peroxide (H₂O₂) and 100 mL potassium permanganate (KMnO₄) and acids were used to collect Hg⁰. The 10% KCl solution was added to the KMnO₄ trap solution after the sampling to remove the SO₂ produced from the reaction. The

OH trap was diluted and immediately analyzed by a cold vapor - atomic fluorescence spectrometer (Tekran 2600, Toronto, ON, Canada). The spectrometer with a detection limit of 1 pg/mL was capable of detecting trace amount of Hg in the OH traps. The system was used for the first 24 hours due to two reasons: the data record length limit of the real-time Hg analyzer, and instability of Hg in the OH trap while feeding continuous air (Laudal and Heidt, 1997).

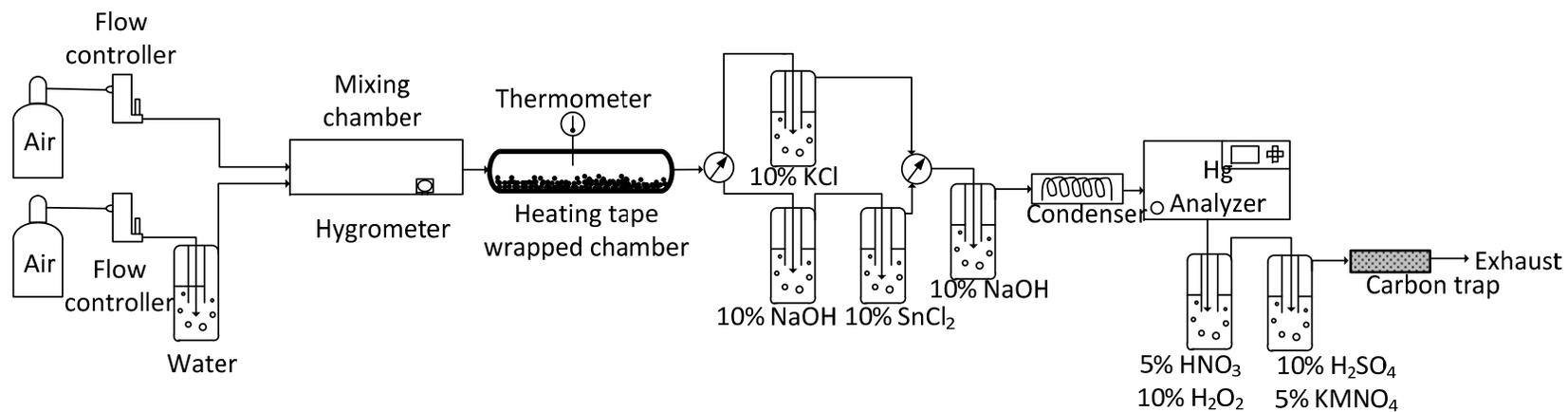


Figure 10: Schematic Diagram of the Laboratory Air Exposure System

6.2.1. Laboratory Air Exposure Experiments on BFD and Cement Blends

Figure 11 shows the total Hg concentration in the gas stream that is released from pure BFD samples as a function of time in 24 hours. Generally, significant Hg release was detectable only in the first 2 hours after the experiment was started; the concentration was at the detection limit of the background level ($2 \text{ ng/m}^3 \text{ s}$) afterward. High RH (relative humidity) and temperature facilitated the Hg release in the earlier stage, while the gas flow rates did not affect the release pattern. High temperature increased the diffusion activity while lowering the adsorption affinity between Hg and the dust. Water in moist air may compete with Hg on adsorption surface (Li et al., 2011). The results of SI-Hg are not seen in Figure 11, due to the fact that early detectable release was mostly NSI-Hg, i.e., switching the channel in the Hg-transformation unit gave an identical result. The Hg analyzer could not detect any significant release from the cement and the 5% BFD/95% cement mixture under all experimental conditions. This was due to the lower total Hg concentration in these materials.

On average, $1.6 \pm 0.4\%$ of the Hg in the 500 g BFD was released to the vapor phase, while almost all released Hg was in NSI-Hg phase ($p < 0.05$). The amount of total Hg released from the BFD and consequently captured by OH trap in different experimental conditions is listed in Table 20. There was no statistical correlation found between total Hg released with any environmental parameter. This indicated the total Hg released in 24 hours was independent of gas flow rate, temperature, and RH. However, the amounts of Hg released from 500 g and from 100 g BFD were identical, regardless the mass difference in total Hg. It was likely due to their similar area of air exchange (Figure 9). This suggests the release was limited to the top layer, and the corresponding effective thickness was determined to be around 0.12 cm. This indicates that the release of Hg from BFD can be correlated to the degree of contact between air and dust.

