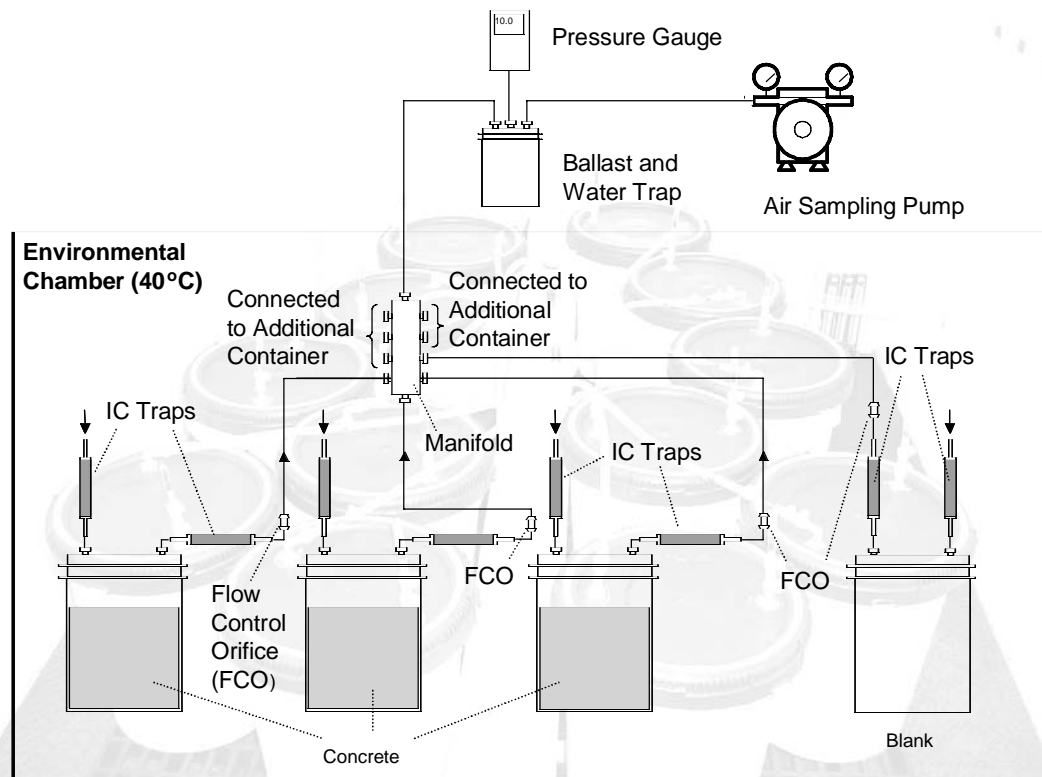


Mercury Emissions from Curing Concretes that Contain Fly Ash and Activated Carbon Sorbents

Technical Report



Mercury Emissions from Curing Concretes that Contain Fly Ash and Activated Carbon Sorbents

1012696

Final Report, September 2006

EPRI Project Manager
K. Ladwig

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

The Ohio State University

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2006 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

The Ohio State University
Department of Civil and Environmental Engineering and Geodetic Science
470 Hitchcock Hall, 2070 Neil Avenue
Columbus, OH 43210

Principal Investigators

C. Cheng
D. Golightly
H. Walker
L. Weavers
W. Wolfe

This report describes research sponsored by the Electric Power Research Institute (EPRI).

The report is a corporate document that should be cited in the literature in the following manner:

Mercury Emissions from Curing Concretes that Contain Fly Ash and Activated Carbon Sorbents.
EPRI, Palo Alto, CA: 2006 1012696.

REPORT SUMMARY

This report presents new laboratory data on the release of mercury from concrete containing fly ash and powdered activated carbon sorbents used to capture mercury. The concretes studied in this project were made with fly ashes from lignite and subbituminous coal, including fly ashes containing powdered activated carbon (PAC). Minute quantities of mercury were emitted from five concretes during the standard 28-day curing process and throughout an additional 28 days of curing for two of these concretes. Generally lower mercury emissions were found with increasing fly ash organic carbon content.

Background

Previous work funded by EPRI examined the release of mercury from concrete containing a single Class F fly ash and mercury sorbent material. These studies demonstrated that minute quantities of mercury are released from fly-ash concretes during the curing process, but more than 99% of the mercury was retained in concrete made with the Class F ash and in concrete that also included mercury-laden PAC. The previous studies examined both air curing of conventional concrete as well as steam curing of aerated cellular concrete. However, the previous work did not examine how the type of fly ash and the related coal source may influence the release of mercury from concrete containing fly ash or systematically evaluate release rates beyond the initial curing times.

Objectives

To investigate the release of mercury during the curing of concretes made from fly ashes derived from lignite and subbituminous coal, with and without PAC injection for mercury capture.

Approach

The project team used a purge-and-trap approach for collection of mercury emissions from curing concrete. Controlled airflow above freshly prepared concrete transported purged volatile mercury species from the headspace air enclosed with the concrete onto an iodated carbon trap. The team tested all samples over a standard 28-day curing period and tested two samples over an extended 56-day curing period. The team conducted three types of sampling experiments: 1) empty containers to evaluate the emission baseline level (blank) for mercury in the experiments, 2) ordinary portland cement (OPC) concrete to establish an emission baseline for mercury that originated from the mix components other than fly ash and PAC, and 3) concrete with 55% of the portland cement replaced by fly ash. In these latter experiments, the team tested four different fly ashes. One fly ash was derived from combustion of lignite coal, and three were derived from combustion of subbituminous coal. Two of the subbituminous fly ash samples also contained PAC for mercury control.

Results

Only very small quantities of mercury were released during the initial 28-day curing period of the concrete containing fly ash and fly ash with mercury sorbent material. Release of mercury from these concretes was less than 0.31% of the total quantity of mercury present from all components of the mixture. The observed emissions of mercury demonstrated a dependency on the presence of sorbent, but mercury concentrations in the concrete and the type of coal burned were poor predictors of mercury release.

Dependence of mercury release on the organic carbon content of the fly ash was notable. The percent mercury released from concrete decreased as the organic carbon content of the fly ash increased. The fly ash with the highest organic carbon content tested, the NRT1019 fly ash, demonstrated the lowest percent mercury release. The fly ash with the lowest carbon content, CCS1, demonstrated the greatest percent mercury release. There is a very strong linear correlation between mercury release and organic carbon content ($r^2=0.99$) for the fly ashes not containing activated carbon, although only three data points were available for this analysis. Lower emissions of mercury were observed for the two ashes containing activated carbon sorbent than would be expected based on the correlation with organic carbon suggesting that the PAC more tightly binds the mercury as compared to carbon originating from unburned coal.

For two fly ashes, air sampling over the concrete samples was conducted for a 56-day period. This extended sampling revealed that mercury release diminished with time. Extrapolating the reduction in mercury release beyond 8 weeks of curing, we estimate that at total curing times of 10.4 weeks for MER032 and 12.3 weeks for MER0357 concrete, mercury emission would decrease to the level observed for OPC concrete at the end of 4 weeks. The decrease in mercury release corresponds to an expected loss of porosity for the concrete and loss of water to hydration reactions by the components of cement.

EPRI Perspective

Replacement of portland cement in concrete is the largest single beneficial use of fly ash, accounting for about 14 million tons of the fly ash produced in 2004. Changes in fly ash characteristics due to increased capture of mercury represent a potential threat to that market. The results presented in this report, as well as previously reported results, indicate that mercury emissions from concrete containing fly ash and powdered activated carbon are insignificant, accounting for less than 0.5 percent of the total mercury content of the concrete in all cases. These data show that higher mercury concentrations in fly ash containing PAC should not inhibit the use of the fly ash in concrete.

Keywords

Fly Ash
Powdered Activated Carbon
Mercury
Concrete
Ash Use

ABSTRACT

One method for reduction of mercury emissions from coal-fired utility boilers is injection of chemically modified powdered activated carbon sorbents into hot flue gas streams and subsequent capture of the mercury-containing sorbent along with fly ash. The trapping of mercury by sorbents boosts the net quantity of mercury in the resulting composite fly ash-sorbent, thus increasing the total mercury content in the final coal combustion product. Because this fly ash-sorbent may be incorporated into various types of concrete, an understanding of the fate of mercury in these concretes is needed to support future applications of the new fly ash-sorbent products.

Possible differences in gaseous mercury releases from curing fly-ash concretes were investigated by collection and measurement of mercury from concretes that contained different fly ashes and carbon-based sorbents. Air above curing concretes was sampled by iodated carbon traps to collect gas-phase mercury over the standard 28-day curing period. Air sampling was extended for an additional 28 days for two selected concretes. All experiments were performed in a laboratory environment and were designed to provide estimates of upper limits on gaseous mercury release from curing concretes that contain fly ash and sorbent material.

The observed emissions of mercury for the complete curing process demonstrated a dependency on mercury concentrations in the concrete, the type of coal burned, and the presence of sorbent. Release of mercury from these concretes was less than 0.31% of the total quantity of mercury present from all sources. The dependence of mercury release on the organic carbon content of the fly ash was particularly notable. Lower emissions of mercury were observed for the ash containing activated carbon sorbent than would be expected based on the correlation with organic carbon, suggesting that the brominated powdered activated carbon more tightly binds the mercury as compared to unburned carbon in the ash. During the extended curing tests, mercury release slowly diminished with time. The decrease in mercury emission corresponds to an expected loss of porosity for the concrete and loss of water to hydration reactions by the components of cement.

