

Mercury Leachability From Concretes That Contain Fly Ashes and Activated Carbon Sorbents

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EPRI Project Manager
K. Ladwig

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CITATIONS

This report was prepared by

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

Principal Investigators

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

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REPORT SUMMARY

This report presents new laboratory data on the leaching of mercury from concrete that contains fly ash and powdered activated carbon (PAC) sorbents used to capture mercury. The concretes studied during this project were made with fly ashes from lignite and subbituminous coal, including fly ashes containing PAC. Only very low levels of mercury—less than 5 parts per trillion—were leached from the fly ash concretes in both 18-hour and 7-day laboratory leach tests.

Background

Increased removal of mercury from power plant air emissions may result in higher concentrations of mercury in the fly ash, depending on the removal technology chosen. Because almost 15 million tons of power plant fly ash are used in concrete products annually, it is critical to understand the fate of mercury in fly ash used in concrete. Previous work funded by the Electric Power Research Institute (EPRI) examined the release of mercury to air from concrete containing fly ash and PAC. These studies demonstrated that minute quantities of mercury are released from concretes during the curing process, but more than 99.5% of the mercury was retained in concrete made with the fly 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.

Objective

- To investigate the release of mercury by leaching of concretes made from fly ashes derived from lignite and subbituminous coal, both with and without PAC injection for mercury capture

Approach

In this study, fly ash cylinders used in previous studies of mercury release to air from concrete curing were used. Five concrete formulations were tested: one with no fly, and four with 55% replacement of the portland cement with fly ash derived from either lignite or subbituminous coal. The cylinders were broken and crushed for leach testing. Leaching experiments were conducted using the toxicity characteristic leaching procedure (TCLP, EPA Method 1311) and the synthetic precipitation leaching procedure (SPLP, EPA Method 1312) to mimic the disposal conditions possible at a municipal solid waste landfill and at a construction and demolition landfill, respectively. Leachate samples were removed for analysis after 18 hours and again after 7 days. All experiments were conducted in a controlled laboratory environment and were designed to provide estimates of the release of soluble mercury forms from cured concretes with and without fly ash and sorbent material.

Results

Only very low levels of mercury were leached from the fly ash concretes at 18 hours and at 7 days, in both the TCLP and SPLP tests. Average mercury concentrations leached from fly ash concretes were less than 4.1 ng/L for all samples analyzed. In fact, levels of mercury leached from fly ash concretes were less than levels observed for ordinary portland cement (OPC) concrete in both TCLP and SPLP tests, perhaps because of the greater amount of carbon and possible lower permeability of the fly ash concretes. Based on the leach testing results, at least 99.98% of the mercury was retained in the fly ash concretes.

Small differences were observed in mercury leaching from the concretes made with the different fly ashes, suggesting that leaching rates for mercury were influenced by the presence of sorbents injected into flue gas prior to capture by air pollution control devices. No clear trends in the percent of mercury leached from concrete as a function of carbon content of the fly ash or initial mercury content of the concrete were observed. Nearly all of the mercury originally present in the fly ash is expected to remain in the concrete and not be released into aqueous media.

EPRI Perspective

Replacement of portland cement in concrete is the largest single beneficial use of fly ash, accounting for about 15 million tons of the fly ash produced in 2005. Changes in fly ash characteristics resulting from the 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 release to air and water from concrete containing fly ash—with or without PAC—are insignificant, accounting for less than 0.5% of the total mercury content of the concrete in all cases. These data show that higher mercury concentrations in fly ash should not inhibit the use of the fly ash in concrete. Separate research is underway to mitigate the negative effect of PAC on the air entrainment characteristics of fly ash in concrete.

Keywords

Fly ash
Powdered activated carbon
Mercury
Concrete
Ash use
Leaching

ABSTRACT

Reduction of mercury emissions from coal-fired utility boilers may be accomplished by the injection of chemically modified powdered activated carbon sorbents into hot flue gas streams followed by capture of the mercury-containing sorbent along with fly ash. Sorbent trapping of mercury 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 the mobility of mercury from fly ash concretes were investigated by measuring the leachability of mercury from concretes that contained different fly ashes and carbon-based sorbents. Standard EPA leaching methods—the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP)—were applied to each concrete. All experiments were conducted in a controlled laboratory environment and were designed to provide estimates of the release of soluble mercury forms from cured concretes with and without fly ash and sorbent material.

Very low levels of mercury were leached from the fly ash concretes at 18 hours and at 7 days in both the TCLP and SPLP tests. Average mercury concentrations leached from fly ash concretes were less than 4.1 ng/L for all samples analyzed, which is significantly below the EPA standard for drinking water of 2 µg/L. In fact, levels of mercury leached from fly ash concretes were less than levels observed for ordinary portland cement concrete in both TCLP and SPLP tests, perhaps because of the greater amount of carbon and possible lower permeability of the fly ash concretes. At least 99.98% of the mercury was retained in the fly ash concretes in all of the leachate samples analyzed.

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1

INTRODUCTION

Background

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.

Previous work funded by EPRI examined the release of mercury to air from concrete containing bituminous, subbituminous and lignite coal fly ashes and mercury sorbent material (Cheng et al. 2006, Cheng et al. 2004, Cheng et al. 2003, Golightly et al. 2005). These studies demonstrated that minute quantities of mercury are released to the gas phase from fly-ash concretes during the curing process, but more than 99% of the mercury was retained in concrete. However, previous work did not examine the potential leaching of mercury, and other elements, to liquid phases from concrete containing fly ash and mercury sorbent material. Such leaching might occur in a landfill environment after useful life of the concrete.

Program Objectives

The goal of this research was to determine whether levels of mercury in leachate solutions may be related to the type of coal fly ashes and carbon sorbents used in preparation of concretes. Our hypothesis was that the concrete mixture (constant matrix for various fly ashes) produces demonstrably different leachabilities of mercury that depend on the fly ash and associated sorbent.

General Approach

Mercury leachability was evaluated by standard methods EPA 1311, toxicity characteristic leaching procedure (TCLP), and EPA 1312, synthetic precipitation leaching procedure (SPLP). These leaching experiments were conducted for 18-hour and 7-day intervals. All parts of this investigation were performed within a conventional laboratory setting.