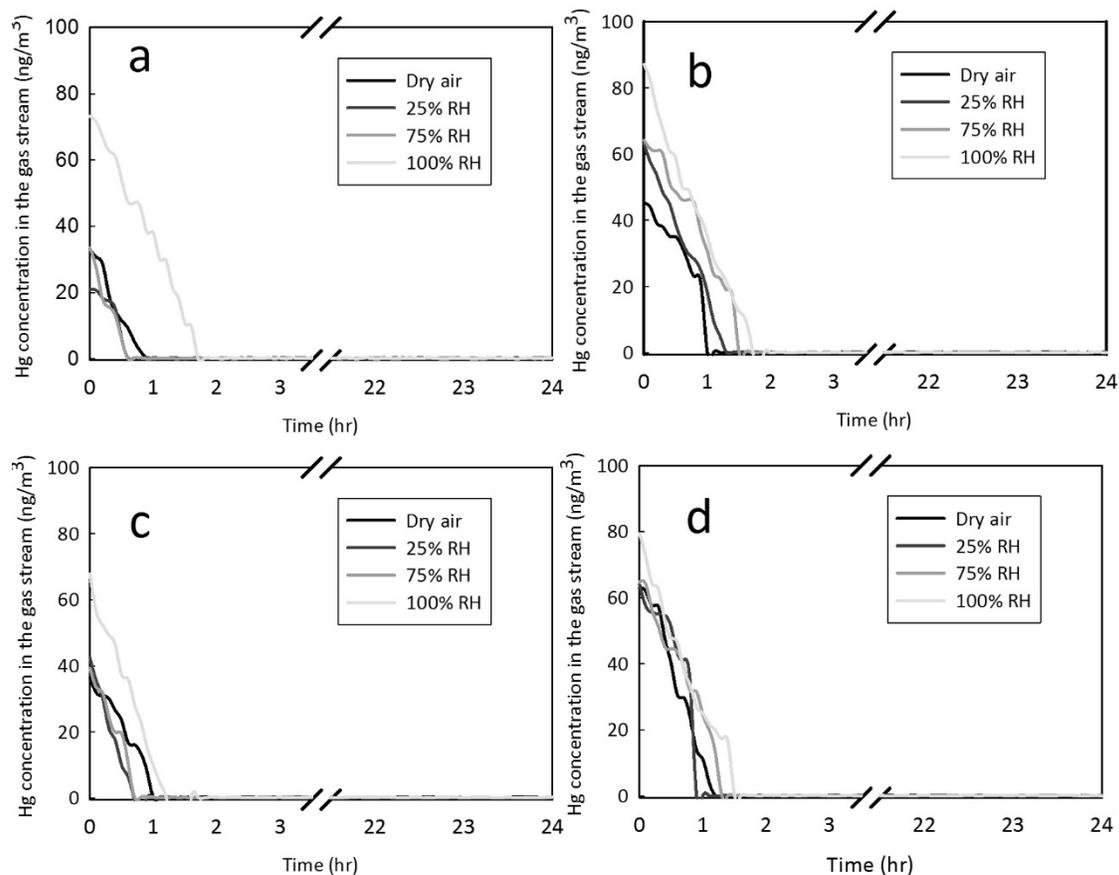


Figure 11: Hg Released from BFD as a Function of Time

(a) 1 Lpm gas flow rate and room temperature; (b) 1 Lpm gas flow rate and elevated temperature; (c) 2 Lpm gas flow rate and room temperature; (d) 2 Lpm gas flow rate and elevated temperature.

The amount of Hg released from the cement was below the detection limit at most environmental conditions, due to the low Hg concentration in the cement. Similarly, the 5% BFD/95% cement mixture did not show any detectable vapor phase Hg released. The higher concentration of Hg and porous structure of the BFD likely contributed to the higher vapor phase Hg released and captured by the OH traps.

Table 150: Total Hg (μg) Released from BFD under Different Experimental Conditions

Amount of BFD	Air flow rate	Temperature	Dry air	25% RH	75% RH	100% RH
500 g	1 Lpm	23 °C	18 (2.4%)*	9 (1.2%)	10 (1.3%)	15 (2.0%)
		80 °C	11 (1.5%)	5 (1.3%)	13 (1.7%)	7 (0.9%)
	2 Lpm	23 °C	13 (1.7%)	18 (2.4%)	14 (1.8%)	13 (1.7%)
		80 °C	11 (1.5%)	11(1.5%)	11 (1.5%)	13 (1.7%)
100 g	2 Lpm	80 °C				13 (8.7%)

* The percentage in the parenthesis denotes total Hg released versus total Hg in the 500 g Feb, 2012 BFD.

7. Bench-Scale Experiments for Release from Concrete

7.1. Bench-Scale Experimental Methodology

Bench scale experiments were conducted in a chamber containing concrete manufactured using cement with 5% and 10%, by mass, additions of BFD at given air exchange rate. This was to emulate the conditions that may be encountered in the handling and use of such materials for two exposure scenarios, i.e., the plastic state and hardened state. Potential metal mobility via water contact was assessed with leaching tests on concrete in the hardened state.

Leaching of materials from the hardened state was assessed using several approaches. First, monolithic sections of concrete created at the different test blends were exposed to water following standardized leaching protocols, i.e., EPA Method 1315, for examining pollutant mobility from monolithic stabilized wastes. Second, sections of the concrete were crushed and tested using standardized leaching tests to assess potential mercury and trace metals mobility. The size-reduced concrete was sieved such that the fraction passing a No. 4 sieve was used in further analysis; this fraction represented ~73% of the total mass of reduced concrete. The sieved, size-reduced fraction was used in the SPLP, pH dependent leaching test, and the MEP described in Section 5.1 of this report.

7.2. Monolith Leaching Test Methodology

Concrete samples were mixed and placed in rectangular molds. Samples and molds were wrapped in plastic sheeting to ensure a high humidity environment for the initial 24-hour curing period. The concrete sample sets created can be seen in Table 21. All constituent amounts were kept constant with the exception of the BFD addition. The cementitious content, water to cementitious content ratio, and coarse and fine aggregate additions were kept constant for all sets

at 2.05 kg, 53%, 3.63 kg, and 2.90 kg, respectively. After the concrete samples had been cured for 24 hours, they were removed from the molds and were placed in 54 gallon HDPE sealed containers. Samples were then ready for extraction by EPA Method 1315: Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test.

Table 161: Concrete Sets Manufactured

Sample Identification	BFD Addition, By Mass
Set A	10%
Set B	5%
Control	0%

EPA Method 1315 is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic material, under diffusion-controlled release conditions, as a function of leaching time. The method comprises leaching of continuously water-saturated monolithic material in an eluent-filled tank with periodic renewal of the leaching solution, refer to Figure 12. Samples are contacted with deionized water at a specified Liquid to Surface Area (LSa) ratio, i.e., 9 mL/cm². The leaching solution is exchanged with new deionized water at nine pre-determined intervals; see Table 22 below (EPA, 2009).

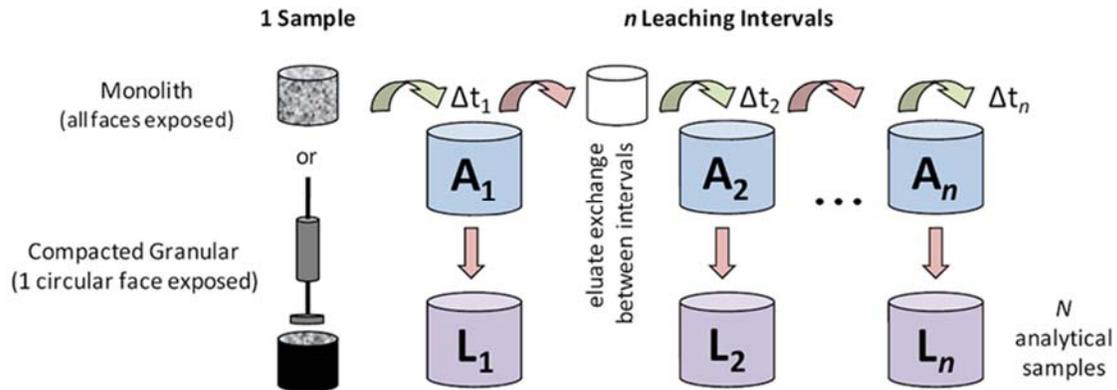


Figure 12: Schematic of Monolithic Leaching Procedure Leaching Intervals

Note: Reprinted from “EPA Draft Method 1315” by United States Environmental Protection Agency, 2009.