ACKNOWLEDGMENTS

This study was funded by the Electric Power Research Institute (EPRI), Palo Alto, California, and done in collaboration with the Department of Civil and Environmental Engineering and Geodetic Science (CEEGS) at The Ohio State University, Columbus, Ohio.

The authors gratefully acknowledge Mr. Kenneth Ladwig, Project Manager, EPRI, for his guidance and interest in this project.

Also, we are greatly indebted to Ms. Jennifer Parker, *Studio Geochimica*, Seattle, WA, for determinations of mercury concentrations for all iodated carbon traps, fly ashes, and concrete ingredients used in this project.

Finally, our sincere thanks go to Mr. Kevin Jewell, OARDC, OSU, Wooster, OH, for measurements of total carbon and inorganic carbon in fly ashes and other concrete components.

CONTENTS

1 INTRODUCTION	1-1
Background	1-1
Program Objectives.....	1-1
General Approach	1-1
Report Organization	1-2
2 TEST METHODS.....	2-1
Concrete Components	2-1
Fly Ash Composition	2-2
Loss on Ignition and Total Organic Carbon.....	2-3
Mercury Content for Each Concrete Ingredient.....	2-3
Mercury Emission Experiments.....	2-3
Concrete Preparation	2-4
Purge and Trap Sampling.....	2-6
Controls for Experiments	2-8
Determination of Mercury in IC Traps.....	2-8
3 RESULTS AND DISCUSSION	3-1
Fly Ash Characterization	3-1
Organic Carbon Content of Concrete Ingredients.....	3-2
Mercury in Concrete Ingredients	3-2
Mercury Emission Experiments.....	3-4
Mercury Emission during Standard 28-day Air Curing	3-4
Mercury Release during Extended Sampling	3-4
Quality Assurance for Mercury Measurements	3-5
Discussion	3-6
Mercury Emission from Ordinary Portland Cement Concrete	3-6
Mercury Emission from Concretes Containing Fly Ash	3-6

Significance of Fly Ash Organic Carbon Content	3-7
Long-Term Trends in Mercury Release	3-10
4 CONCLUSIONS AND RECOMMENDATIONS	4-1
Conclusions.....	4-1
Recommendations	4-1
5 REFERENCES	5-1
A INSTRUMENTS, EQUIPMENT, AND SUPPLIES	A-1
B FLY ASH COMPOSITION DATA	B-1
C MERCURY COLLECTED IN INDIVIDUAL TRAPS.....	C-1

LIST OF FIGURES

Figure 2-1 Dry components mixed by tumbling.	2-5
Figure 2-2 Schematic diagram of the sampling setup.....	2-5
Figure 2-3 Air sampling of multiple containers of concrete in the environmental chamber.....	2-6
Figure 2-4 Air pump, water trap, and pressure gauge.	2-7
Figure 3-1 Mercury release and mercury content of the different fly ash concretes	3-8
Figure 3-2 Mercury release as a function of fly ash organic carbon content.....	3-9
Figure 3-3 Mercury release rate during extended curing	3-10

LIST OF TABLES

Table 2-1 Background Information on Fly Ashes Used in This Study.....	2-2
Table 2-2 Concrete Formulations for Individual 20-kg Batches	2-4
Table 3-1 Silica, Iron Oxide, Alumina, and Sulfur Trioxide in Fly Ashes (%)	3-1
Table 3-2 LOI, Organic Carbon, and Inorganic Carbon in Fly Ashes.....	3-2
Table 3-3 Carbon Content of Cement, Coarse Aggregate, and Sand.	3-2
Table 3-4 Mercury Concentration in Concrete Ingredients	3-3
Table 3-5 Estimated Mercury in 20-kg Batches of Concrete	3-3
Table 3-6 Mercury Collected on Iodated-Carbon Traps over 28-day Curing Period.....	3-4
Table 3-7 Mercury in Air above Select Fly-Ash Concretes during Extended Curing (n=3) ^a	3-5
Table 3-8 Mercury Recoveries for Spikes and NIST Standard Reference Material.....	3-5
Table 3-9 Sample Blanks: Total Mercury Collected on Individual IC Traps.....	3-6

1

INTRODUCTION

Background

Previous EPRI-sponsored studies in our laboratories have documented the release of sub-microgram quantities of mercury from kilogram masses of curing concretes that contain fly ash generated by the combustion of bituminous coal (Cheng *et al.* 2002-2005; Golightly *et al.* 2005). These studies utilized a single, Class F fly ash and activated carbon sorbent exposed to mercury under laboratory conditions. Less than 0.1% of the total mercury contained in these concretes was released over the initial curing period, suggesting that nearly all of the mercury was retained in the concrete. The investigation summarized herein focuses on differences in rates of mercury release that reflect both the source of the fly ash and the types of sorbents that accompany the fly ash.

Lignite and subbituminous coals, sources of fly ashes used in the current study, produce fly ashes that contain levels of calcium oxide somewhat higher than concentrations observed for most anthracite and bituminous coals. High-calcium fly ashes, as components of concretes, are reported to produce concretes that exhibit good durability, that is, reduced permeability and chloride diffusivity, relative to equivalent-strength ordinary portland cement (OPC) concretes. Furthermore, these concretes offer excellent freeze-thaw resistance and de-icer salt scaling performance (Thomas *et al.* 1999). The potential differences in the physical and chemical properties of these concretes, compared to the Class F fly ash studied previously, necessitate the study of mercury release from these materials.

Program Objectives

The goal of this research was to determine whether differences in releases of mercury occur during the curing process for concretes that contain dissimilar coal fly ashes and carbon sorbents. The mercury release rates were compared with emphasis on the fly ash source. Our hypothesis was that the controlled curing and large fractions of fly ash (55% replacement of cement) in an unchanging concrete mixture (constant matrix for various fly ashes) produce demonstrably different releases of mercury that depend on the fly ash and associated sorbent.

General Approach

Gaseous mercury release was monitored for concrete samples contained within closed vessels continuously purged by mercury-free air in a temperature-controlled environment. These purge-and-trap experiments were configured to enable precise estimates of the gaseous mercury release

from dry curing concretes that contain fly ash and associated sorbent materials. All aspects of this investigation were performed within a laboratory setting.

Experiments were conducted to observe mercury release from: 1) an empty sampling container to establish the emission baseline level of mercury (blank) for each experiment, 2) an OPC concrete that contained no fly ash to establish a mercury emission level for the basic concrete mixture, and 3) concretes for which fly ash replaced 55% of the portland cement.

Report Organization

Subsequent chapters of this report describe the test methods used (Chapter 2), test results and discussion (Chapter 3), and conclusions and recommendations for future work (Chapter 4).

2

TEST METHODS

Instruments, equipment, and supplies used in this investigation are detailed in Appendix A.

Concrete Components

The ingredients used in concrete prepared in this study were commercially available type I portland cement, sand, coarse aggregate, and coal fly ash. Four Class C fly ashes, originating from power plants that burn either lignite or subbituminous coal, were characterized for loss on ignition (LOI), organic carbon content, and mercury content. High-purity water (18.2 M Ω -cm) was used to prepare all concretes.

One sample of fly ash (CCS1) used in our study originated from a 1100-MW plant that burns ~ 7.4 million tons of lignite coal annually. Fly ash is collected in a cold-side electrostatic precipitator (ESP). No special mercury controls were employed at this plant. Most of the fly ash from this plant is used as a portland cement replacement in concrete.

A second fly ash (NRT1019) used in concrete preparation originated from a 1200-MW power plant burning subbituminous coal. Fly ash is collected in a cold-side ESP after conditioning with SO₃. All of the fly ash is typically used as a portland cement replacement in concrete. The fly ash used in this study was collected during a demonstration test of powdered activated carbon (PAC) injection for mercury capture. PAC was injected prior to the primary ESP, and was collected with the fly ash in the ESP.

Finally, two fly ashes (MER032, MER0357) were from a power plant (858 MW) burning subbituminous coal. This plant was conducting full-scale tests on the Norit bromine-containing activated carbon sorbent Darco[®] Hg-LH (Feeley *et al.* 2005). Thus, MER032 is baseline fly ash without sorbent and MER0357 contains Darco[®] Hg-LH in the fly ash. This sorbent is designed for application to flue gases in power plants burning coals that contain low concentrations of halogens, and is thought to have less impact on the air entraining characteristics of concrete. Mercury capture rates over 90% are reported for applications of Darco[®] Hg-LH to fabric filter and ESP-only particulate removal devices.

Descriptive information on the fly ashes used in our study on mercury release from concretes is presented in Table 2-1.