Experiments were conducted to observe mercury leachability from: 1) an empty sampling container to establish a baseline level of mercury (blank) for each concrete, 2) an OPC concrete that contained no fly ash to establish a baseline mercury release from 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

Concretes used in this study were prepared in 2005 from commercially available type I portland cement, sand, coarse aggregate, and coal fly ash (Cheng et al. 2006).

Fly Ash

One sample of fly ash (CCS1) used in preparation of concrete originated from a 1100-MW plant that burns ~7.4 million tons of lignite coal annually. This fly ash was collected from a unit with 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 from a unit with a cold-side ESP. 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.

The final, two fly ashes (MER032, MER0357) were from an 858-MW power plant 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 this study on mercury release from concretes is presented in Table 2-1.

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

	Fly Ash ID			
	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	ESPh	ESPh	ESPc
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

Concrete Preparation

The formulation used for preparation of each 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 on the cement and on each fly ash used in these experiments.

For each batch of concrete, dry components were first mixed in a polypropylene (PP) container by tumbling the closed container for 10 minutes. A weighed quantity of high-purity water (18 MΩ-cm) was then poured gradually into the powder mix as stirring occurred (open container). The resulting wet concrete mixture was then sealed inside the PP container. Following air sampling for mercury release conducted for an earlier study (Cheng et al., 2006), the concretes were stored at 23 °C with sampling ports blocked by polyethylene wrap (*Glad Press'n Seal*).

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

Preparation of Concrete Samples for Leaching

Concrete for leachate studies was removed from individual polypropylene (PP) containers with conventional tools. Lids had been tightly sealed onto the “twist-lock” PP containers by silicone adhesive. Thus, the top portion of each container was first removed by sawing through the container wall with an electrically powered reciprocating saw. Then, the concrete in each topless container was released onto stacked sheets of cardboard that rested on the laboratory floor by vigorously tapping the bottom of the inverted container with a 1.4-kg steel drilling hammer. The freed 20-kg body of concrete, shaped as a truncated cone, was tipped onto its side and split lengthwise by forceful application of a steel chisel (2.5-cm blade) driven by the 1.4-kg hammer. Then, pieces from the central portions of the resulting concrete masses were broken loose by the chisel. Some of these smaller pieces of concrete were transferred into two 0.1-mm thick polyethylene bags for further crushing and for storage. One bag of these concrete fragments (~1 kg) was set aside as a “backup” sample for possible later use. The other bag of concrete pieces (~0.8 kg) was subjected to further crushing (inside the bag) with the drilling hammer until all the resulting material passed through a 0.95-cm stainless steel sieve (ASTM E-11). A weighed portion, 100 g, of each pulverized sample was placed into a labeled 2-L FLPE bottle (Nalgene® fluorinated high-density polyethylene), and the FLPP-capped (Nalgene® fluorinated polypropylene closure) bottle was then wrapped in aluminum foil to reduce the possibility of photochemical reduction of any mercury potentially on particle surfaces. The balance of pulverized concrete was transferred from the stainless-steel sieve pan into a new polyethylene bag suitably labeled for future use. All ten concrete samples, including those from two containers of OPC, CCS1, MER032, MER0357, and NRT1019, were then ready to be subjected to leaching processes.

Preparation of Concretes for Bulk Analysis

A subsample of each of the 10 concretes was prepared from the dry coarse (< 1 cm) material made for leachate studies (EPA methods 1311 and 1312) as described above. Multiple quantities

(0.5 to 2 g) of each coarse sample were removed from the bulk material with a stainless steel spatula and combined (10 to 15 g) in a stainless steel shattering vessel. The powder and fragments produced by the shattering process were transferred into a small alumina mortar and hand ground with an alumina pestle to create a fine powder. This powder was poured onto a folded piece of glassine paper and then transferred into a labeled HDPE tube (15 mL capacity, Becton-Dickenson). Each capped container was placed into a zip-lock polyethylene bag for courier shipment to *Studio Geochimica* for analysis of mercury content.

Leaching Experiments

Leaching experiments were conducted using TCLP and SPLP test protocols to mimic disposal conditions possible at a municipal solid waste landfill and at a construction and demolition landfill, respectively. Concrete samples prepared as described above were subjected to standard leaching procedures described in EPA methods 1311 and 1312. Leachate samples were removed for testing after 18 hours and again after 7 days. Two sampling times were chosen in order to determine if the leaching of mercury increases or decreases with time.

The TCLP leaching of concretes followed the protocol described in USEPA Method 1311. A weighed portion, 100 g, of each pulverized (< 0.95 cm) concrete sample was subjected to 18 hours of agitation (28-rpm rotator) in 2 L of dilute acetic acid using a rotary agitator apparatus as shown in Figure 2-1. Following the 18-hour sampling, a leachate sample was collected and the closed 2-L bottles were returned to the rotator and agitated continuously for an additional 150 hours. Then, samples were again taken for determination of mercury concentration in the filtered (<0.7 μm) leachate. A reagent blank was included in the leaching process along with each group of concretes (OPC, CCS1, MER032, MER0357 and NRT1019). Each sample, ~200 mL, was placed into a trace metal-free glass bottle provided by *Studio Geochimica*. Thus, 24 leachate samples (5 samples run for 18 hrs and 7 d in duplicate and 4 reagent blanks) were generated in this part of our leachate study. All samples, including blanks, were sent to *Studio Geochimica* for mercury determinations by CVAFS.

The SPLP leaching of concretes followed the protocol described in USEPA Method 1312. Leachate samples were taken after 18 hours of agitation (adhering to Method 1312) and again after 7 days (total) of continuous agitation. The SPLP testing was carried out in a similar fashion as to the TCLP, except a mixture of nitric and sulfuric acid with an initial pH of 4.2 was used as the leaching fluid, per Method 1312. Similar to TCLP samples, portions of the filtered (<0.7 μm) samples were sent to *Studio Geochimica* for mercury determinations by CVAFS and a reagent blank was included in the leaching process along with each group of concretes.