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Table 172: Monolith Leaching Test Exchange Intervals

Interval Duration (hr.)	Interval Duration (days)	Cumulative Leaching Time (days)
2.0 ± 0.25	-	0.08
23.0 ± 0.5	-	1.0
23.0 ± 0.5	-	2.0
-	5.0 ± 0.1	7.0
-	7.0 ± 0.1	14.0
-	14.0 ± 0.1	28.0
-	14.0 ± 0.1	42.0
-	7.0 ± 0.1	49.0
-	14.0 ± 0.1	63.0

7.3. Bench-Scale Air Exposure Experimental Methodology

Real-time measurement of vapor phase Hg release from the concrete during mixing and curing was performed in a sealed glove box (Plas Lab 818-GB, Lansing, MI) with an interior volume of 489 L. The conceptual illustration of the bench scale system is shown in Figure 13. Gas

flows from two air cylinders were mixed at a chamber to create a total flow of 1~2 liter per minute (Lpm). The ratio of flow rates between water saturated air and dry air was used to control the relative humidity (RH), which was monitored by a hygrometer inside the mixing chamber. The gas stream then went through the glove box to simulate concrete mixing and curing. Thermometers mounted inside the concrete were used to monitor the temperature during the early stage of mixing.

The gas stream carrying any released vapor phase Hg was sent through a mercury transformation unit (Figure 13) similar to the laboratory air exposure experiment system. A real-time Hg analyzer (Ohio Lumex RA915+, Twinsburg, OH) monitored the Hg concentration in the gas stream, with a detection limit of 2 ng /m³ s. The vapor phase Hg passed the Zeeman atomic absorption spectrometer in the real-time Hg analyzer, and then entered the OH trap.

The bench system was used for the first 24 hours due to two reasons: the data record length limit of the real-time Hg analyzer, and instability of Hg in the OH trap while feeding continuous air (Laudal and Heidt, 1997). A long-term head-space experiment was therefore performed using the glove box as a supplement to the 24 hour study. The solidified concrete was put into the box without air exchange. After a predetermined period, vacuum was used to extract 20 L air from the glove box through the OH trap. The concentration in the OH trap was used to calculate the Hg vapor released from the solidified concrete.

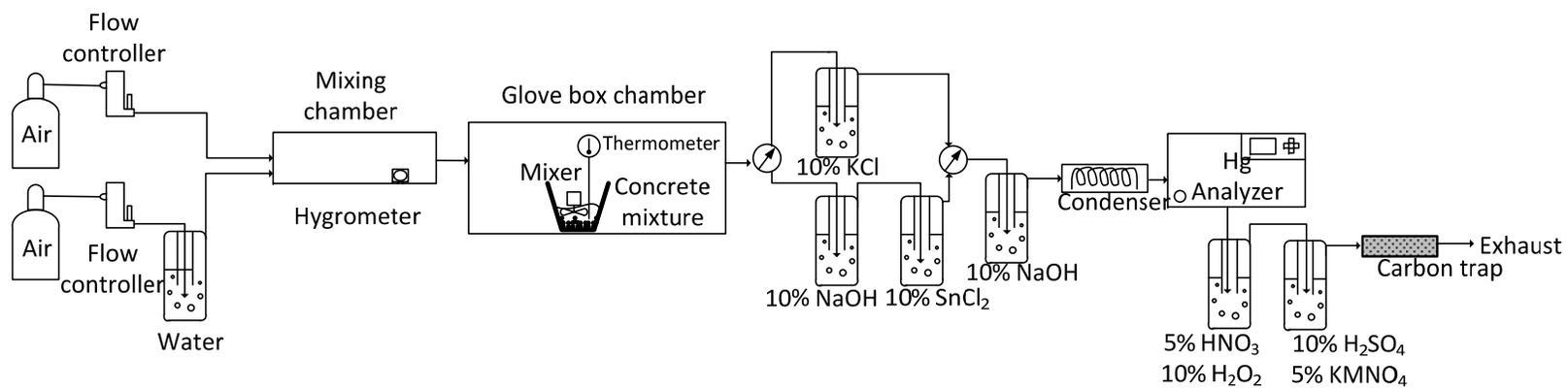


Figure 13: Schematic Diagram of the Bench-Scale System

The Feb, 2012 BFD sample was used in all concrete mixes prepared in the air exposure experiments. The mixing ratio of different constituents followed the design mix in Section 7.2 of this report. It should be noted that, the gas stream's RH was fixed at 50% as opposed to previous experiments in this report for simulation of BFD or cement storage. During concrete mixing and curing, large amounts of water were supplied to the mixture and the humidity was already at constant 100%. The air exchange rate of the glove box was set at 1.5 Lpm. The mixing of BFD, cement, water, and aggregates was done using a drill attachment mixer and lasted approximately 3 minutes, and then the concrete remained undisturbed and became completely solidified in 8 hours. The concrete processing was repeated five times using 5% BFD/95% cement mixture and 10% BFD/90% cement mixture, respectively. After 24 hours of curing, one of the concrete samples from each mixing ratio was subjected to a 7-day head-space study with OH trap.

7.4. Results of Bench-Scale Experiments

7.4.1. Bench-Scale Leaching Experimental Results

The release of the constituent trace metals in the monolith leaching test was minimal. Indeed, only barium and zinc were above the detection limit of the ICP-AES, while the mercury concentration, determined via CV-AFS, in the extractions was not significantly different than that found in deionized water, i.e., < 0.2 ng/L. Due to this fact, limited data is available from the study; the mass release rate of barium as a function of time can be seen in Figure 14 below. It should also be noted that the concentrations in the graph of Figure 14 have been normalized with respect to the LSa ratio of the monolith. Additionally, the interval release of barium was two orders of magnitude below the GCTL for all extractions. The release of zinc was recorded only during the first 48 hours of leaching after which the concentration of zinc in the extraction fluid fell below

the detection limit of the ICP-AES. This result leads to the conclusion that zinc was released in an initial wash-off period and did not release via diffusion. The minimal release of all trace metals leads to the conclusion that these constituents are encapsulated and immobilized in the concrete matrix.