Table 2-1
Background Information on Fly Ashes Used in This Study

	CCS1	MER032	MER0357	NRT1019
Unit Capacity (MW)	500	138	138	600
Primary Coal Type	lignite	subbituminous	subbituminous	subbituminous
Sorbent	—	—	Darco® Hg-LH	Darco®
Primary Coal Source^a	ND	WY	WY	WY
Boiler Type	Tangential	Tangential	Tangential	Opposed
Particulate Control Device^b	ESPC ^a	ESPh ^a	ESPh ^a	ESPC ^a
NOx Control^c	OFA	--	--	LNB
Sampling Date	7/2005	8/26/2004	11/16/2004	11/12/2001

a. ND = North Dakota; WY = Wyoming

b. ESP: Electrostatic Precipitator (c=cold-side; h=hot-side)

c. OFA = Over-Fired Air; LNB = Low-NOx Boiler

Fly Ash Composition

The American Society for Testing and Materials (ASTM) standard for Class C fly ash currently specifies: 1) LOI of less than 6%, 2) maximum water content of 3%, and 3) a sum of the concentrations of $\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ greater than or equal to 50%. This latter composition requirement was verified by elemental analysis of each fly ash sample (Appendix B). Cold vapor atomic adsorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectrometry (CVAFS) were used to determine mercury concentration, and inductively coupled plasma–atomic emission spectrometry (ICP–AES) was used to verify concentrations of Si, Fe, Al, and S.

The elemental composition of the fly ash was determined by a procedure based on EPA method 3052. A solution of the fly ash was prepared by microwave-heated digestion of a closed vessel containing 300 mg of fly ash in an acid mixture of nitric, hydrochloric, and hydrofluoric acids. The accuracy of our method has been validated for Class F (low Ca) fly ash using NIST SRM 1633b, coal fly ash standard reference material (SRM).

Determinations of aluminum, iron, and silicon in a fly ash were accomplished by inductively coupled plasma–atomic emission spectrometry (ICP–AES). Calibration of the Varian VISTA AX™ ICP spectrometer was achieved with 5 accurately diluted aliquots of a custom multiple-element standard solution and one blank. Calibration solutions were “matrix matched” with the sample solution so that every solution introduced into the ICP consisted of the aqueous acid mixture of 6% HNO_3 , 2% HCl , 2% HF , and 20% H_2BO_3 . The concentration of each element in the custom standard is certified traceable to NIST by the supplier (Inorganic Ventures). Measurements of background-corrected relative intensities for 9 spectral lines (total lines for Al, Fe, and Si) were made simultaneously for axial emission from a 1.20-kW, 40-MHz plasma.

Calibration functions were either first- or second-degree polynomial least-square regression fits with correlation coefficients greater than 0.995. Concentration values obtained by this approach typically are within 10% of actual concentrations.

Loss on Ignition and Total Organic Carbon

LOI values were measured in our laboratory by the method established by ASTM C-311-04 (ASTM 2004). After a determination of water loss at 105°C, each dry sample was heated to constant weight at 750°C for 4 hours in a Vulcan Model 3-130 muffle furnace.

All fly ashes, cement, sand, and coarse aggregate were analyzed for total carbon and inorganic carbon by the STAR laboratory of the Ohio Agricultural Research and Development Center (OARDC), The Ohio State University, Wooster, OH. The sand and coarse aggregate had been ground to fine powders with an alumina mortar and pestle in our laboratory.

Organic carbon contents were determined by a procedure in which samples were “burned” under pure O₂ at 900°C in an Elementar Americas, VarioMax Carbon/Nitrogen Analyzer to measure total carbon (TC). Total inorganic carbon (TIC) was determined by coulometry on an instrument manufactured by UIC Inc. Upon introduction of sample into the sample flask, the system was purged with a CO₂-free carrier gas to eliminate atmospheric carbon dioxide. Then, 2N perchloric acid was added and heated to oxidize organic carbon to gaseous CO₂ that was measured by a sensitive CO₂ detector. The difference between TC and TIC is the organic carbon content.

Mercury Content for Each Concrete Ingredient

CVAFS was used by *Studio Geochimica* to determine mercury concentrations in cement, coarse aggregate, sand, fly ash, and air entrainment admixture (AEA). This information enabled later estimates of the background mercury concentration in all concretes prepared for this study.

Individual samples of the listed components were reacted with concentrated nitric acid inside a sealed PTFE vessel heated within a CEM microwave oven. Mercury concentrations in the resulting solutions were determined using a Tekran™ Series 2600 CVAFS system. The technique uses amalgamation of elemental mercury onto a gold surface as the mercury is released from an aqueous sample solution to which stannous chloride solution has been added to reduce Hg(II) to Hg(0). Subsequently, the mercury, as Hg(0), is thermally released from the gold amalgam and transported into a fluorescence cell (253.7 nm) where fluorescence is excited and measured (Bloom *et al.* 1995). Calibration of the fluorescence spectrometer system is achieved with NIST-traceable standard solutions. The 18.2 MΩ-cm water (Millipore) used in all concretes consistently had mercury concentrations below the method detection limit (0.5 ppt).

Mercury Emission Experiments

All concretes were prepared and cured in cleaned, new polypropylene (PP) containers.

Concrete Preparation

The formulation used for preparation of each curing concrete is presented in Table 2-2. A batch of ordinary portland cement concrete, which contained no fly ash, was prepared to establish an emission baseline level for mercury that might originate from all non-ash components. Four additional batches of concrete mixes were prepared with fly ash replacing 55% of the portland cement. The percentage cited here refers to the mass fraction of fly ash relative to the original amount of cement used in OPC. Quantities of air entrainment admixture, AEA, added to each batch of concrete were based on foam index measurements (Kulaots *et al.* 2003) on the cement and on each fly ash used in these experiments.

For each batch of concrete, dry components first were mixed in a PP container by tumbling the closed container for 10 minutes (Figure 2-1). A weighed quantity of high-purity water (18 M Ω -cm) then was poured gradually into the powder mix as stirring occurred (open container). Vigorous mixing of this wet mixture was accomplished with a steel helical impeller driven at ≤ 450 rpm by a high-torque electric drill. The resulting wet concrete mixture then was sealed inside the PP container. A bead of silicone adhesive sealant (GE RTV-6700 series) provided assurance of a gas-tight seal at the lid-container interface. This arrangement defined a sampling volume of ~ 4 L (headspace) for air in direct contact with the upper surface of the curing concrete. Iodated carbon (IC) traps were affixed at entrance and exit ports of the sampling container, and the container then was placed inside an environmental chamber where gas lines from a manifold were connected to the sampling IC traps.

Table 2-2
Concrete Formulations for Individual 20-kg Batches

Concrete	Fly Ash kg	Coarse Aggregate kg	Sand kg	Cement kg	Water kg	AEA ^a kg
OPC	0	10.0750	6.0670	2.6450	1.2130	0.0026
CCS1	1.4550	10.0750	6.0670	1.1900	1.2130	0.0085
NRT1019	1.4550	10.0750	6.0670	1.1900	1.2130	0.0543
MER032	1.4550	10.0750	6.0670	1.1900	1.2130	0.0201
MER0357	1.4550	10.0750	6.0670	1.1900	1.2130	0.0376

a. AEA: air entrainment admixture MicroAir 100™



Figure 2-1
Dry components mixed by tumbling.

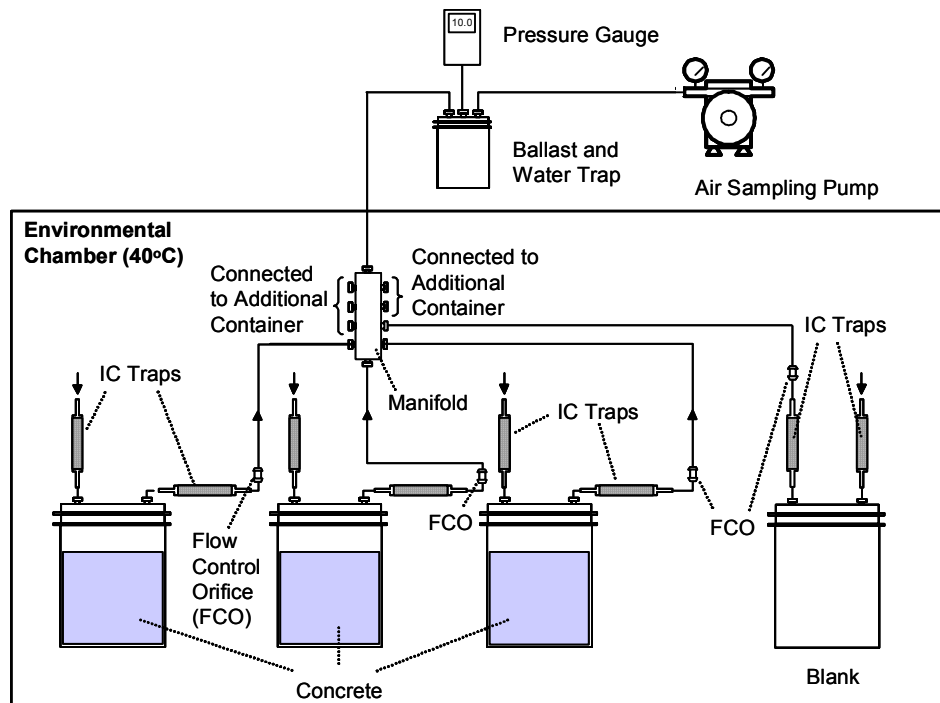


Figure 2-2
Schematic diagram of the sampling setup

Purge and Trap Sampling

Mercury was sampled from headspace air using an air sampling pump and IC traps that served as collectors for multiple mercury species in air (Figure 2-2). Each freshly prepared concrete was sealed within a 20-L PP container (*Curtec*) (Figure 2-3). Sampling of the headspace gas, above each concrete mass, was accomplished by pulling air (pumped) through an entry port, located near the edge of the lid, at a rate of 0.285 L/min. En route to the headspace, the air was pulled through an IC trap [*Studio Geochimica*] to remove background levels of mercury present in ambient air within the environmental chamber. As it entered the PP container, the mercury-free air displaced headspace air that was being pumped, in turn, through an exit port where a second IC trap (sampling trap) collected gaseous mercury species emitted from the concrete surface. The sampling trap was located immediately above an exit port in the lid diagonally across from the entry port. Thus, an induced air stream through the headspace provided the principal means for transport of released mercury into an IC trap.