For both TCLP and SPLP experiments, a 10-mL aliquot of each filtered leachate sample was placed into a 15-mL polypropylene tube and acidified with 0.5 mL concentrated nitric acid (Trace Metal grade; Fisher Scientific) to provide a solution for multiple-element analysis by ICP-AES.



Figure 2-1
Rotary agitation apparatus, driven by gear motor at 28 rpm

Measurements of Total Mercury and Elemental Composition

Mercury Analysis

Samples for mercury analysis were processed at *Studio Geochimica* by ultra-clean sample handling techniques in a laboratory known to be low in atmospheric Hg. Reagents, gases, and DI water were all reagent or ultra-pure grade, and previously analyzed for Hg and trace metals to ensure very low blanks.

Concrete leachate samples were oxidized using BrCl (5% v/v) in the original sample bottles and, when appropriate, transferred to glass bottles. Inorganic Hg standards were prepared by direct dilution of NIST certified NBS-3133 (10.00 mg/mL Hg) standard solution, and results were independently verified by the analysis of NIST-1641d (fresh water CRM, 200x dilution; 7,950 ng/L Hg). Mercury was then determined by cold vapor atomic fluorescence spectrometry (CVAFS) as a detector (Bloom and Fitzgerald, 1988). In the chart recorder output, a single peak of Hg(0) (all Hg compounds adsorbed to gold are released as Hg(0)) appears at about 1.0 minute retention time. All results were corrected both for the mean reagent blank and for instrumental drift. Generally, the total correction ranged from 2 to 15% of the raw measured values.

For pulverized concretes, individual samples of the listed components were reacted with an acid mixture (nitric, hydrochloric, and hydrofluoric acids) 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. Calibration of the fluorescence spectrometer system is achieved with NIST-traceable standard solutions.

Method detection limits of 0.08 to 0.55 ng/L were estimated for the CVAFS method used by *Studio Geochimica*. Spike recoveries of 96.4 to 103.9 percent were reported for Hg spike concentrations within the range 11 to 475 ng/L. Also, recoveries of 98.3 to 103.9 percent were reported for Hg determinations on NIST SRM 1641d (Mercury in Water) and NIST 2709 as shown in Table 2-3.

**Table 2-3
Mercury Recoveries for Spikes and NIST Standard Reference Material**

Sample Set	Sample Material	Recoveries for Mercury Spikes of 11 ng ^a , 16 ng ^a , 39 ng ^b , 53 ng ^c and 475 ng ^d (%)	Recoveries for Mercury in NIST-SRM 1641d ^e and SRM 2709 ^f (%)	Mercury Detection limit [3σ] (ng/L)
1	Leachate	100.0 ± 0.1 ^b	101.2 ^e	0.18
2	Leachate	109.3 ± 1.3 ^c	99.9 ^e	0.09
3	Leachate	96.4 ± 5.8 ^a	98.3 ^e	0.08
4	Concretes	99.8 ± 2.8 ^d	103.9 ^f	0.55

Elemental Analysis

The TCLP- and SPLP-leachate samples were analyzed for 30 elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in the OSU Environmental Engineering laboratory. Calibration of the Varian VISTA AX™ ICP spectrometer was achieved with five accurately diluted aliquots of a custom multiple-element standard solution and one blank. Calibration solutions were “matrix matched” with the sample solution. Matching was done for acetic acid and nitric-sulfuric acid, as appropriate. 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 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 are typically within 10% of actual concentrations. Detection limits are shown in Table 2-4.

Table 2-4
Detection Limits of Elements in Leaching Solutions

Element	Detection Limit
Silver	3 µg/L
Aluminum	10 µg/L
Arsenic	24 µg/L
Boron	0.01 mg/L
Barium	1 µg/L
Beryllium	1 µg/L
Calcium	1 µg/L
Cadmium	1 µg/L
Cobalt	4 µg/L
Chromium	2 µg/L
Copper	1 µg/L
Iron	1 µg/L
Potassium	0.1 mg/L
Lithium	5 µg/L
Magnesium	0.02 mg/L
Manganese	1 µg/L
Molybdenum	10 µg/L
Sodium	0.01 mg/L
Nickel	4 µg/L
Phosphorus	25 µg/L
Lead	10 µg/L
Sulfur	0.25 mg/L
Antimony	30 µg/L
Selenium	35 µg/L
Silicon	10 mg/L
Tin	10 µg/L
Strontium	1 µg/L
Titanium	1 µg/L
Thallium	20 µg/L
Vanadium	5 µg/L
Zinc	10 µg/L

3

RESULTS AND DISCUSSION

Mercury in Concrete Ingredients

Mercury was measured in each component as shown in Table 3-1. As described in previous work (Cheng et al., 2006), the mercury concentrations fall within an expected range for each of the components used in the concretes. In addition, mercury values measured by CVAFS for each concrete are shown in Table 3-2. Direct analysis represents the values measured by grinding concrete samples as described in Chapter 2. Ingredient analysis refers to values determined from summing the mercury in each component.

As indicated in Table 3-2, the mercury contents for each concrete measured by direct measurement are consistent with mercury contents determined from mercury measured in initial ingredients. This verifies previous work on mercury release from concrete during curing that shows between 99.7% and 99.98% of mercury in concrete ingredients is retained in concrete after curing. It is notable that these direct mercury measurements were performed many months after curing was complete. During this time, samples were maintained in closed polypropylene containers.

Mercury in Concrete Leachates

Average mercury concentrations and pH values for all concrete leachates in this study are summarized in Table 3-3. Reagent blank Hg concentrations have been subtracted from the total Hg values measured for concrete leachates. Average mercury concentrations in the leachate solutions ranged from 0.1 to 31 ng/L for the 18-hour samples and from <0.08 to 9.9 ng/L for the 7-day samples.