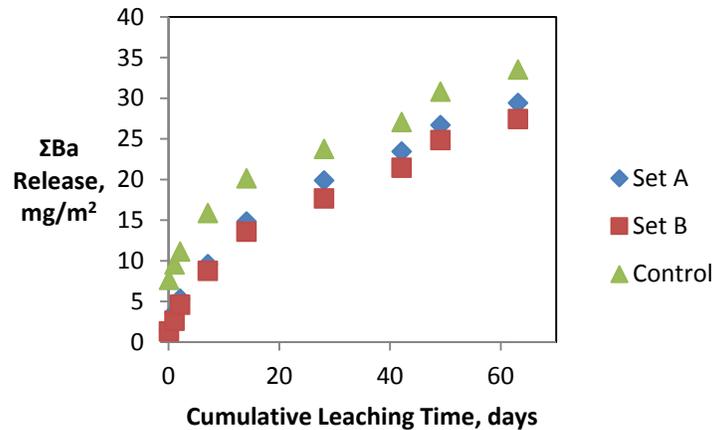


Figure 14: Cumulative Aqueous-Phase Release of Barium from Concrete Monoliths

The results of the SPLP on the crushed concrete samples can be seen in Table 23 below. As can be seen in the table, all elemental concentrations were lower than those SPLP results seen in the BFD D and Cement A used in the concrete mix. Additionally, all releases of analytes were well below the GCTLs for those elements. The results of the SPLP on the crushed concrete and the results from the monolith leaching tests strongly support the conclusion that little to no effect can be seen on the leachability of metals due to the addition of BFD in the amounts currently allowed. Furthermore, it can be concluded, as suspected, that there is little concern of metals leachability from concrete in general in this study.

Table 183: SPLP Results for Crushed Concrete Samples

Element	Control (mg/L)	Set A (mg/L)	Set B (mg/L)	GCTL (mg/L)
Ag	< 0.0025*	< 0.0025*	< 0.0025*	0.1
As	< 0.0096*	< 0.0096*	< 0.0096*	0.01
Ba	0.718 ± 0.0327	0.848 ± 0.0191	0.798 ± 0.0145	2
Cd	< 0.0006*	< 0.0006*	< 0.0006*	0.005
Cr	0.0205 ± 0.0005	0.0238 ± 0.0003	0.0226 ± 0.0007	0.1
Hg (ng/L)	36.0 ± 6.9	48.0 ± 5.9	32.0 ± 2.2	2000
Pb	< 0.0085*	< 0.0085*	< 0.0085*	0.015
Se	< 0.0155*	< 0.0155*	< 0.0155*	0.05
V	< 0.0014	< 0.0014	< 0.0014	0.049
Zn	0.0318 ± 0.0064	0.0288 ± 0.0079	0.0321 ± 0.0073	5

The results from the multiple extraction procedure (MEP, Method 1320) can be seen in Figures 15-18 below. Only barium, chromium, zinc, and vanadium were above the detection limits of the ICP-AES. With the exception of chromium, all analytes were below the GCTL. After the first extraction, the level of chromium in the leachate fell below the GCTL. As can be observed from the graphs, chromium and barium followed a predictable pattern of decreasing release after each extraction likely due to depletion of the initial barium and chromium found in the concrete samples. The release of zinc was variable and showed no discernible pattern. Release of vanadium exhibited an interesting trend, with increasing release over several extractions. It is likely that the solubility of vanadium was controlled by the dissolution of its complex with other minerals or compounds.