Airflow through headspaces within multiple containers was accomplished by a single air pump [*Welch*] (Figure 2-4), located outside the environmental chamber, and a pair of PP manifolds located inside the chamber. All gas lines used to interconnect components of the gas sampling system were silicone tubing [*Silastic™*, 6.35 mm i.d., 12.7 mm o.d.]. Gas-tight ball valves (PVC) were used in gas lines as on-off switches for gas flow to the pump.

Regulation of gas flow through the head space and IC traps was achieved by maintaining a constant pressure drop of 3.00 ± 0.15 psig [*Manometer – Fisher Scientific*] across a fixed aperture (0.200 mm diameter) in a stainless steel fitting [*Lenox Laser*] inserted into the gas line just after the sampling IC trap. Airflows were measured by glass-float rotameters [*Cole Parmer*] that have calibrations traceable to NIST.



Figure 2-3
Air sampling of multiple containers of concrete in the environmental chamber



Figure 2-4
Air pump, water trap, and pressure gauge.

Carbon traps are cited by the EPA “Appendix K” method as effective collectors for mercury in air sampling methods (U.S. EPA 2005). The collection efficiency of these traps is reputed to be greater than 90%. Orientation of the small-capacity (100 μg for Hg) sampling trap is not associated with channeling.

One large-capacity (500 μg for Hg) trap was mounted at the opening on each lid through which air passed into the headspace. Each of these traps was kept vertical to minimize possible channeling through the IC granules packed into the glass tube.

Collection of gaseous mercury species released from the curing concrete relied on physicochemical adsorption onto the IC granules contained in small-diameter glass tubes (IC traps). The sampling setup is described schematically in Figure 2-2. A single sampling pump, specially designed for controlled movement of air through small columns of collector particles, pulled air through the headspace above curing concrete. Airflow through the container was 0.285 ± 0.010 L/min. This flow was accomplished by connecting the output from 3 containers to a PP

manifold which, in turn, was connected to a single pump operated at -3.0 ± 0.15 psig. An IC trap (500 μg Hg capacity) placed at the input port of the sampling chamber removed mercury from the air stream that entered the chamber. This “mercury-free” air passed over exposed surfaces of freshly mixed concrete to facilitate curing of the concrete and to transport gaseous mercury released by the concrete into a small IC trap (100 μg Hg capacity) located at the exit port of the chamber.

When an IC trap was removed from an air sampling line, each end of a sampling trap immediately was blocked with a Teflon™ plug. Then, each sealed tube was enclosed within a labeled zip-lock polyethylene bag that was rolled into a cylindrical shape around the tube and then, placed inside a plastic bubble envelope for packaging and shipment. Groups of these protected IC traps then were shipped by courier to the *Studio Geochimica* laboratory for analysis.

Controls for Experiments

Removal of any background mercury from air pulled into each container of concrete was important to achieving low blanks in these experiments. Therefore, a single IC trap, with a capacity for 500 μg of Hg, was attached at the intake port of each PP sampling chamber to preclude entry of mercury into the air atmosphere above the curing concrete. Mercury accumulated on these “cleanup” traps ranged from 1349 ng to 1642 ng ($n=2$). These quantities of mercury are well below the 500- μg capacity of the IC traps used to capture mercury.

For control experiments, background mercury from within a container was determined as a “sampling blank” by pulling mercury-free air through an empty sampling container. A sampling blank container accompanied each set of three identical concrete samples through the air sampling interval. Mercury from the air that passed through the container was collected at the exit port by a small IC trap. This sampling blank was subtracted from quantities of mercury collected on individual traps for the associated set of concretes sampled at the same time.

Furthermore, the OPC concrete, described elsewhere in this report, served as a control reference for emissions from concretes that contained fly ash.

Determination of Mercury in IC Traps

Mercury determinations for IC traps used in sampling air were accomplished by CVAFS in the laboratories of *Studio Geochimica*, Seattle, Washington. The iodated carbon from each trap used in air sampling was digested in 15 mL of a mixture of nitric and sulfuric acids (70% HNO_3 and 30% H_2SO_4 , by volume). Following digestion, the resulting mixture was diluted to 40 mL with 0.07 N BrCl solution. Then, mercury measurements were started by SnCl_2 reduction of mercury to Hg (0) which subsequently was adsorbed onto gold-coated sand. Finally, thermal desorption of the elemental mercury into a calibrated cold vapor atomic fluorescence spectrometer enabled determination of the quantity of mercury present in the sample (Bloom *et al.* 1995). The detection limit of mercury in IC traps is 0.3 to 0.7 ng per IC trap.

3

RESULTS AND DISCUSSION

Fly Ash Characterization

Concentrations for the oxides of aluminum, iron, silicon, and sulfur in the fly ashes used in preparation of concretes appear in Table 3-1. The sums of the concentrations of $\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ were $\geq 50\%$, which meets a basic criterion for Class C fly ashes. Concentrations of CaO range from 14 to 26.9%. Sulfur concentrations, expressed as % SO_3 , varied from 0.9% to 1.9%. More detailed compositions, measured primarily by ICP-AES, are presented in Appendix B.

Table 3-1
Silica, Iron Oxide, Alumina, and Sulfur Trioxide in Fly Ashes (%)

Oxide	CCS1	MER032	MER0357	NRT1019
Al_2O_3	13.9	16.5	18.0	19.3
CaO^1	14-16	23-26	23-26	26.9
Fe_2O_3	6.2	8.6	8.4	4.8
SiO_2	40.8	32.0	31.5	31.3
SO_3	0.9	1.3	1.3	1.9
$\Sigma \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{SiO}_2$	60.9	57.1	57.9	55.4

¹ CaO data were obtained from plant personnel due to an analytical discrepancy

LOI values for fly ashes (Table 3-2) ranged from 0.043 to 4.44. LOIs determined for the fly ashes used in this study were well below the upper limit of 6% prescribed by the American Concrete Institute (ACI) for fly ash use in concrete (ACI 232.2R-96), and significantly less than the 10% limit for use of fly ash in transportation projects as specified by the American Association of State Highway and Transportation Officials (AASHTO).

The organic carbon contents for the four fly ashes (Table 3-2) ranged from 0.054% to 3.9%. Concentrations of inorganic carbon were quite low for all the fly ashes (0.0064% to 0.018%). Importantly, the organic carbon contents correlated well with the average LOI values determined. None of the fly ashes had measurable water content.

Table 3-2
LOI, Organic Carbon, and Inorganic Carbon in Fly Ashes

Fly Ash	LOI (n=2) %	Organic Carbon %	Inorganic Carbon %
CCS1	0.043± 0.005	0.054	0.008
NRT1019	4.44 ± 0.03	3.91	0.018
MER032	1.59 ± 0.03	1.40	0.0064

Organic Carbon Content of Concrete Ingredients

Insignificant quantities of carbon, 0.008% total, were associated with the sand used in concretes prepared in this study (Table 3-3). However, quite small amounts of organic carbon, 0.2% to 0.53%, were attached to the coarse aggregate and cement. For the coarse aggregate and sand, the source for this carbon probably is non-specific plant debris that was not removed by commercial washing and sieving processes. Interactions of this type of carbonaceous material with mercury currently are unknown. Carbonate mineral phases most likely account for the inorganic carbon found in coarse aggregate and cement. Interactions of carbon-containing air entrainment admixture with mercury remain unexplored.

Table 3-3
Carbon Content of Cement, Coarse Aggregate, and Sand.

Material	Organic Carbon %	Inorganic Carbon %
Cement	0.201	0.334
Coarse Aggregate	0.530	4.320
Sand	0.006	0.002

Mercury in Concrete Ingredients

Mercury values measured in each of the concrete ingredients are shown in Table 3-4. The total quantities of mercury contributed to each batch of concrete from sand, coarse aggregate cement, and fly ash components were estimated from CVAFS measurements of samples shown in Table 3-5. These data provided a basis for estimates of the mercury concentrations in each 20-kg batch of curing concrete.

Table 3-4
Mercury Concentration in Concrete Ingredients

Ingredient	Hg ($\mu\text{g}/\text{kg}$)	Other Studies ($\mu\text{g}/\text{kg}$)
MER0357 Fly Ash	1372 \pm 37	100-2300 ^a
NRT1019 Fly Ash	1164 \pm 19	
MER032 Fly Ash	354 \pm 21	
CCS1 Fly Ash	12.8 \pm 1.7	
Cement	8.01	60 ^b
Coarse Aggregate	7.42	5-460 ^c
MicroAir100™	1.52	NA ^d
Sand	1.37	20-100

a. Gustin and Ladwig, 2004.

b. Verein Deutscher Zementwerke e.V., 2001

c. Johansen and Hawkins, 2003.

d. NA: not available.