Table 3-1
Mercury and Carbon Concentration in Concrete Ingredients

Ingredient	Hg ($\mu\text{g}/\text{kg}$)	% Carbon
MER0357 Fly Ash	1372 \pm 37	1.89
NRT1019 Fly Ash	1164 \pm 19	3.91
MER032 Fly Ash	354 \pm 21	1.4
CCS1 Fly Ash	12.8 \pm 1.7	0.054
Cement	8.01	
Coarse Aggregate	7.42	
MicroAir100™	1.52	
Sand	1.37	

Table 3-2
Mercury Concentrations in Fly Ash Concretes ($\mu\text{g}/\text{kg}$)

Concrete	Direct Analysis ^a ($\mu\text{g}/\text{kg}$) (n = 2)	Ingredient Analysis ^b ($\mu\text{g}/\text{kg}$) (n=1)
OPC	4.6 \pm 0.6	5.2
CCS1	16.0 \pm 15.5	5.6
MER032	31.3 \pm 4.6	30.4
MER357	102 \pm 11	104.4
NRT1019	98.5 \pm 40.3	89.3

a. Total Hg determined by CVAFS analysis of solution prepared by microwave digestion of concrete sample in HNO_3 -HCl-HF mixture.

b. Summation of Hg measured for individual ingredients in Table 3-1 used in preparation of concretes. Hg determinations were by CVAFS analysis of solutions prepared by microwave digestion of individual concrete ingredients in HNO_3 -HCl-HF mixture.

Table 3-3
Mercury Concentrations^a and pH Values^b for Concrete Leachates

Concrete	TCLP				SPLP			
	18 hour		7 day		18 hour		7 day	
	Hg (ng/L)	pH	Hg (ng/L)	pH	Hg (ng/L)	pH	Hg (ng/L)	pH
OPC	31 \pm 20	7.6	9.9 \pm 1.6	10.6 \pm 1.1	8.4 \pm 3.8	12.3 \pm 0.1	3.6 \pm 0.6	12.4 \pm 0.0
CCS1	0.1 \pm 1.6	6.6	UDL ^c	6.8 \pm 0.2	1.1 \pm 0.3	11.9 \pm 0.1	0.2 \pm 0.3	12.0 \pm 0.1
MER032	2.4 \pm 1.6	6.6	1.7 \pm 1.7	7.0 \pm 0.4	1.9 \pm 0.3	11.8 \pm 0.1	0.6 \pm 0.3	11.9 \pm 0.1
MER0357	1.1 \pm 0.6	6.5	4.1 \pm 3.9	7.2 \pm 0.7	3.2 \pm 0.6	11.8 \pm 0.0	1.4 \pm 1.3	11.9 \pm 0.1
NRT1019	3.2 \pm 1.7	6.4	UDL	7.1 \pm 0.6	0.9 \pm 0.2	11.8 \pm 0.1	0.5 \pm 0.7	11.8 \pm 0.0

a. Average mercury concentrations (n=2) are corrected for reagent blank concentrations (n=2). Uncertainties are expressed as one standard deviation, that is, ± 1 .

b. pH values were measured for only one set of the 18-hour TCLP leachates.

c. under detection limit.

Elemental Composition in Concrete Leachates

Tables 3-4 and 3-5 show elemental release and pH of TCLP leachate solutions from OPC and fly ash concretes. Tables 3-6 and 3-7 show elemental release and pH of SPLP leachate solutions from OPC and fly ash concretes. Reagent blank concentrations of elements have been subtracted from all values.

Table 3-4
Release of Elements in OPC, CCS1 and NRT 1019 Concretes by TCLP Leaching

Element*	Unit	OPC		CCS1		NRT1019	
		18 hour	7 day	18 hour	7 day	18 hour	7 day
Al	µg/L	<10	80 ± 100	110 ± 30	<10	650 ± 900	<10
B	mg/L	0.13 ± 0.07	0.05 ± 0.06	2.68 ± 0.01	2.54 ± 0.07	1.38 ± 0.14	1.39 ± 0.14
Ba	µg/L	290 ± 40	280 ± 60	760 ± 20	420 ± 30	580 ± 80	340 ± 40
Ca	mg/L	1200	1100	1100	1000	1100	1000
Co	µg/L	<4	<4	7.5 ± 0.7	<4	12 ± 4	<4
Cr	µg/L	70 ± 7	76 ± 8	40 ± 6	<2	60 ± 40	20 ± 20
Cu	µg/L	<1	<1	2.5 ± 0.7	<1	16 ± 3	9 ± 4
Fe	µg/L	<1	<1	11 ± 7	4 ± 2	60 ± 70	17 ± 5
K	mg/L	27 ± 1	31 ± 1	28	28 ± 1	22.4 ± 0.7	22 ± 4
Li	µg/L	93 ± 4	82 ± 6	61 ± 3	59 ± 3	51 ± 3	47 ± 1
Mg	mg/L	92 ± 1	96 ± 3	50 ± 40	8 ± 11	83.5 ± 0.7	85 ± 4
Mn	µg/L	35 ± 50	<1	1100 ± 200	780 ± 60	900 ± 500	500 ± 400
Mo	µg/L	3.5 ± 0.7	9 ± 1	26 ± 1	31 ± 3	17 ± 6	24 ± 3
Na	mg/L	9.05 ± 0.2	10.2 ± 0.8	24.1 ± 0.7	23.3 ± 0.7	28 ± 1	26.8 ± 0
Ni	µg/L	26 ± 40	<4	79 ± 2	54 ± 4	84 ± 8	40 ± 20
S	mg/L	44.3 ± 0.7	40 ± 10	42.3 ± 0.7	38.8	53 ± 8	50 ± 7
Si	mg/L	17 ± 20	<10	36 ± 6	<10	14 ± 10	<10
Sr	µg/L	2000 ± 100	2000 ± 200	4800 ± 70	4600 ± 100	6400 ± 600	6000 ± 300
V	µg/L	28 ± 20	19 ± 20	11 ± 1	3 ± 1	14.5 ± 0.7	6.5 ± 0.7
pH	SU	7.6	10.6 ± 1.1	6.6	6.8 ± 0.2	6.4	7.1 ± 0.6

* Note: Ag, As, Be, Cd, P, Pb, Sb, Se, Sn, Ti, Tl, and Zn were below detection limits.