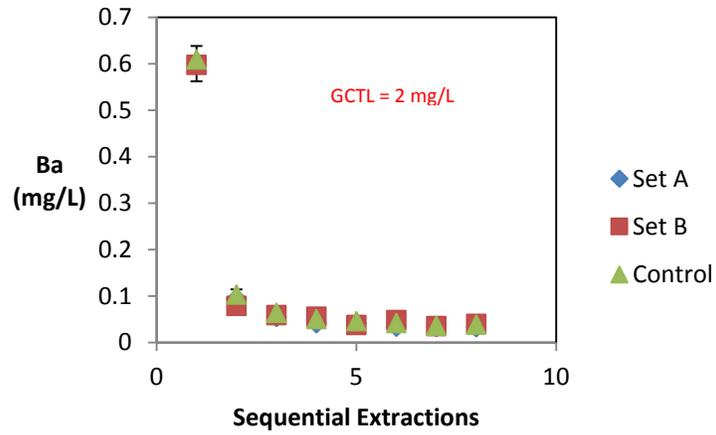


Figure 15: Multiple Extraction Release of Barium from Concrete

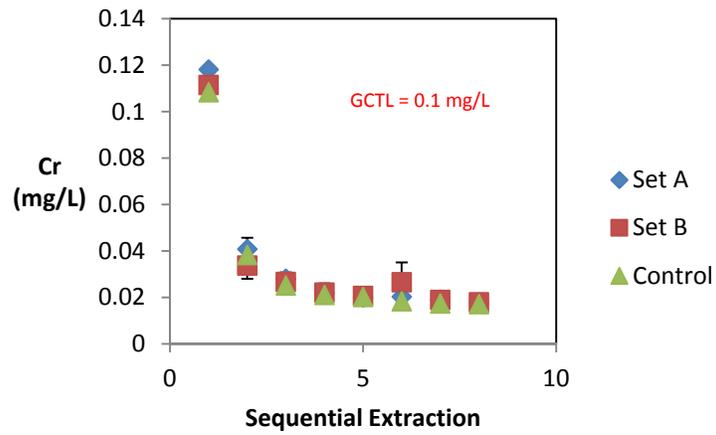


Figure 16: Multiple Extraction Release of Chromium from Concrete

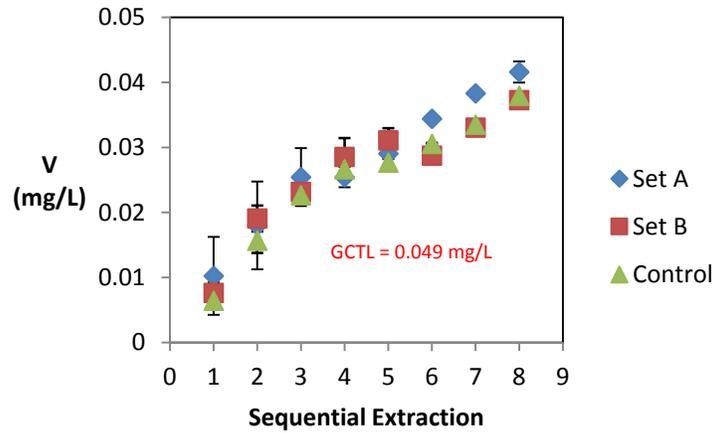


Figure 17: Multiple Extraction Release of Vanadium from Concrete

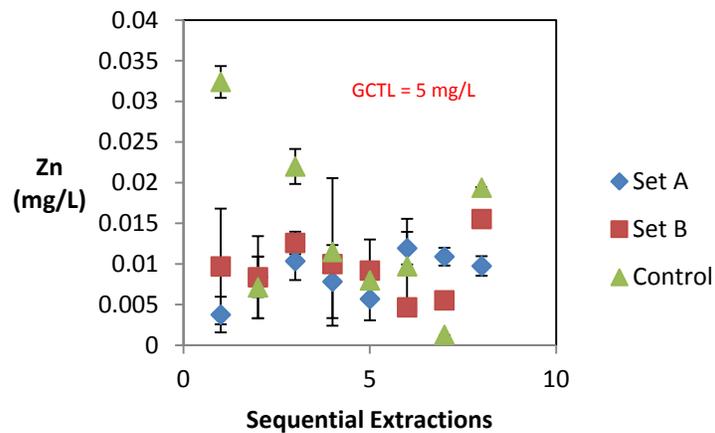


Figure 18: Multiple Extraction Release of Zinc from Concrete

The results from the pH variable leaching test (Method 1313) can be seen in Figures 19-27. All analytes were measured at concentration above their respective GCTL in the lower pH range (2 to 4) with the exception of mercury and selenium. This should not be cause for concern since these low pH regimes are unlikely to occur in almost all scenarios found in field conditions. A more likely leaching scenario would occur in the 6 to 12 regime. The only analyte to leach above GCTL in this more reasonable pH range was barium. It should be noted, that the

barium leached at much higher levels from the cement in the SPLP analysis seen in Table 19 above. This leads to the conclusion that the leaching of barium seen in Figure 20 is largely due to the presence of cement in the concrete mix and not the BFD.