Table 3-5
Estimated Mercury in 20-kg Batches of Concrete

Concrete	Fly Ash	Coarse Aggregate	Cement	Sand	AEA ^a	Water	Total Mercury in Concrete	Mercury Concentration in Concrete
	$\mu\text{g}/\text{batch}$							$\mu\text{g}/\text{kg}$
OPC	–	74.8	21.2	8.3	<0.01	0.0006	104	5.2
CCS1	18.6	74.8	9.5	8.3	0.01	0.0006	111	5.6
NRT1019	1693.6	74.8	9.5	8.3	0.08	0.0006	1786	89.3
MER032	515.1	74.8	9.5	8.3	0.03	0.0006	608	30.4
MER0357	1996.3	74.8	9.5	8.3	0.06	0.0006	2089	104.4

a. AEA: Air entrainment admixture MicroAir 100™

Mercury Emission Experiments

Mercury Emission during Standard 28-day Air Curing

In the 28-day curing process, total quantities of mercury collected by small sampling traps ranged from 149 ng to 1549 ng (Table 3-6). An air volume of 10.4 m³ was sampled for each concrete container during this curing interval.

Table 3-6
Mercury Collected on Iodated-Carbon Traps over 28-day Curing Period

Concrete ID	Hg Concentration in Fly Ash ^a (µg/kg)	Hg Concentration in Concrete (µg/kg)	n	Hg Collected (ng/trap ^a)	Hg Released from Concrete ^a (ng per kg Concrete)	Hg Released from Concrete ^b (%)
OPC	—	5.2	3	116.0 ± 15.3	5.8 ± 0.8	0.112
CCS1	12.8 ± 1.7	5.6	3	343.6 ± 50.5	17.3 ± 2.5	0.307
NRT1019	1164 ± 19	89.3	2	345.4 ± 17.7	17.3 ± 0.9	0.019
MER032	354 ± 21	30.4	3	1447.8 ± 77.1	72.4 ± 3.9	0.238
MER0357	1372 ± 37	104.4	3	1207.3 ± 95.6	60.4 ± 4.8	0.058
OPC-2003 ^c	—	4.1	4	77.5 ± 17.7	2.8 ± 0.7	0.068
FA-2003 ^c	119	12.6	3	254.4 ± 67.2	9.5 ± 2.4	0.075

- Average ± 1σ for n samples (Appendix C). All values for trapped mercury have been blank-corrected.
- Percent Hg collected on trap (blank corrected) relative to total Hg in concrete.
- Values from ordinary portland cement and fly ash containing concrete derived from bituminous coal determined in Cheng et al., 2003.

Mercury Release during Extended Sampling

After the initial 28-day curing interval, mercury release over an extended 4-week sampling period was monitored for two fly ashes at 40 ± 1 °C. Quantities of mercury collected weekly in outlet IC traps are summarized in Table 3-7. Blanks, that is any mercury originating from the container or sources other than concrete, have been subtracted from the total quantity of mercury measured on each IC trap. Importantly, all blank values, summarized later in Table 3-9, were small relative to quantities of Hg collected for air samples above these two concretes.

The time-based decrease in mercury release during extended curing, fit by “least-squares” to an exponential decay function ($y = ae^{-bx}$), intercepts the OPC value (116.0 ± 15.3 ng at 4 weeks) after a total curing time of 10.4 weeks for the MER032 concrete and 12.3 weeks for MER0357 concrete. Thus, first approximations have been established for the curing times necessary for mercury release from these fly-ash concretes to diminish to a level similar to that observed for OPC concrete.

Table 3-7
Mercury in Air above Select Fly-Ash Concretes during Extended Curing (n=3)^a

Week →	1 thru 4	5	6	7	8
Concrete ↓	ng				
MER0357	1207.3 ± 95.6	360.4 ± 20.6	325.0 ± 26.1	265.7 ± 23.9	232.7 ± 60.6
MER032	1447.8 ± 77.1	244.8 ± 18.4	215.6 ± 38.4	192.9 ± 3.0	162.1 ± 44.4

a. Average ± 1σ. See Appendix C for full data set.

Quality Assurance for Mercury Measurements

Average recoveries of mercury from spikes of the blank and from determinations of mercury in NIST 1641d standard reference material were 92% and 96%, respectively (Table 3-8). Limits of detection for mercury were in the range from 0.23 to 0.62 ng per trap.

Table 3-8
Mercury Recoveries for Spikes and NIST Standard Reference Material

Sample Set	Recoveries for 10ng and 100 ng Mercury Spikes (%)	Recoveries for Mercury in NIST-SRM 1641d (%)	Mercury Detection limit [3σ] (ng/trap)
1	99.0 ± 5.9	94.4	0.62
2	99.0 ± 4.2	94.4	0.62
3	90.3 ± 2.8	99.4	0.23

In previous EPRI-sponsored studies conducted in our laboratories (Cheng *et al.* 2002-2005; Golightly *et al.* 2005), mercury collected on partitioned segments of iodated carbon in individual traps indicated that no significant breakthrough from segment A to B occurred ($\leq 2\%$) for any sampling experiment. Thus, measurements on Hg breakthrough were not repeated in the current study.

Mercury blank levels were quite low, relative to mercury collected from air samples above concretes (Table 3-9). Quantities of mercury captured on individual traps ranged from 19.4 to 46.3 ng for the initial 28-day curing interval. For the 1-week sampling periods used during extended curing, blanks ranged from 4.3 to 13.9 ng. Blank averages were 29.4 ± 11.3 ng for the standard 28-day maturation and 9.5 ± 3.4 ng for each week of extended curing.

Table 3-9
Sample Blanks: Total Mercury Collected on Individual IC Traps

Concrete ID →	MER032	MER0357	NRT1019	CCS1	OPC
Curing Period ↓	ng/trap				
Initial 28 days	22.5	19.4	23.1	35.7	46.3
First week, extended	7.9	4.3	—	—	—
Second week, extended	9.5	6.0	—	—	—
Third week, extended	13.1	11.6	—	—	—
Fourth week, extended	13.9	9.3	—	—	—

Discussion

Mercury Emission from Ordinary Portland Cement Concrete

Release of small quantities of mercury from OPC concrete (concrete without fly ash) occurred during the curing process. After deducting the blank, the average mercury release from OPC concrete was 5.8 ± 0.8 ng/kg. Thus, the amount of mercury released from the ingredients mixed into OPC concrete, including cement, sand, coarse aggregate, and water, was 0.11% of the total mercury present. This value is close to, but slightly higher than, the mercury release measured from OPC concrete in 2003 of 0.068%.

Mercury Emission from Concretes Containing Fly Ash

The release of mercury from concrete containing fly ash varied depending on the source of the fly ash. For the group of fly ashes included in this study, mercury associated with the lignite fly ash (CCS1) was the least tightly bound, as demonstrated by the highest percent mercury release of the different fly ashes examined as shown in Figure 3-1. For this fly ash, the organic carbon content was low (0.054%) and no manufactured carbon-based sorbent was present. The quantity of gas-phase mercury captured by IC traps above the curing concrete represents 0.3% of the total mercury in the concrete. Importantly, the mercury concentration (12.8 $\mu\text{g}/\text{kg}$) in this lignite fly ash is quite low relative to other fly ashes included in our investigation. Therefore, while this fly ash demonstrated the highest percent release of the different ashes examined, the lignite fly ash had the lowest mercury content and 99.7% of the mercury was not volatilized.

Previous studies examining mercury release from coal fly ash performed by Gustin and Ladwig (2004) showed that lignite-derived coal fly ash released mercury, while other fly ash types

usually acted as sinks for atmospheric mercury. These data are consistent with our results in that we observed the greatest percent mercury release from the concrete containing lignite-derived coal fly ash. In contrast, our results demonstrate release of mercury for concrete made from all the fly ashes. In our experiments, mercury-free air was used rather than ambient mercury in atmospheric air as in the Gustin and Ladwig (2004) study.

The higher release of mercury from the concrete containing lignite-derived ash may be related to factors similar to those controlling the removal of mercury by this ash in combustion flue gases. It has been observed that mercury capture from flue gas generated from the combustion of lignite coal is low (Kilgroe and Senior, 2003). The low level of mercury capture in systems burning lignite coal has been attributed to the low carbon content of these ashes and the low chlorine levels, which reduce oxidation of elemental mercury (Senior and Johnson, 2005). Huggins et al. (1999) have shown by x-ray absorbance spectroscopy that mercury forms a variety of surface species on unburned carbon, and most involve interactions with chlorine. Because of the relatively low carbon and chlorine levels of lignite coals, the speciation of mercury in lignite-derived coal fly ash may be significantly different than the speciation of mercury in the other types of ash. Therefore, the higher release of mercury from concrete containing lignite-derived fly ash is potentially due to differences in the surface speciation of mercury in this material.

In previous work using a single fly ash (Cheng *et al.* 2002-2005), we found that mercury release generally increased with increasing mercury concentration in the concrete. Mercury release and mercury content for the different concretes examined in the current work are shown in Figure 3-1. No clear trend was observed between the mercury content of the concrete and the percent mercury release. For example, the highest percent release was for the concrete containing CCS1 fly ash which also had the lowest mercury content of any of the fly ashes tested. This again suggests that differences in the interactions of mercury with various components of fly ash (e.g. carbon) are potentially more important than the total mercury content. For the work in 2003, a single fly ash was used and therefore, the speciation of mercury, or interactions of mercury with various fly ash components, was conserved for each batch. As a result, as the amount of fly ash in the concrete increased, so did the mercury content and the mercury release. For the different fly ashes examined in the current study, total mercury content is not a predictive parameter for estimating mercury release.