Table 3-5
Release of Elements in OPC, MER032 and MER0357 Concretes by TCLP Leaching

Element*	Unit	OPC		MER032		MER0357	
		18 hour	7 day	18 hour	7 day	18 hour	7 day
Al	µg/L	<10	80 ± 100	230 ± 150	<10	120 ± 180	<10
B	mg/L	0.13 ± 0.07	0.05 ± 0.06	1.23 ± 0.07	1.04 ± 0.07	1.23 ± 0.07	1.14 ± 0.07
Ba	µg/L	290 ± 40	280 ± 60	550 ± 90	350 ± 40	590 ± 70	400 ± 20
Ca	mg/L	1200	1100	1200	1000	1000	1000
Co	µg/L	<4	<4	18 ± 0	4 ± 1	16 ± 9	5 ± 5
Cr	µg/L	70 ± 7	76 ± 8	49 ± 5	2 ± 3	33 ± 15	4 ± 5
Cu	µg/L	<1	<1	8.5 ± 0.7	3.5 ± 0.7	11 ± 1	5.5 ± 0.7
Fe	µg/L	<1	<1	14 ± 10	7 ± 1	16 ± 14	11 ± 7
K	mg/L	27 ± 1	31 ± 1	21 ± 1	20 ± 2	21 ± 1	20 ± 1
Li	µg/L	93 ± 4	82 ± 6	63.5 ± 0.7	57	58 ± 2	53 ± 2
Mg	mg/L	92 ± 1	96 ± 3	89 ± 6	90 ± 3	89 ± 5	94 ± 1
Mn	µg/L	35 ± 50	<1	840 ± 10	500 ± 80	600 ± 400	400 ± 300
Mo	µg/L	3.5 ± 0.7	9 ± 1	22 ± 3	27 ± 5	28 ± 10	30 ± 10
Na	mg/L	9.05 ± 0.2	10.2 ± 0.8	22.6 ± 0	21.3 ± 0.7	31.1 ± 0.7	29.8 ± 0
Ni	µg/L	26 ± 40	<4	116 ± 0	70 ± 10	120 ± 30	60 ± 40
S	mg/L	44.3 ± 0.7	40 ± 10	50 ± 5	45 ± 6	50 ± 8	47 ± 8
Si	mg/L	17 ± 20	<10	23 ± 6	<10	15 ± 14	<10
Sr	µg/L	2000 ± 100	2000 ± 200	4800 ± 200	4500 ± 100	5200 ± 300	4850 ± 70
V	µg/L	28 ± 20	19 ± 20	16.5 ± 0.7	7 ± 0	15.5 ± 0.7	7.5 ± 0.7
pH	SU	7.6	10.6 ± 1.1	6.6	7.0 ± 0.4	6.5	7.2 ± 0.7

* Note: Ag, As, Be, Cd, P, Pb, Sb, Se, Sn, Ti, Tl, and Zn were below detection limits.

Table 3-6
Release of Elements in OPC, CCS1 and NRT 1019 Concretes by SPLP Leaching

Element*	unit	OPC		CCS1		NRT1019	
		18 hour	7 day	18 hour	7 day	18 hour	7 day
B	mg/L	0.01	0.01	0.09 ± 0.06	0.01	0.01	0.01
Ba	µg/L	320 ± 20	430 ± 20	450 ± 40	1200 ± 700	370 ± 40	430 ± 40
Ca	mg/L	470 ± 20	660 ± 10	145 ± 7	180 ± 40	120 ± 0	130 ± 0
Cr	µg/L	10 ± 0	5.65 ± 0.07	26 ± 5	25 ± 4	54 ± 0	60.5 ± 0.7
Fe	µg/L	1.5 ± 0.7	1	4 ± 3	3 ± 0	0.5 ± 0.7	0.5 ± 0.7
K	mg/L	18 ± 1	26 ± 0.00	15.5 ± 0.7	19.5 ± 0.7	12 ± 1	15 ± 1
Mo	µg/L	<10	<10	5 ± 4	10 ± 4	6 ± 1	24 ± 9
Na	mg/L	6.5 ± 0.3	9.3 ± 0.2	16 ± 1	18 ± 2	17.2 ± 0.7	18.7 ± 0
S	mg/L	1.7 ± 0	0.05 ± 0.07	7.3 ± 0.1	3 ± 3	12.0 ± 0.7	9.1 ± 0.2
Sr	µg/L	1150 ± 70	1899 ± 0	1200 ± 200	2500 ± 400	1550 ± 70	2700 ± 200
pH	SU	12.3 ± 0.1	12.4 ± 0.0	11.9 ± 0.1	12.0 ± 0.1	11.8 ± 0.1	11.8 ± 0.0

*Note: Al, Ag, As, Be, Cd, Co, Cu, Li, Mg, Mn, Ni, P, Pb, Sb, Se, Si, Sn, Ti, Tl, V, and Zn were below detection limits.

Table 3-7
Release of Elements in OPC, MER032 and MER0357 Concretes by SPLP Leaching

Element*	unit	OPC		MER032		MER0357	
		18 hour	7 day	18 hour	7 day	18 hour	7 day
B	mg/L	0.01	0.01	0.01	0.01	0.01	0.01
Ba	µg/L	320 ± 20	430 ± 20	400 ± 70	600 ± 200	400 ± 100	500 ± 100
Ca	mg/L	470 ± 20	660 ± 10	145 ± 7	150 ± 10	140 ± 10	140 ± 0
Cr	µg/L	10 ± 0	5.65 ± 0.07	32 ± 3	31 ± 4	32 ± 3	29 ± 5
Fe	µg/L	1.5 ± 0.7	1	4 ± 3	2.5 ± 0.7	1 ± 0	1.5 ± 0.7
K	mg/L	18 ± 1	26 ± 0.00	10.5 ± 0.7	15 ± 1	12 ± 0	16.5 ± 0.7
Mo	µg/L	<10	<10	2.5 ± 0.7	16 ± 4	10	23 ± 3
Na	mg/L	6.5 ± 0.3	9.3 ± 0.2	13.2 ± 0.7	15.2 ± 0.7	20.2 ± 0.7	22.2 ± 0.7
S	mg/L	1.7 ± 0	0.05 ± 0.07	9 ± 2	4 ± 2	10 ± 3	5 ± 2
Sr	µg/L	1150 ± 70	1899 ± 0	1200 ± 100	1200 ± 300	1300 ± 100	2000 ± 200
pH	SU	12.3 ± 0.1	12.4 ± 0.0	11.8 ± 0.1	11.9 ± 0.1	11.8 ± 0.0	11.9 ± 0.1

*Note: Al, Ag, As, Be, Cd, Co, Cu, Li, Mg, Mn, Ni, P, Pb, Sb, Se, Si, Sn, Ti, Tl, V, and Zn were below detection limits.