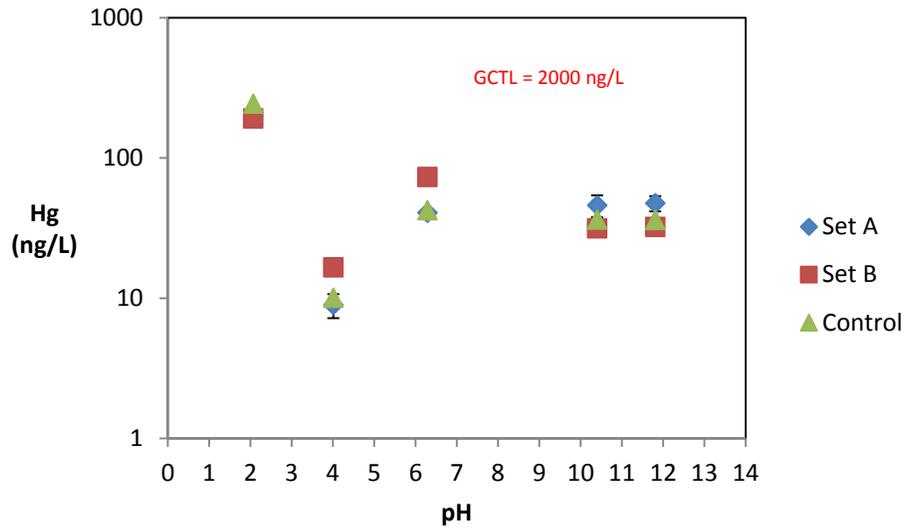


Figure 19: pH Variable Leaching of Mercury from Concrete

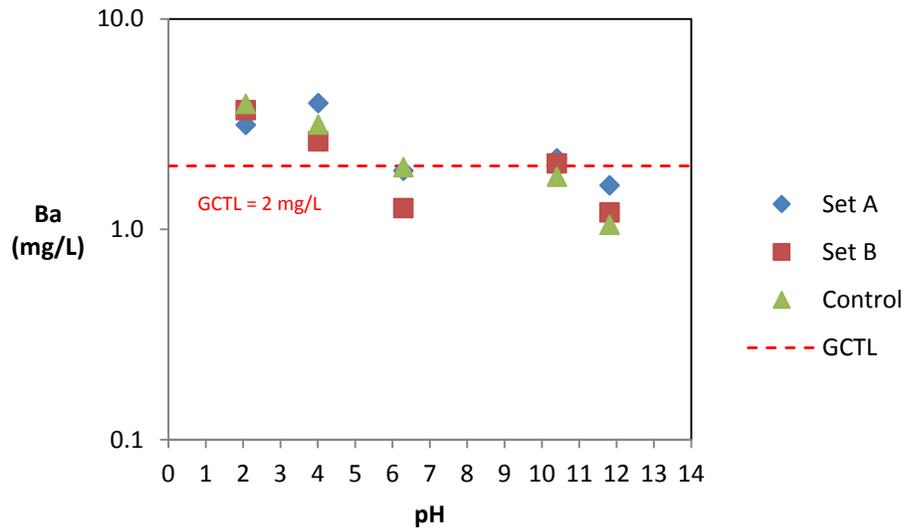


Figure 20: pH Variable Leaching of Barium from Concrete

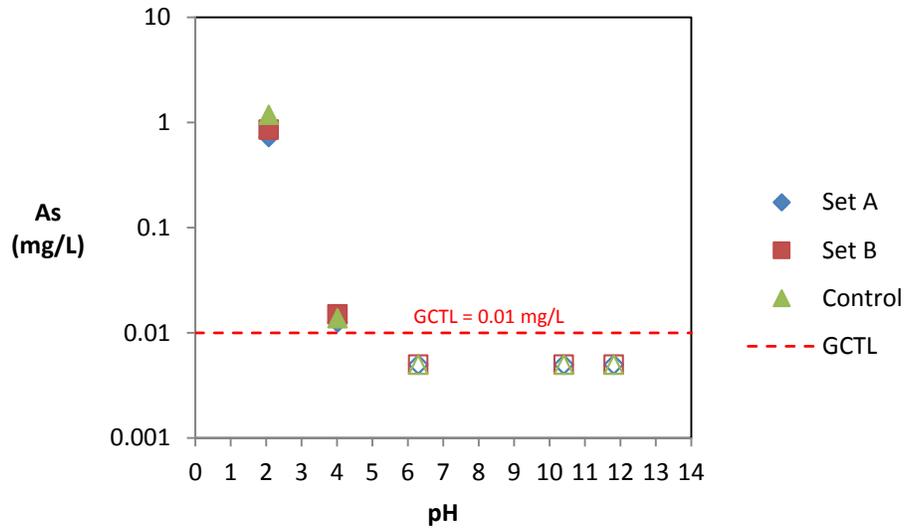


Figure 21: pH Variable Leaching of Arsenic from Concrete

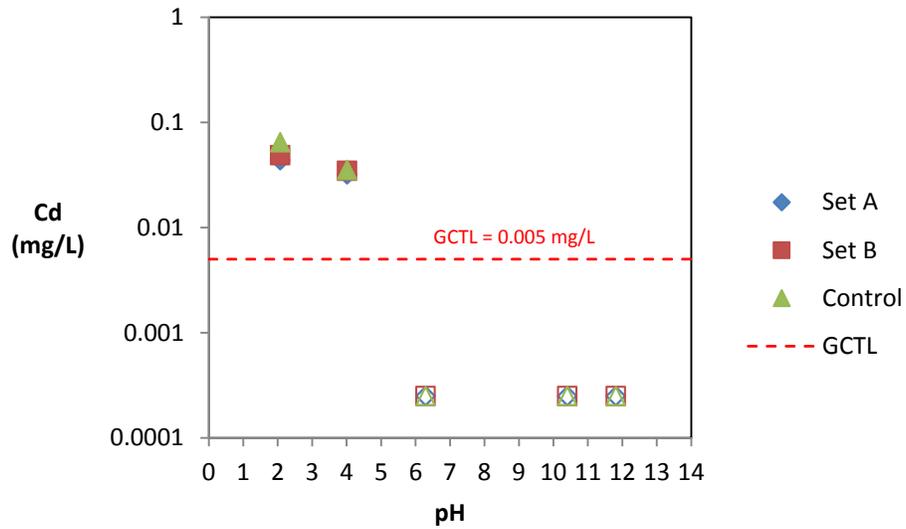


Figure 22: pH Variable Leaching of Cadmium from Concrete

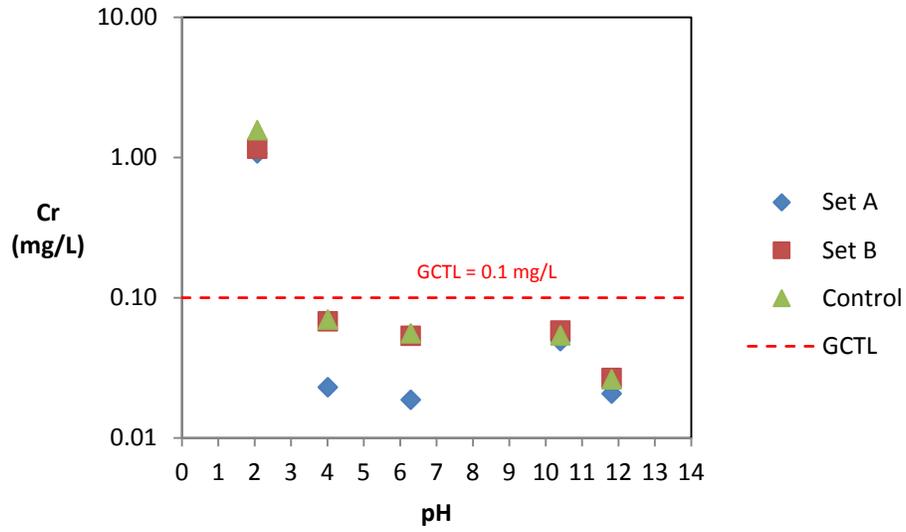


Figure 23: pH Variable Leaching of Chromium from Concrete

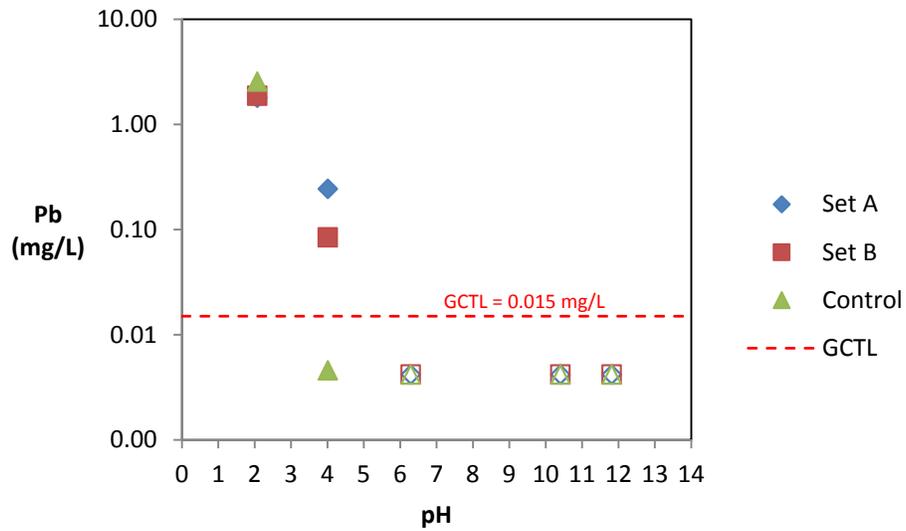


Figure 24: pH Variable Leaching of Lead from Concrete

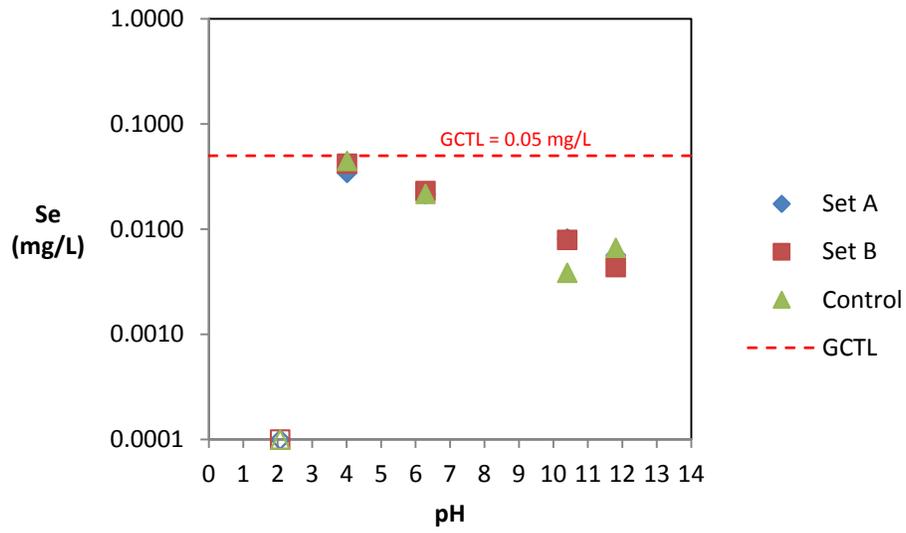


Figure 25: pH Variable Leaching of Selenium from Concrete

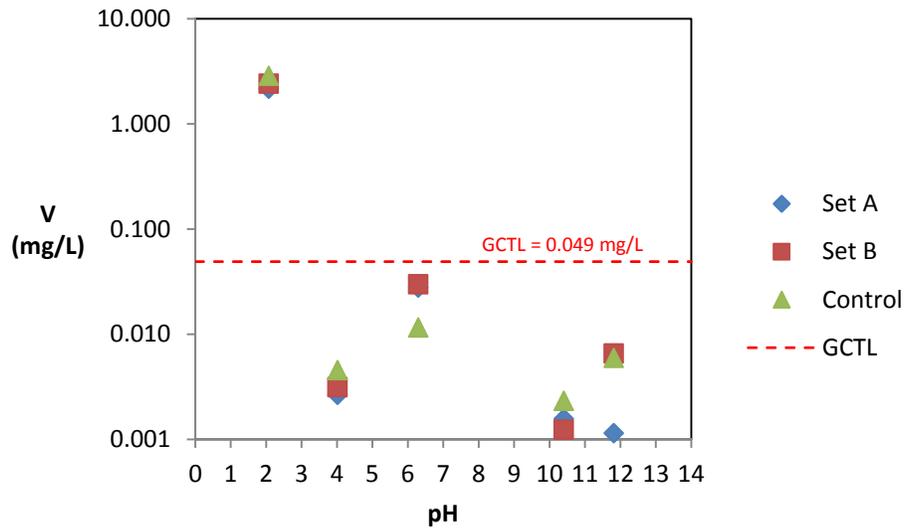


Figure 26: pH Variable Leaching of Vanadium from Concrete

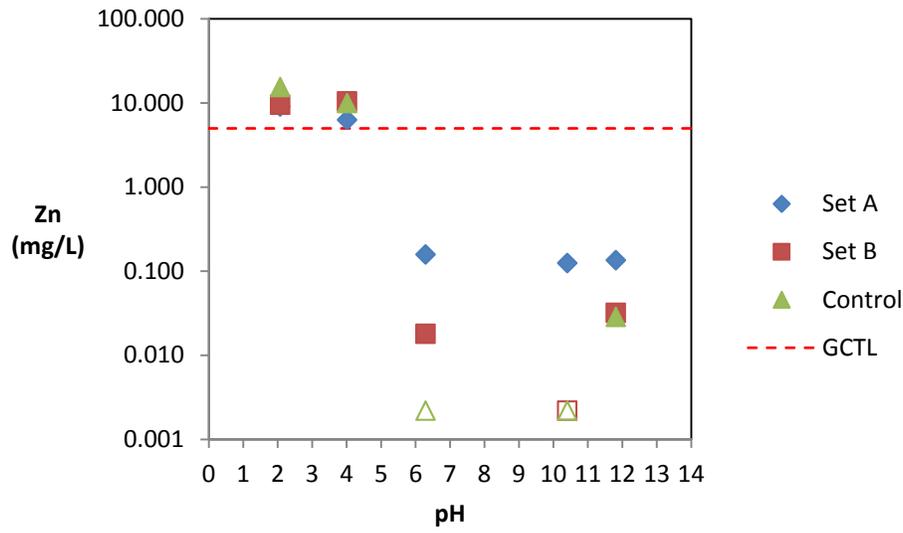


Figure 27: pH Variable Leaching of Zinc from Concrete

7.4.2. Air Exposure Bench-Scale Experimental Results

The release of Hg from mixing and curing cement was more complicated than the BFD and the cement in the laboratory air exposure experiments. The mixing process involved several minutes of high speed blending. Considerable amount of water was added into the mixture during this process. However, the temperature was raised only about 11 °C during the mixing, which could be considered to be negligible. In this study, the BFD and the cement contributed 1-2% and 18-20% of the mass to the concrete mixture, respectively. The rest of the concrete mixture was coarse and fine aggregates, which contained much less Hg. The total mass of concrete constituents was 4.8 kg for each batch of experiment and the material contained about 0.15~0.22 mg of total Hg.

During the mixing and curing of the 5% BFD/95% cement and the 10% BFD/90% cement, there was no detectable Hg release activity from the real-time monitoring. This may be due to the