Significance of Fly Ash Organic Carbon Content

The different fly ashes examined in this work varied significantly with respect to organic carbon content (Table 3-2). The relationship between mercury release and organic carbon content for the different fly ashes is shown in Figure 3-2. The percent mercury release decreased as the organic carbon content of the fly ash increased. The fly ash with the highest organic carbon content tested in 2005 was the NRT1019 fly ash, and this fly ash demonstrated the lowest percent mercury release. Also shown in Figure 3-2 is the percent mercury release from concrete containing fly ash tested in 2003. This fly ash had an organic carbon content of 4.1% and demonstrated similarly low mercury release as the NRT1019. The fly ash with the lowest carbon content (CCS1) demonstrated the greatest percent mercury release. There is a very strong linear correlation between mercury release and organic carbon content ($r^2=0.9985$) for the fly ashes not containing activated carbon, though only 3 data points were available for this analysis.

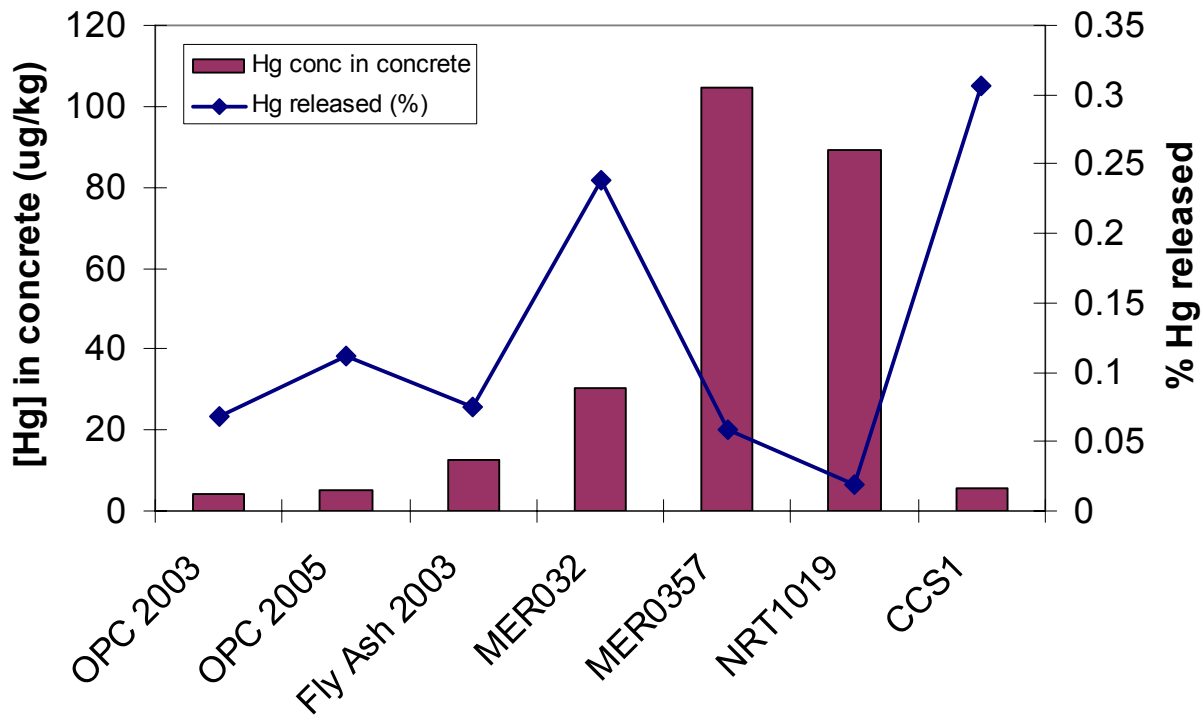


Figure 3-1
Mercury release and mercury content of the different fly ash concretes

The fly ashes containing activated carbon sorbent (MER0357 and NRT1019) had lower percent mercury release than would be expected given the organic carbon content of this ash and the correlation established above. This suggests that the manufactured activated carbon is more effective at limiting mercury release than organic carbon originating from the bulk coal. The MER032 (Hg: 354 $\mu\text{g}/\text{kg}$) and MER0357 (Hg: 1372 $\mu\text{g}/\text{kg}$) ashes are from a power plant burning subbituminous coal. MER032 (1.40% organic carbon) is labeled as a baseline fly ash that contains no sorbent. In contrast, MER0357 (1.89% organic carbon) contains Norit Darco Hg-LHTM carbon sorbent. The mercury release from concrete for MER0357 (0.058%) is four-times less than that for MER032 (0.238%). Thus, just a slight increase in the organic carbon in the MER0357 fly ash compared to the MER032 ash resulted in a large decrease in mercury release. In instances where powdered carbon sorbents are used to capture mercury in flue gas, a significant fraction of mercury is expected to be sorbed to carbon sites on unburned coal particles and to reactive sites on brominated carbon powders, such as Norit Darco Hg-LHTM, injected into the flue gas. Our measurements cannot differentiate directly between these potential binding sites. However, the data suggest that for the MER0357 ash the manufactured activated carbon binds the mercury more strongly, resulting in less mercury release compared to organic carbon formed during the combustion process.

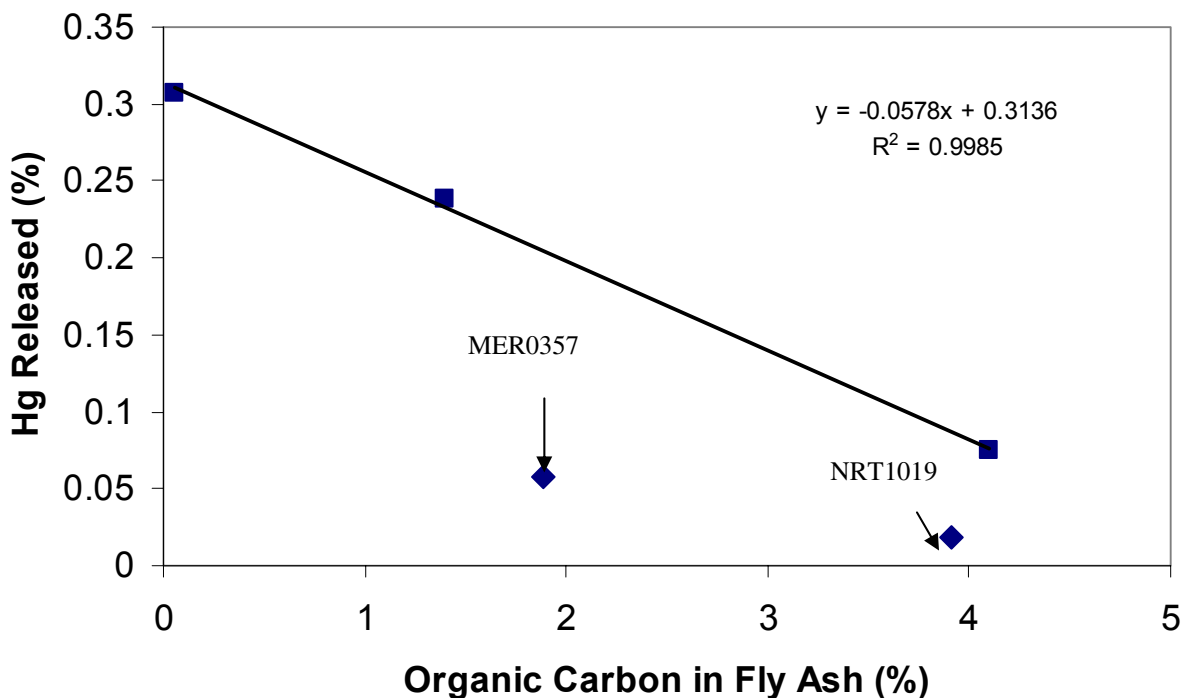


Figure 3-2
Mercury release as a function of fly ash organic carbon content

Other differences in the fly ash properties, in addition to organic carbon content, may have influenced the extent of mercury release from the concretes. For example, the levels of sulfur also varied (Table 3-1) between the ashes, with the NRT1019 ash having the highest sulfur (1.9%) and CCS1 having the lowest sulfur level (0.9%). Mercury emissions from concrete made with the NRT1019 ash were the largest of the different concretes, while emissions from concrete made from the CCS1 were the lowest. Krishnan *et al.* (1994) suggested that the activated sites causing Hg(0) adsorption in activated carbon may include oxygenated organic species and functional groups containing inorganic elements, i.e. chlorine (Cl) or sulfur (S). Our data suggest that increasing sulfur content of ash does not noticeably decrease the release of mercury from concrete made with this ash, and, in fact, the opposite correlation was seen. However, the variation in sulfur content (0.9%-1.9%) among the different fly ashes was relatively small. The levels of chlorine and bromine in the different fly ashes were not measured, and therefore, possible effects by these halogens on the mercury release process are unresolved.

The release rates observed also indicate the effectiveness of certain components of the ash to continue binding mercury within the chemically reactive matrix (pH 10 to 12) presented by freshly prepared concrete. During the initial curing phase the physical desorption of mercury into the pore water of the curing concrete is likely an important step leading to mercury volatilization. Therefore, the effect of pH on the leaching of mercury from fly ash and unburned/activated carbon is an important consideration. Previous studies indicate that the adsorption of mercury on ash (Feng *et al.* 2004) and activated carbon (Zhang *et al.* 2005) increases as the pH increases. This suggests that the high pH of the curing concrete is favorable for binding of mercury to ash

and carbon and is consistent with the low mercury volatilization rates measured in our experiments.

Long-Term Trends in Mercury Release

For MER032 and MER0357 concretes, air sampling conducted over 4 weeks of curing beyond the initial 4 weeks revealed that mercury release diminished with time, as shown in Figure 3-3. At expected total curing times of 10.4 weeks for MER032 concrete and 12.3 weeks for MER0357, mercury emission is expected to decrease to the level observed for OPC concrete at the end of 4 weeks of curing. This corresponds to an expected loss of porosity for the concrete and loss of water to hydration reactions by the components of cement. Studies on water adsorption by activated carbon report that H₂O is adsorbed on the carbon surfaces by means of hydrogen bonding (Bansal *et al.* 1988). Oxygen complexes on carbon surfaces form primary adsorption centers, while adsorbed H₂O molecules then can become secondary adsorption centers as the H₂O vapor pressure increases. Chemisorption of Hg(0) is a dominant process for moisture-containing samples (Li *et al.* 2002). Thus, the mercury emitted from other components in the concrete making process may be adsorbed onto these secondary adsorption centers due to the water-to-binder ratio of 0.459 during concrete curing. As the hydration of cement proceeds, a build-up of a gel-membrane outside the carbon pores has been postulated. Once in the solidified waste form, activated carbon particles will retain most of the adsorbed mercury by forming a barrier outside of the activated carbon particles (Zhang and Bishop, 2002), which accounts for the overall low release rate of mercury in our experiments.

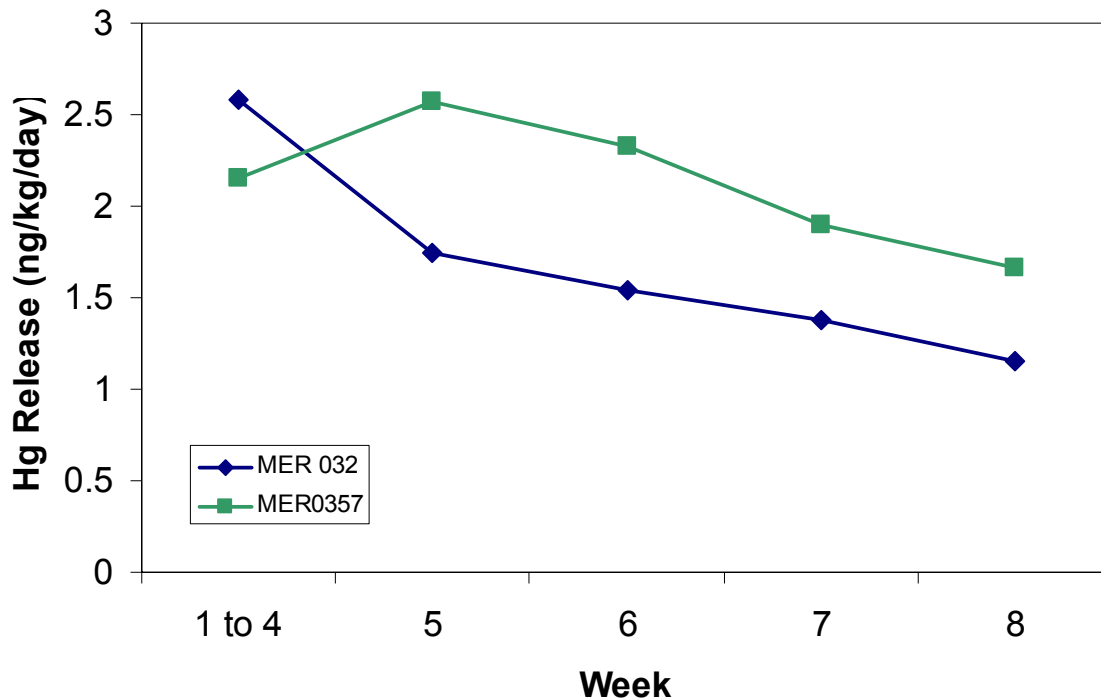


Figure 3-3
Mercury release rate during extended curing

4

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Conclusions from this investigation are based on purge-trap measurements using purified air, and thus, deal with upper limits for rates of mercury release. Measurements within an ambient air environment may result in lower release rates due to a higher concentration of mercury in the transport medium.

During the curing process, concretes that contained various fly ashes were observed to emit less than 0.31% of the total mercury present in the concrete mixture. Release rates for gas-phase mercury are significantly influenced by the presence of sorbents injected into flue gas prior to capture by air pollution control devices. The percent mercury release from concrete decreased with increasing carbon content of the fly ash. Long-term curing data suggest that the mercury release from fly-ash-containing concretes diminishes to levels found for OPC concrete in 12 weeks or less. Therefore, nearly all of the mercury originally present in the fly ash is expected to remain in the concrete and not be released to the atmosphere.

Recommendations

Field measurements at industrial sites that routinely cure concretes containing either fly ash or fly ash-sorbent combinations are recommended as a source of practical information on the release of mercury. Also, measurements of mercury release to water and air phases from concrete under different disposal scenarios are recommended.

5

REFERENCES

ASTM C311-04, Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland cement concrete. American Society for Testing and Materials. 2004.

Bansal RC; Donnet JB; Stoeckli F. Active Carbon; Dekker: New York, 1988. 504pp.

Bloom NS; Prestbo EM; Hall B; Von Der Geest EJ. Determination of atmospheric Hg by collection on iodated carbon, acid digestion and CVAFS detection. *Water Air Soil Pollut.* 1995;80(1-4):1315-1318.

Cheng C; Golightly D; Sun P; Taerakul P; Walker H; Weavers L; Wolfe W. Release of mercury during curing of concrete containing fly ash and mercury sorbent material, EPRI, Palo Alto, CA: 2002. 1004697.

Cheng C; Golightly D; Sun P; Taerakul P; Walker H; Weavers L; Wolfe W. Mercury emissions from concrete containing fly ash and mercury-loaded powdered activated carbon, EPRI, Palo Alto, CA: 2003. 1004402.

Cheng C; Golightly D; Sun P; Taerakul P; Walker H; Weavers L; Wolfe W. Mercury emissions during steam-curing of cellular concretes that contain fly ash and mercury-loaded powdered activated carbon, EPRI, Palo Alto, CA: 2005. 1008308.

Feeley TJ; Brickett LA; O'Palko BA; Murphy JT. Field testing of mercury control technologies for coal-fired power plants. DOE/NETL Mercury R&D Program Review. May 2005. 21pp.

Feng Q; Lin Q; Gong F; Sugita S; Shoya M. Adsorption of lead and mercury by rice husk ash. *J. Colloid Interf. Sci.* 2004; 278(1):1-8.

Golightly DW; Sun P; Cheng C-M; Taerakul P; Walker HW; Weavers LK; Golden DM. Gaseous mercury from curing concretes that contain fly ash: Laboratory Measurements. *Environ. Sci. Technol.* 2005;39(15):5689-5693.

Gustin M; Ladwig K. An assessment of the release of mercury emissions from coal fly ash. *J Air Waste Manage. Assoc.* 2004;54(3):320-330.

Huggins FE; Yap N; Huffman GP; Senior CL. Identification of mercury species in unburned carbon from pulverized coal combustion. *Proceedings Air and Waste Management Association, 92 Annual Conference* 1999: 2116-2127.

References

- International Organization for Standardization. ISO 10694:1995(E). Soil Quality – Determination of Organic and Total Carbon after Dry Combustion (elemental analysis). International Organization for Standardization. Geneva, Switzerland.
- Johansen, V.C.; Hawkins, G.J.; Portland Cement Association R&D Serial No.2567, 2003.
- Kilgroe J; Senior C. Fundamental Science and Engineering of Mercury Control in Coal-Fired Power Plants. Proceedings, Air Quality IV Conference 2003.
- Kulaots I; Hsu A; Hurt RH; Suuberg EM. Adsorption of surfactants on unburned carbon in fly ash and development of a standardized foam index test. Cement and Concrete Research 2003;33:2091-2099.
- Krishnan SV; Gullett BK; Jozewicz W. Sorption of elemental mercury by activated carbons. Environ. Sci. Technol. 1994;28:1506-1512.
- Li YH; Lee CW; Gullett BK. The effect of activated carbon surface moisture on low temperature mercury adsorption. Carbon 2002;40(1):65-72.
- Senior CL; Johnson SA. Impact of carbon-in-ash on mercury removal across particulate control devices in coal-fired power plants. Energy Fuel 2005;19(3):859-863.
- Thomas MD; Shehata A; Shashiprakash MH. The use of fly ash in concrete: classification by composition. Cement, Concrete, and Aggregates, CCAGDP, 1999;21(2):105-110.
- U.S. Environmental Protection Agency. Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units; Final Rule. Code of Federal Regulations, Title 40, Parts 60, 72 and 75; in the Federal Register v. 70, no. 95, May 18, 2005. Appendix K to Part 75 – Quality assurance and operating procedures for sorbent trap monitoring systems, pp 28695 – 28700.
- U.S. Environmental Protection Agency. Test Method for Evaluating Solid Wastes. Chapter 5. Miscellaneous Test Methods. Method 9060A: Total Organic Carbon. SW-846. 3rd Ed.
- Verein Deutscher Zementwerke e.V.; Trace Elements in German Standard Cements, 2001.
- Zhang FS; Nriagu JO; Itoh H. Mercury removal from water using activated carbons derived from organic sewage sludge. Water Res. 2005;39(2-3):389-395.
- Zhang J; Bishop PL. Stabilization/solidification of mercury-containing wastes using reactivated carbon and Portland cement. J. Haz. Materials 2002;92(2):199-212.

A

INSTRUMENTS, EQUIPMENT, AND SUPPLIES

	Equipment/Supplies	Description or Function	Material	Source
1	Flow control apertures	¼-inch diameter barbed tubing insert, orifice 200 micrometers	304 stainless steel; orifice created by laser	Lennox Laser
2	Manometer/pressure/vacuum gauge	Provided 3-digit LCD digital display of pressure difference between ballast chamber and atmosphere.	Model 06-664-21, Calibration traceable to NIST meter and compliant with ISO 17025. Accurate to ±0.3% of full scale at 25°C.	Control Company
3	Containers	20 liters, white with blue lid, Click-Pak™, concrete was sealed inside these containers during headspace sampling.	Polypropylene; white container with blue top; silicone sealant was used on all gas fittings and around normal sealing lip for top.	Curtec Nederland, from M.O. Industries (USA)
4	Air sampling pump	Vacuum pump, adjustable pressure, 22 L/min capacity, continuous duty.		Welch
5	Rotary tumbler	Mixer for dry powder ingredients of concrete	Model 65T, heavy-duty rotary tumbler, load capacity 65 lbs, modified.	Diamond Pacific Tool Corp.
6	Stainless steel barrel	Container in which dry powder ingredients were mixed by tumbling.	304 stainless steel, 15-inch o.d., 8 gallons, open head drum with lid, EPDM gasket, modified for use on tumbler	McMaster-Carr
7	Electric drill	Concrete mixing, rotated spiral impeller for mixing wet concrete in HDPE bucket.	500 rpm, high torque, 0.5-inch chuck.	Milwaukee Tool Co.
8	Spiral mixer blade	Spinning steel blade inserted into wet concrete to mix ingredients.	Modified, shaft diameter 7/16 inch, maximum 500 rpm.	Fabricated in Germany

	Equipment/Supplies	Description or Function	Material	Source
9	Timer	Records elapsed time in days, hours, minutes, seconds, 1/100 second. Operated in Mode IV, chronometer mode, battery powered.	Project timer MC2100	Cole-Parmer
10	Inline water trap, pulsation damper	Protects air pump from condensed water; damps any pulsations from pump; located in air line before air sampling pump.	10 L volume, thick-walled for vacuum use; cap has 3 ports for connection of gas lines; cap tightly sealed onto container with silicone adhesive	Cole-Parmer
11	Flowmeters	Rotameter, 150-mm, air, 374 mL/minute max. STP flow rate; accuracy $\pm 2\%$ full scale; calibration provided by manufacturer.	Aluminum construction, borosilicate flow tube; glass float; operating temperature -26 to 121 °C.	Cole-Parmer
12	Gas manifold	Enabled interconnection of air pump with multiple polypropylene containers.	Polypropylene manifold, 10 outlets, 3/8" NPT outlet, 1/2" NPT inlet.	Cole-Parmer
13	Gas lines	Silastic™ laboratory tubing, 6.4 mm i.d., 12.7 mm o.d.	High-temperature silicone.	Dow
14	Gas line clamps	White hose/tubing clamps firmly attached tubing to gas line fittings.	Acetal copolymer; nylon.	Cole-Parmer; Fisher Scientific
15	Iodated carbon traps	Air sampling traps for collection of mercury and mercury compounds	Glass cylinder filled with 2 partitioned, equal portions of iodated carbon	Studio Geochimica
16	Heating tape	Impeded water condensation on small IC traps. Operated at 60°C .	Flexible, silicone-insulated, electric, 52 watts, 120 VAC, with controller unit.	Barnstead-Thermolyne
17	Portland cement	Type I, Commercial grade	Complies with ASTM C150 and Federal Specifications; 42.6 kg bag.	Quikrete
18	Fly ashes (4 sources)	Two types	Fly ashes from coal combustion at electric power plants.	EPRI

	Equipment/Supplies	Description or Function	Material	Source
19	Sand	Commercial grade	22.7 kg bags	Quikrete
20	Coarse aggregate	All purpose gravel	Washed and graded, conforms to ASTM C-33 specifications; 22.7 kg bags	Quikrete
21	Thermometer	Blue spirit oil fill, -10° to 50°C, ±0.5°C accuracy, NIST traceable*, reference thermometers for air temperature	Ever-Safe™	Cole-Parmer
22	Water	High-purity, 18.2 MΩ-cm	Type I, ASTM D1193	MilliPore
23	Nitric acid	Trace metal purity, concentrated.		Fisher Scientific
24	Hydrochloric acid	Trace metal purity, concentrated.		Fisher Scientific
25	Muffle furnace	LOI measurements on fly ash	Model 3-130	Vulcan
26	Analytical balance*	Electronic, 0.1 mg sensitivity	100 g capacity	Mettler
27	Top Loading balance	Electronic, 0.1 g sensitivity	4.0 kg capacity	Mettler
28	Top Loading balance	Electronic, 0.1 g sensitivity	32.0 kg capacity, Explorer- E1M210	Ohaus
29	Bags, zip-lip	Protective container for exposed IC traps used in storage and shipment.	LDPE, assorted sizes	Cole-Parmer
30	Silicone adhesive	Silicone rubber adhesive sealant, general purpose	RTV6700, GE Silicones	Grainger
31	Sampler for powders	Enabled sampling of cement, sand, and coarse aggregate.	Powder sampler, multipro sector probe, 20 mL capacity	Cole-Parmer

* Traceable to physical standard or chemical standard reference material maintained by the National Institute of Standards and Technology of the U.S. Department of Commerce.

B

FLY ASH COMPOSITION DATA

Component	Units	Fly Ash Sample ID			
		CCS1	MER032	MER0357	NRT1019
Hg ^a	ppb	12.8	354	1372	1164
LOI ^a	%	0.043	1.59	1.96	4.44
Carbon (organic) ^a	%	0.054	1.40	1.89	3.91
Al ₂ O ₃	%	13.9	16.5	18.0	19.3
CaO	%	4.4	6.0	5.9	3.4
Fe ₂ O ₃	%	6.2	8.6	8.4	4.8
MgO	%	4.7	4.2	4.3	4.1
K ₂ O	%	1.9	0.6	0.6	0.6
SiO ₂	%	40.8	32.0	31.5	31.3
Na ₂ O	%	2.4	1.1	1.6	1.3
SO ₃	%	0.9	1.3	1.3	1.9
TiO ₂	%	0.5	1.1	1.1	1.5
Σ Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂	%	60.9	57.1	57.9	55.4
As	ppm	73	33	44	16
Ba	ppm	5190	4850	5230	5500
Cr	ppm	68	68	73	104
Cu	ppm	57	160	150	210
Mn	ppm	375	203	188	151
Ni	ppm	30	120	120	50
Sr	ppm	2790	2460	2740	3360
V	ppm	110	220	240	260
P	ppm	520	3470	4240	4400

C

MERCURY COLLECTED IN INDIVIDUAL TRAPS


Concrete	Batch	ng/trap				
		Normal	Extended Curing			
		28 Days	1 st Week	2 nd Week	3 rd Week	4 th Week
OPC	Blank	46.3	—	—	—	—
	1	159	—	—	—	—
	2	149	—	—	—	—
	3	179	—	—	—	—
CCS1	Blank	35.7	—	—	—	—
	1	379	—	—	—	—
	2	329	—	—	—	—
	3	430	—	—	—	—
NRT1019	Blank	23.1	—	—	—	—
	1	356	—	—	—	—
	2	— ^a	—	—	—	—
	3	381	—	—	—	—
MER0357	Blank	19.4	4.26	6.00	11.6	9.27
	1	1337	363	358	288	295
	2	1174	345	329	250	255
	3	1169	386	306	294	176
MER032	Blank	22.5	7.90	9.45	13.1	13.9
	1	1549	248	260	206	226
	2	1467	237	184	209	161
	3	1395	273	231	203	141

a. Rejected value (713 ng) attributed to air leak.

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

© 2006 Electric Power Research Institute (EPRI), Inc. All rights reserved.
Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

 Printed on recycled paper in the United States of America

The Electric Power Research Institute (EPRI)

The Electric Power Research Institute (EPRI), with major locations in Palo Alto, California, and Charlotte, North Carolina, was established in 1973 as an independent, nonprofit center for public interest energy and environmental research. EPRI brings together members, participants, the Institute's scientists and engineers, and other leading experts to work collaboratively on solutions to the challenges of electric power. These solutions span nearly every area of electricity generation, delivery, and use, including health, safety, and environment. EPRI's members represent over 90% of the electricity generated in the United States. International participation represents nearly 15% of EPRI's total research, development, and demonstration program.

Together...Shaping the Future of Electricity

Program:

Coal Combustion Product Use

1012696

ELECTRIC POWER RESEARCH INSTITUTE

3420 Hillview Avenue, Palo Alto, California 94304-1395 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com