Discussion

Mercury Leachability From Ordinary Portland Cement Concrete

Very low levels of mercury were leached from the OPC concrete after 18 hours and 7 days, in both the TCLP and SPLP tests (see Table 3-3 and Figures 3-1, 3-2). Average mercury concentrations leached from OPC were less than 31 ng/L for all samples analyzed, which is significantly below the United States Environmental Protection Agency (USEPA) standard for RCRA hazardous waste limit is established for mercury of 0.2 mg/L. (USEPA, 2007)

Mercury release was greater from OPC concretes compared to concretes containing fly ash in both TCLP and SPLP tests. In the fly ash concrete samples, the majority of mercury was contributed from the fly ash. Previous studies have demonstrated that mercury primarily associates with the unburned carbon fraction of the ash (Hower et al. 2000). For the fly ash samples that contained mercury sorbent material, the mercury was largely associated with the sorbent. For the OPC concrete, the coarse aggregate was the primary source of mercury. The adsorption of mercury, either Hg(II) or Hg(0), on fly ash occurs via either physisorption, chemisorption, chemical reaction, or a combination of these processes (Galbreath and Zygarlicke 2000). Similar interactions control the binding of mercury to activated carbon sorbent (Li et al. 2002). This suggests that stronger associations between mercury and carbon, compared to the interactions between mercury and aggregate material, resulted in lower release of mercury during leaching. Replacement of cement with fly ash also generally results in concrete with lower permeability, lower sulfate resistance, and higher durability (King 2005). The lower permeability of the fly ash concrete possibly resulted in less reaction of the leaching fluid with the fly ash concrete, compared to the OPC concrete.

Greater release of mercury from OPC concrete was observed in the TCLP testing compared to during SPLP leaching. The data in Table 3-3 indicate that the pH of the leachate was significantly lower, at both 18 hours and 7 days, in the TCLP testing compared to the SPLP testing. The highest amount of mercury release for OPC concrete also had the lowest pH, suggesting that pH is important in controlling leaching. In general, mercury is expected to be more leachable at low pH, but this is also dependent on the mercury speciation in the solid and on the composition of the solid (Kim et al. 2003, Theis and Wirth 1977). Previous studies have also shown that adsorption of mercury on fly ash decreases as pH decreases (Feng et al 2004). In addition to solution pH, the acetic acid used in the TCLP testing is a more aggressive leaching agent. For example, acetate may participate in ligand-promoted dissolution reactions during the leaching process (Stumm 1992).

In comparing 18-hour leaching results to 7-day leaching results, both TCLP and SPLP testing showed a decrease in mercury from OPC concrete over the longer time period. This suggests that a fraction of the mercury released during the early stages was re-adsorbed onto components of the concrete or incorporated into secondary mineral phases formed from other leached elements.

Mercury Leachability from Concretes Containing Fly Ash

Similar to the results for OPC, very low levels of mercury were leached from the fly ash concretes at both 18 hours and 7 days, in both the TCLP and SPLP tests (see Table 3-3 and Figures 3-1, 3-2). Average mercury concentrations leached from fly ash concretes were less than 4.1 ng/L for all samples analyzed, which is significantly below the United States Environmental Protection Agency (USEPA) standard for drinking water of 2 µg/L. As mentioned above, leaching of mercury from fly ash concretes was less than the release for the OPC concretes in both TCLP and SPLP tests, perhaps due to the greater amount of carbon and possible lower permeability of the fly ash concretes. At least 99.98% of the mercury was retained in the fly ash concretes in all the leachate samples analyzed.

The leaching of mercury from fly ash concretes, during both TCLP and SPLP testing, was low and no clear trend was evident in comparing the two procedures. For most fly ash concretes the leaching of mercury during the two different leaching protocols was similar within the error of the measurements. An exception to this was the MER0357 concrete which showed greater release of mercury at 18 hours in the SPLP test compared to the TCLP test. The NRT1019 fly ash concrete, on the other hand, showed slightly greater leaching of mercury in the TCLP test at 18 hours compared to the SPLP leaching over the same time interval. Differences in final leachate pH between the SPLP and TCLP tests were greater for the fly ash concretes compared to the OPC concretes, but do not explain the results. Thus, differences in the leaching fluid and final leachate pH were apparently less important for the fly ash concretes, perhaps due to the very low levels of mercury released.

For the SPLP testing, mercury concentration in the leachate decreased with time for CCS1, MER032, and MER357. No statistical difference was observed in the leaching of mercury from MER357 and NRT1019 in the SPLP test at the different time intervals. As mentioned for OPC concrete, the decrease in mercury at the longer leaching times suggests a fraction of the mercury released during the early stages was re-adsorbed onto components of the concrete or incorporated into secondary mineral phases formed from other leached elements. For the MER0357 and NRT1019, the statistically similar concentrations of mercury at the two leaching times were potentially related to the higher carbon contents of these ashes. For the TCLP testing, no statistically significant difference was observed in leaching over 18 hours versus 7 days for any of the fly ash concretes.

Some differences in leaching between the ashes were observed during the SPLP testing. Comparing the different fly ashes after 18 hours of SPLP testing, NRT1019 and CCS1 fly ash concretes showed similar levels of mercury release, MER032 had higher mercury release compared to NRT1019 and CCS1, while MER0357 showed the highest mercury release. After 7 days in the SPLP test, CCS1 had the lowest mercury release, MER032 and NRT1019 had similar and higher mercury release compared to CCS1, and MER0357 again showed the highest mercury release. Previously, we have shown that gaseous mercury emissions from curing concrete were related to the carbon content of the fly ash, with release decreasing with increasing carbon content (Cheng et al. 2006). The carbon content of the different fly ash samples were determined previously (Cheng et al. 2006) and are reproduced in Table 3-1. When comparing the leaching of mercury from these concretes, however, no clear relationship between carbon content and mercury release was observed. While mercury release was lowest from the concrete containing NRT1019, which had the highest carbon content, mercury release increased with

carbon content for the other fly ash concretes. Also, mercury leaching did not directly correlate with the mercury content in the ashes. While mercury release increased with mercury content for CCS1, MER032, and MER357, the lowest mercury release was observed for the NRT1019 concrete, which had the second highest mercury content. These data suggest that mercury may be bound more strongly to the NRT1019 ash, resulting in lower release during leaching in the SPLP test, compared to the other ash samples. Little or no statistical difference was observed in the amount of leaching of mercury from the different fly ash concretes during the TCLP testing.

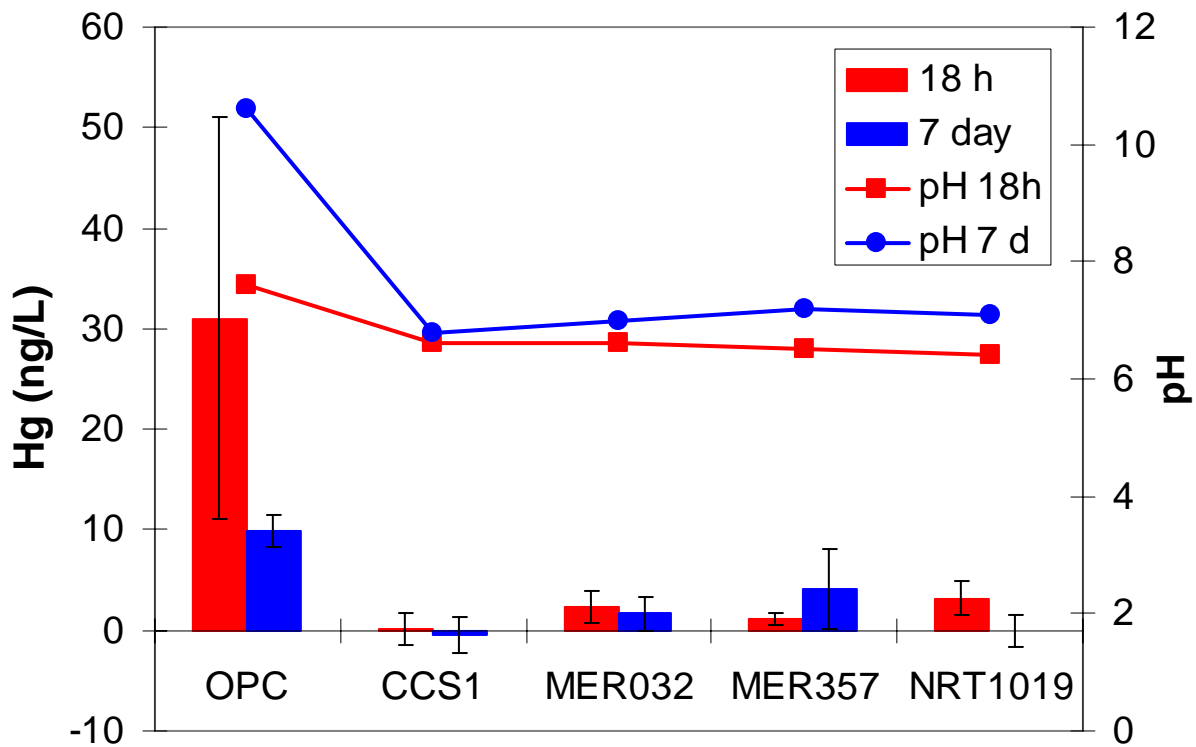


Figure 3-1
Mercury leached from concrete by TCLP and final pH of leached solutions

Leachability of Other Inorganic Elements

In the TCLP tests, calcium, potassium, magnesium, silicon, sulfur and vanadium show similar concentrations in the leachate of OPC and fly ash concretes. Fly ash concretes released more boron, barium, cobalt, copper, iron, manganese, molybdenum, sodium, nickel and strontium concentrations into solution during TCLP leaching than OPC concrete. Levels of aluminum in TCLP leachate were higher for the fly ash concretes at 18 hours, but lower after 7 days compared to OPC concrete. Chromium and lithium leached into solution more for OPC than fly ash concretes. All other elements analyzed (Table 3-4, 3-5) were below the limits of detection (Table 2-4). Levels of arsenic, barium, cadmium, chromium, and selenium were all below the established RCRA limits for the TCLP test.

In SPLP tests, levels of barium, chromium, sodium, and sulfur were generally greater in the leachate of fly ash concretes compared to OPC concrete. Similar levels of boron, potassium, molybdenum, and strontium were observed in OPC and fly ash concrete SPLP leachates. Levels of calcium were observed to be lower in fly ash concrete SPLP leachate than in OPC leachate. All other elements analyzed (Tables 3-6, 3-7) were below the limits of detection (Table 2-4).

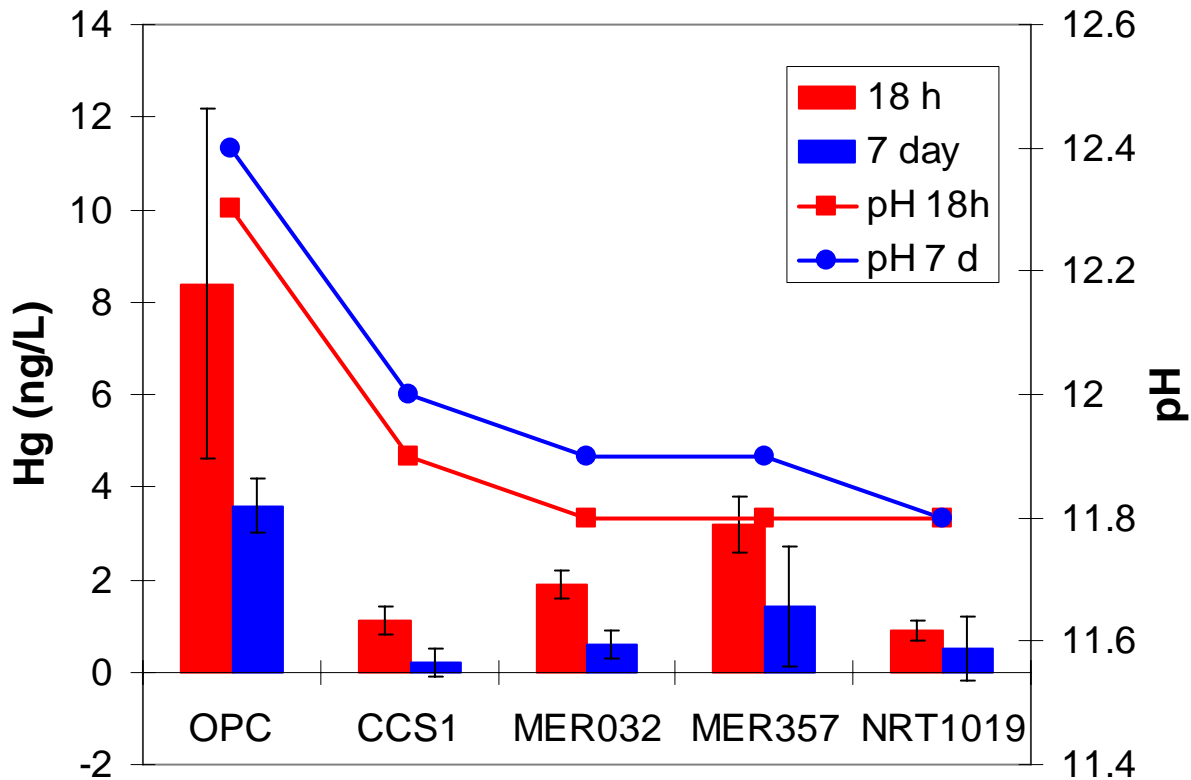


Figure 3-2
Mercury leached from concrete by SPLP and final pH of leached solutions

Comparing 18-hour leaching to 7-day leaching of OPC concrete, calcium and lithium showed a decrease in leaching with time, whereas potassium and molybdenum showed an increase in leaching with time. All other elements in OPC leaching solutions did not change over the time period monitored. However, for fly ash concretes, all elements measured showed either no statistical change with time or a decrease in release into the leaching solution at 7 days compared to 18 hours. Decreases in leached elements with time suggests that elements leached during early stages were reabsorbed onto concrete or incorporated into mineral phases from leached elements. Paired samples, MER032 and MER357, generally (with the exception of copper, sodium and lithium) do not show differences among elemental concentrations leached.

In general, higher levels of boron, calcium, aluminum, cobalt, copper, iron, lithium, magnesium, manganese, sodium, nickel, sulfur, silicon, strontium, and vanadium were seen in TCLP leachate compared to the SPLP tests. Similar levels of barium, chromium, potassium and molybdenum were observed in TCLP and SPLP leachate. No elements were observed at higher levels in SPLP

leachate compared to TCLP leachate. As mentioned with mercury leaching, the acetic acid used in the TCLP testing is a more aggressive leaching agent as it results in a lower final pH of the leachate solution and can also participate in ligand-promoted dissolution reactions during the leaching process (Stumm 1992). These effects likely explain the greater leaching observed in the TCLP testing compared to the SPLP.

4

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Conclusions from this investigation are based on laboratory measurements of leachable mercury determined by standard EPA methods. Measurements within a real-world environment may result in different leachability rates.

Concretes that contained various fly ashes were observed to retain at least 99.98% of the total initial mercury present in the concrete mixture. Differences were observed in mercury leaching of the different fly ashes, suggesting that leaching rates for mercury were influenced by the presence of sorbents injected into flue gas prior to capture by air pollution control devices. No clear trends in the percent mercury leached from concrete as a function of carbon content of the fly ash or initial mercury content of the concrete were observed. Nearly all of the mercury originally present in the fly ash is expected to remain in the concrete and not be released into aqueous media.

Recommendations

Field measurements at sites that utilize concretes containing either fly ash or fly ash–sorbent combinations are recommended as a source of practical information on the potential release of mercury.

5

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INSTRUMENTS, EQUIPMENT, AND SUPPLIES

Equipment/Supplies	Description or Function	Material	Source
Leaching containers	2 liters, dedicated to leaching experiments	FLPE container with FLPP closure (lid)	Nalgene
Rotary agitator	Capacity for 6 two-liter leaching containers; 28 rpm	Milled aluminum alloy, driven by electric gear-motor	CEEGS, The Ohio State University
Bottles	250 mL, cleaned for trace metal use by EPA methods	HDPE, glass	Fisher Scientific
Timer	Recorded leaching intervals. Operated in Mode IV, chronometer mode, battery powered	Project timer MC2100	Cole-Parmer
Filters	0.7 μ m fiber filter for filtration step in EPA methods 1311 and 1312	Filter funnel, F1525T	Environmental Express
Water	High-purity, 18.2 M -cm	Type I, ASTM D1193	MilliPore
Nitric acid	Trace metal purity, concentrated		Fisher Scientific
Hydrochloric acid	Trace metal purity, concentrated		Fisher Scientific
Acetic Acid	Trace metal purity, concentrated		Fisher Scientific
Analytical balance*	Electronic, 0.1 mg sensitivity	100 g capacity	Mettler
Top Loading balance*	Electronic, 0.1 g sensitivity	4.0 kg capacity	Mettler
Bags, zip-lip	Protective container for samples; used in storage and shipment	LDPE, assorted sizes	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.

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3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com