lower total Hg content in the concrete mixture (3.4 times less) than the 100% BFD. Total Hg released from the 10% BFD/90% cement mixture captured by the OH trap was $0.8 \pm 0.09 \mu\text{g}$, higher than $0.7 \pm 0.07 \mu\text{g}$ from the 5% BFD/95% cement mixture ($p < 0.05$). Again, all total Hg released was in NSI-Hg phase ($p < 0.05$). The total Hg released from the concrete mixing was about 0.4~0.5% of the total Hg in the concrete constituents. This was higher than a 2005 study using coal fly ash-added cement, which recorded a release of 0.1% of Hg (Golightly et al., 2005). There was no detectable Hg in the OH trap for the 7-day head-space study on solidified concrete. It indicated that the majority of Hg release occurred in the first 24 hour.

8. Summary and Conclusions

8.1. Evaluation of Potential Concerns from Mercury Volatilization

During concrete curing and after being solidified, less than 0.5% of Hg was released in the vapor phase. Assuming 5% of the cement is replaced with the BFD containing 1 mg/kg of Hg, about 0.05 mg Hg per ton of concrete could be released. In a typical scenario of workers placing and finishing the concrete floor (about 16.5 ton concrete) in an enclosed room (6.72 m in length, 5 m in width, 3 m in height), the maximum ceiling concentration of Hg is less than 0.01 mg/m³, if no ventilation at all. This is much lower than the permissible exposure limit (PEL) of 0.1 mg Hg/m³ ceiling concentration set by the Occupational Safety and Health Administration (OSHA). (OSHA, 2006) The Hg will be quickly diluted by ambient air in an outdoor concrete curing scenario, and should cause no violation to the PEL.

From the experimental results, storing BFD in an open area contributed the highest Hg loss up to 21% (Section 6.2). The Hg loss is related to the degree of contact between air and BFD, i.e., area of air exchange surface. Hence, it is recommended that cement kiln plant operators do not store unused BFD in an open area to avoid additional Hg emission from the plant.

The finish mill, where clinker is ground and BFD can be added to the final product, is constantly rotating. Thus, it creates good mixing between air and BFD. All the volatile Hg (NSI-Hg) can be possibly released from rotating and feeding air. However, there will be likely no oxidized Hg (SI-Hg) loss due to the low temperature profile (~240 °F/116 °C) of the finish mill.

Based on mass balance of 1.0 mg/kg Hg and one million short tons of clinker (containing 5% BFD) production annually, there could be up to 30 lb of Hg transferred from the kiln system to the finish mill system and potentially emitted from the finish mill, assuming all of 30% NSI-

Hg is released and not captured in an air pollution control device for Hg. This 30 percent value is discussed in the experimental Section 6.2. Based on these experiments, it is recommended that cement plant operators continue to direct flue gas from the finish mill through a low temperature air pollution control device that can capture Hg to limit potential Hg emission to the ambient. The worst case scenario is that if the 73 million tons of cement US produced in 2012 (USGS, 2013) all contained 5% BFD without Hg-removal device attached. This would potentially create 2190 lb additional Hg emission; for comparison, the total Hg emission in 2008 from the cement industry estimated by EPA was 9658.2 lb. The research team contacted several industrial people knowledgeable of dust shuttling in the cement industry, and they expected no major mercury emission from the finish mill. They anticipated only oxidized mercury in BFD and the temperature at the finish mill would not be high enough to vaporize oxidized mercury. Several factors may be responsible for the differences between their opinions and our worst-case estimate, such as the halogen content or carbon content in the fly ash or the combustion condition of the studied facilities. The total Hg concentration in the concrete constituents may also vary by orders of magnitude from different geological location, hence affecting the released amount. Nevertheless, it should be noted that the industry people who were consulted have neither mercury speciation data in BFD nor mercury emission data from finish mill, whilst our experimental data are the first-time mercury speciation data albeit limited to one facility only. Hence, it will be valuable future work to directly sample stack emission from the finish mill to determine the true mercury emission level, coupled with data of mercury speciation in BFD from multiple facilities to explain the emission pattern. Understanding the mechanism how Hg is trapped in the concrete will provide knowledge how to avoid potential release from concrete in the long term. It should be emphasized that the worst-case estimate sets the maximum emission

level and serves as a preliminary screening. It should not be interpreted as a proof against the dust shuttling practice, as the true emission level is likely to be lower and can only be accurately determined through field measurement.

8.2. Assessment of Potential Concerns from Product Leaching and End-of-Life Management

The total (mg/kg) and leachable (mg/L) concentration of trace inorganic chemicals in concrete manufactured with BFD were evaluated to assess the potential for increased environmental risk associated with the use of the BFD. When the total concentrations of elements in the BFD were assessed as part of a risk screening evaluation, they were compared to concentrations both in cement and in a final concrete product, and to a set of risk-based regulatory thresholds normally used to assess contaminated soils. While most BFD elements were of similar composition to cement, mercury was greater in concentration in the BFD. For perspective, however, the BFD mercury concentration was below Florida's risk-based threshold for residential clean soil. The only element in the BFD that was consistently above the clean-soil threshold was arsenic, and this was elevated in the cement as well. The experimental results from the samples collected in this study, along with an estimated final concrete composition based on individual measurements, suggest that the final concrete product made from similar materials should not be expected to differ dramatically in overall composition from that of concrete made without BFD.

The potential of chemical mobility (i.e., leaching when in contact with water) from a concrete product manufactured with BFD was examined using different testing procedures. In batch leaching tests, leachate from BFD did exceed risk-based thresholds for several elements, but leachate from the concrete product resulted in no concentrations above such thresholds. Furthermore, when leaching on monolithic concrete forms were examined over time in submerged

conditions, the elements of concern were rarely detectable and no potential risk of exceeding regulatory thresholds were noted. The results of these different assays do not suggest that leaching of inorganic elements from concrete products manufactured with BFD of similar composition as tested in this study and at similar mix designs will pose additional risk beyond any normal (without BFD) concrete production use.

9. Recommendations

Based on the previous results, following recommendations were made:

- (1) The results of the laboratory experiment indicated that the addition of BFD (of characteristics similar to those in the samples tested in this study) to cement does not pose added risk to human health and the environment as part of typical FDOT applications.
- (2) Mass balance estimates suggest that BFD with greater Hg concentrations (up to 10 ppm) than those encountered in this study should also not pose added worker exposure risk in typical FDOT applications.
- (3) The following studies are essential for further understanding of the potential issues and may be accomplished if more research resources become available:
 - a. Field sampling of Hg concentration and speciation from the stack of cement finish mills;
 - b. Collection and analysis of more varieties of BFD samples from different cement facilities;
 - c. The effects of a wider range of concrete mixes should be explored, as well, as the effects concrete admixtures, i.e., air-entrainment agents, might have on leaching of trace elements and the efficacy of those admixtures used in conjunction with BFD additions;
 - d. If more cement facilities continue to investigate the use of alternative fuels in conjunction with dust shuttling; the BFD should be characterized to ensure no significant changes occur in its material properties and elemental composition.

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Appendix

Fate of Heavy Metals in Cement and the Recycling of Baghouse Dust

To address potential concern associated with the use of baghouse dust, the Florida Department of Transportation is working with the Hinkley Center for Solid and Hazardous Waste Management and the University of Florida to carry out a study on this subject. Baghouse is commonly used downstream of the cement kiln to collect dust particles produced in the process, and baghouse dust is then used as an admixture in the cement production process. Mercury and other heavy metals from raw material, fuels, and coal fly ash in cement production can be concentrated in the baghouse dust, and hence may pose hazards to environmental and occupational safety by emission into the air, water, and soil. This project will provide a detailed and in-depth examination of the impact of mercury and other heavy metals in baghouse dust to be added to cement.

Your response to the questions below will assist researchers with their review. A final report which will include the responses to this survey will be prepared and made available to those participating in this survey. We are grateful for your time and your commitment to the safety of our workers.

1. Have you had complaints, issues, or questions about mercury and other heavy metals as it relates to cement? (Yes/No/Unknown) If so, from what industries, or sources?
2. Is baghouse dust recycled in the cement production process in your state? (Yes/No/Unknown) If yes, is there any regulation regarding how much baghouse dust is allowable? For example, up to 5% is allowable in Florida.
3. Is the release of mercury and other heavy metals from cement and concrete a concern in your state? (Yes/No/Unknown)
4. Does your agency enforce or recommend any specifications regarding mercury or other trace metals in cements? (Yes/No/Unknown) If yes, could you give some brief information or code citation?
5. What actions (research, regulations, monitoring, etc.) have been taken in your state to address the issue of mercury and other metals in cement?

We would greatly appreciate any additional information related, or the contact information of someone in your state who is experienced with these issues.

Name:

Agency:

Title: