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Gaseous Mercury Release during Steam Curing of Aerated Concretes That Contain Fly Ash and Activated Carbon Sorbent

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Gaseous mercury released from aerated concrete during both presteam curing at 25 °C and steam curing at 80 °C was measured in controlled laboratory experiments. Mercury release originated from two major components in the concrete mixture: (1) class F coal fly ash and (2) a mixture of the fly ash and powdered activated carbon onto which elemental mercury was adsorbed. Mercury emitted during each curing cycle was collected on iodated carbon traps in a purge-and-trap arrangement and subsequently measured by cold-vapor atomic fluorescence spectrometry. Through 3 h of presteam curing, the release of mercury from the freshly prepared mixture was less than 0.03 ng/kg of concrete. Releases of total mercury over the 21 h steam curing process ranged from 0.4 to 5.8 ng of mercury/kg of concrete and depended upon mercury concentrations in the concrete. The steam-cured concrete had a higher mercury release rate (ng kg^{-1} h^{-1}) compared to air-cured concrete containing fly ash, but the shorter curing interval resulted in less total release of mercury from the steam-cured concrete. The mercury flux from exposed concrete surfaces to mercury-free air ranged from 0.77 to 11.1 ng m^{-2} h^{-1}, which was similar to mercury fluxes for natural soils to ambient air of 4.2 ng m^{-2} h^{-1} reported by others. Less than 0.022% of the total quantity of mercury present from all mercury sources in the concrete was released during the curing process, and therefore, nearly all of the mercury was retained in the concrete.

Introduction

Production of coal fly ash from electric power generators in the United States reached 66 million tons in 2006.[1] Approximately 17 million tons of this fly ash was incorporated into concrete, concrete products, grout, cement, and raw feed for clinker.[1] The silica in fly ash behaves as a pozzolan to form desired hydrated silicates important to the microstructure of concrete. Accordingly, fly ash has become an effective replacement for cement in portland cement concretes and for pulverized sands used in steam-cured aerated concretes. This significant application of fly ash continues to grow as the recognition of quality factors and cost benefits to concrete production using fly ash becomes more widespread.

Fly ashes contain mercury at total average concentrations of 0.1−0.2 mg/kg.[2] Mercury may be present in fly ash as both Hg^0 and Hg^{II}, with the primary forms of oxidized mercury being HgCl$_2$ and HgO.[3] The mercury present in fly ash primarily is adsorbed, both chemically and physically, onto surface sites of carbonaceous phases created from partially oxidized coal particles in the high-temperature environments of a combustion chamber and flue gas.[3−6] The presence of mercury in fly ash necessitates an understanding of the fate of mercury in products made from fly ash, including conventional fly ash concretes and aerated concretes.

Low-level emission of gaseous mercury from conventional fly ash concretes during air-curing at 40 °C has been reported.[7] For these concretes, fly ash replaced a significant portion (≤55%) of the cement, although it constituted only 7.8% of the total concrete mass. The fluxes of mercury from conventional fly ash concretes during air curing were similar to fluxes observed for natural soils. The release of mercury from these concretes was less than 0.1% of the total mercury content over an initial 28 day curing period, indicating that nearly all of the mercury was retained in the concrete.

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The release of mercury from aerated concrete containing fly ash has not been examined. Aerated concrete resembles a mortar in which fly ash may replace part or all of the pulverized sand. Subsequently, fly ash makes up a greater fraction of the total concrete mass in aerated concretes as compared to conventional fly ash concretes. Maximum temperatures applied in low-pressure stream curing of aerated concrete range from 40 to 100 °C, with optimal temperatures being in the 65–80 °C range,[8] significantly higher than the temperatures encountered during typical air-curing of conventional concretes. Also, the porosity of aerated concretes is significantly greater than conventional fly ash concretes. Thus, the collective features of composition, porosity, abundant water, and high-temperature curing support the possibility of gaseous mercury release from fly ash-containing aerated concretes.

Further, aerated concretes may incorporate significant amounts of fly ash containing mercury-laden powdered activated carbon. A likely technology for the reduction of mercury emissions from coal-fired power plants is the injection of powdered activated carbon (PAC) into the flue gas stream. The mercury-laden PAC is removed from the flue gas stream, along with fly ash, by either fabric filters or electrostatic precipitators. The presence of PAC in fly ash may significantly impact the use of fly ash in conventional concretes, because the carbon exerts a demand for polymer-based air entrainment additives, which ensure adequate levels of concrete porosity. In aerated concretes, however, the desired porosity is obtained by the addition of aluminum powder, which reacts during the curing process to form hydrogen gas.[9] As curing advances, the bubble volumes within the hardening concrete become fixed structural features and the hydrogen ultimately is displaced by air in the fully cured product. Unburned carbon and PAC do not significantly impact hydrogen generation, and therefore, there is greater potential for the incorporation of fly ash containing mercury-laden PAC into aerated concretes as compared to conventional fly ash concretes.

This research reports the first measured releases of gaseous mercury from a steam-curing process for aerated concretes that contain coal fly ash and activated carbon sorbent. All experiments, conducted in the laboratory, were designed to collect and measure any gaseous mercury released from steam-curing aerated concretes that contained different quantities of fly ash and mercury-loaded PAC (HgPAC). Comparisons were made between the mercury released from steam-curing aerated concrete to those from air-curing concrete and natural soils.

Experimental Section

Concrete. Ingredients used in concretes were type-III portland cement (Holcim), Chardon 110 silica sand (100–270 mesh, 99.5% silica, Fairmount Minerals), pulverized burnt lime containing a silica flow aid (Carmeuse), Class F[10] coal fly ash (Headwaters Resources), and 0.6 μm aluminum powder (99.9% pure, Aldrich). The fly ash, originating from an electrical utility that burns Eastern bituminous coal, served both as a replacement material for fine silica sand and as a principal source of mercury. Aluminum, iron, and silicon in fly ash were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES, Varian). The sum of the concentrations determined for $SiO_2 + Fe_2O_3 + Al_2O_3$ was 79.5%,
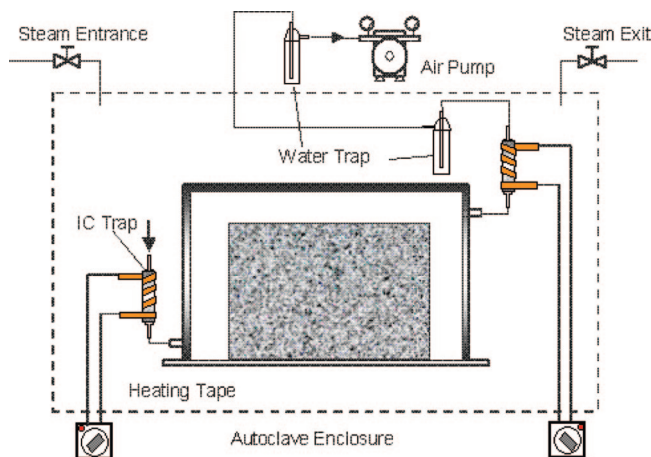

Figure 1. Diagram of the autoclave and sampling setup.

confirming the fly ash as American Society for Testing and Materials (ASTM) Class F in terms of minerals ($SiO_2 + Fe_2O_3 + Al_2O_3 > 70\%$). The average loss on ignition (LOI) value measured following ASTM C-311-00[11] was determined to be $3.17 \pm 0.11\%$ ($n = 7$). The total organic carbon content and the content of inorganic carbon were 2.30 ± 0.44 and $0.059 \pm 0.039\%$, respectively. Powdered activated carbon (PAC), Norit Americas DARCO-FGD, was used in select experiments and determined to have a Brunauer–Emmett–Teller (BET) specific surface area of 481 ± 7 m^2/g. Mercury-loaded PAC was prepared in the laboratory by exposing powdered activated carbon (DARCO-FGD) to air saturated with mercury from metallic mercury in a closed glass desiccator for approximately 6 weeks. High-purity water (18.2 MΩ cm, Millipore) was a component of all concretes prepared.

The mass of each ingredient, including water, cement, sand, fly ash, lime, Al powder, and PAC for each batch was based on Hu[12] and is shown in Table S1 in the Supporting Information. For each batch of concrete, dry components were first mixed in a closed 30 L 304 stainless-steel barrel by tumbling for 30 min. The resulting dry mix was then poured into preweighed high-purity water contained within a clean HDPE bucket. The wet mixture was mixed vigorously for approximately 2 min with a helical impeller at 450 rpm.

Individual samples of the concrete components were reacted with concentrated nitric acid inside a sealed PTFE vessel heated within a CEM microwave oven. Cold vapor atomic absorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectrometry (CVAFS) were used by a commercial laboratory to determine mercury concentrations in cement, sand, lime, loaded PAC, fly ash, and water by standard methods.[13] The 18.2 MΩ cm water (Millipore) used in all concretes consistently had mercury concentrations below the method detection limit (0.5 ppt).

Steam Curing. Steam curing of concretes was accomplished in a four-step process: (a) presteaming, (b) temperature rise, (c) maximum-temperature hold, and (d) soaking. A chemically inert sampling chamber was designed to provide rigid support for 20 kg of concrete during the curing process (see Figure 1). The rectangular chamber was constructed from 0.95 cm thick, cast aluminum alloy. High-temperature silicone adhesive sealant (Loctite Superflex Clear RTV) provided gastight seals along plate edges and around holes for screws. A perfluoro-alkoxyalkane (PFA) layer, nominally 76

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μm thick, was applied to all aluminum alloy surfaces (E.L. Stone Company, Norton, OH). All other exposed metallic surfaces were coated with a thin layer of white epoxy paint.

Mercury release measurements were made for five different sampling arrangements: (1) an empty sampling container to evaluate the emission baseline level of mercury in the experimental system, (2) an ordinary steam-cured concrete that contained no fly ash (OSCC) to establish an emission level for mercury that originated from the noncoal combustion byproduct components of the mix, (3) a concrete (FA50) for which fly ash replaced 50% of the sand, (4) a concrete (FA100) for which fly ash replaced 100% of the sand, and (5) a concrete (HgPAC) with 50% fly ash plus mercury-loaded PAC.

Presteaming. Each freshly prepared concrete mixture was first placed into a rectangular "mold" (61.0 × 20.3 × 22.9 cm) made of PFA-coated aluminum alloy. The mold was centered on the rectangular base of the sampling chamber and held in place by thumb screws. The exterior cover of the sampling chamber was then placed over the curing concrete, sealed at the base with Kapton tape. Mercury sampling at ambient temperature was conducted over the next 3 h. During this period, curing progressed to form a soft but physically stable, "cake" of concrete. After formation of the aerated concrete "cake," the sidewalls of the rectangular mold were removed (exposed surface area = 0.3 m²).

Steam Curing. After presteaming, the exterior box was positioned over the concrete "cake" and resealed to the base plate, creating a sampling volume of 34.1 L for steam and air to contact the curing concrete. The sampling chamber was then placed inside a carbon-steel autoclave (restored unit, McGill AirPressure Corporation).

Steam for curing concrete was supplied by an electrical boiler (Sussman Electric Boilers, model MBA3, 3 kW). Filtered city water (AquaPure AP51T filter) was supplied to the boiler through an automated pump to maintain a constant level of water in the boiler chamber. The operating pressure of the boiler was set at 80 psig. Steam flow into the autoclave chamber (approximate volume: 0.75 m³) passed through a compressed air-driven rotary valve controlled by a microprocessor-based ramping controller (Watlow Series 982 Controller) programmed to elevate temperature at set rates ranging from 0.23 to 0.56 °C/min.

Temperature in the autoclave chamber was increased from 21 to 80 °C over an interval of 5 h and 26 min. After the temperature reached 80 °C, the regulated supply of steam was continued for 1 h to maintain the temperature at 80 °C. At the end of the hour at 80 °C, the steam supply was switched off. Over the next ∼15 h, the ceramic-insulated autoclave cooled to near 27 °C. A typical temperature profile over the curing process is shown in Figure S1 in the Supporting Information. The pressure inside the steam chamber was maintained near atmospheric pressure by keeping open the major vent valve at the back of the autoclave chamber. Continuous sampling for gaseous mercury emissions from each curing concrete was conducted over the total interval of ∼21 h.

Purge and Trap Sampling. The sampling setup is illustrated in Figure 1. Air sampling pumps (AirCheck 2000, SKC), specially designed for controlled movement of air through small columns of collector particles, pulled steam–air through the headspace above curing concrete. Airflow through the sampling chamber was 0.350 L/min. Iodated carbon (IC) traps (Studio Geochimica and Frontier Geosciences) served as collectors for multiple mercury species in air.[14] An IC trap (either 100 or 500 μg Hg capacity) placed at the input port of the sampling chamber removed mercury from the steam–air stream that entered the chamber. This "mercury-free" steam passed over exposed surfaces of freshly mixed concrete to facilitate curing of the concrete and transport gaseous mercury released by the concrete into a small IC trap (100 μg of Hg capacity) located at the exit port of the chamber. Iodated carbon traps are accepted by the Environmental Protection Agency (EPA) for collection of mercury in air-sampling methods applied to stationary

stacks[13] The collection efficiency for Hg by these traps has been reported to be greater than 90%.[15,16]

Inside the autoclave, IC traps were kept at temperatures in the range from 90 to 100 °C by silicone-insulated heating tape (52 W) to inhibit water condensation while maintaining adsorption capabilities for mercury.[15] Two PTFE water traps were placed inline, one after the sampling IC trap and another just before the pump, to protect both the sampling IC trap and the air pump. When an IC trap was removed from an air-sampling line, each end of a sampling trap was immediately blocked with a PTFE plug and placed into a zip-lock polyethylene bag.

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, WA, using published methods.[15] The limit of detection for mercury in the IC traps is 0.3–0.7 ng/IC trap.

Controls. In control experiments, "background" mercury was determined as a "system blank" by pulling steam–air through the empty sampling chamber. The average value for the system blank, adjusted to the sampled gas volume, was subtracted from the quantity of mercury collected on a trap in each sampling experiment on concrete.

Quality Assurance. Several steps were taken to ensure the quality of measurements for the ultratrace levels of mercury observed in these experiments. Measured recoveries of mercury from spikes (25 and 50 ng of Hg) of the blank ranged from 90.0 to 92.3%. Recoveries for determinations of mercury in National Institute of Standards and Technology (NIST) 1641d Standard Reference Material (SRM) were in the range of 103.5–103.8%. SRM 1641d, mercury in water, was certified by NIST to contain mercury at the concentration of 1.590 ± 0.018 mg/kg.

Mercury collected on "cleanup" traps (n = 7 analyzed) ranged from 20.4 to 70.5 ng, thus demonstrating that the 100 or 500 μg capacity of cleanup traps was more than adequate to remove mercury from steam entering the curing chamber. Moreover, measurements of mercury collected on partitioned segments of iodated carbon in several individual traps indicate that no significant breakthrough from segment A to B occurred (≤2%) for any sampling experiment. Thus, potential mercury contamination from steam–air intake was trapped effectively before entering into the sampling chamber that contained the curing concrete. The quantity of mercury collected in the intake (cleanup) IC trap during the extended sampling period was 2.5 ng. Measurement of mercury in the "B" segment of the intake IC trap showed little breakthrough of mercury during this extended sampling interval.

Results and Discussion

Mercury in Concrete and Concrete Ingredients. The concentrations of mercury in ingredients used in concretes investigated here were similar to those published by other researchers for comparable materials (Table 1).[17-19] The mercury concentration measured for the fly ash, 72.3 ± 4.9 μg/kg, was within the range but below the median for fly ashes generated from combustion of Eastern coals. The concentration of mercury in Eastern coal fly ash ranges from 20 to 4200 μg/

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Table 1. Mercury Content in Concrete Ingredients and Aerated Concretes

	water	cement	sand	fly ash	burnt lime	HgPAC	Al powder	total mercury in concrete	mercury concentration in concrete
ingredients				(μg/kg)					
this work	$>0.5 \times 10^{-3}$	3	1.7	72	1.8	1880	7		
other studies[17−19]	N/A	60	20−100	13−651	5−460	1090−963 900	N/A		
concrete				(μg/batch)					(μg/kg)
OSCC	<0.004	13.3	11.9	0	1.9	0	0.14	27	1.4
FA50	<0.004	13.3	6.0	261	1.9	0	0.14	283	14.2
Hg PAC	<0.004	13.3	5.8	261	1.9	186	0.14	468	23.4
FA100	<0.004	13.3	0	523	1.9	0	0.14	538	26.9

Table 2. Release of Mercury from Steam-Curing Concretes

concrete	description	Hg release		Hg release rate
		ng/kg	%	ng kg^{-1} day^{-1}
OSCC	0% fly ash	0.4 ± 0.6	0.03 ± 0.05	0.46 ± 0.69
FA50	50% fly ash	1.9 ± 0.4	0.013 ± 0.003	2.2± 0.5
HgPAC	FA50 plus Hg-loaded PAC	2.5 ± 1.1	0.011 ± 0.005	2.9 ± 1.3
FA100	100% fly ash	5.8 ± 1.3	0.022 ± 0.005	6.6± 1.5
FA100 ext	release over 10 days following curing for 100% fly ash	0.073	0.005	0.0073

kg, with a median of 192 μg/kg.[20] A recent study found the mercury content of fly ash from a variety of coal types ranged from 13.0 ± 0.2 to 650.6 ± 6.8 μg/kg without activated carbon injection (ACI) and 37.7 ± 1.3 to 1529.6 ± 1.1 with ACI.[21] The total quantity of mercury in each batch of concrete, estimated as the sum of mercury contributions from all ingredients, including water, aluminum powder, sand, cement, burnt lime, fly ash, and activated carbon, ranged from 27 to 538 μg (Table 1). These data provided a basis for estimates of the initial mercury concentrations, 1.4−26.9 μg/kg, in each batch of steam-cured concrete. For every batch of fly ash concrete, fly ash and mercury-loaded PAC were the major sources of mercury. The total initial mercury concentration in different concrete mixtures increased with each rise in the quantity of fly ash in the concrete. FA100 concrete had the highest initial mercury concentration because of the large fraction of fly ash. Because of the addition of mercury-loaded PAC to the FA50 mixture, the HgPAC concrete had the second highest mercury concentration.

Mercury Release. *Presteam Stage.* During air sampling over the initial 3 h of curing at ambient temperature, the quantities of mercury released into 0.045 m³ of air were at or below the limit of detection (0.28−0.65 ng/trap). Thus, mercury release was less than 0.03 ng/kg of concrete for the 3 h presteam curing interval.

Steam-Curing Stage. During the steam-curing process, quantities of mercury collected in IC traps ranged from 21.9 to 169 ng. An average steam−air volume of 0.44 ± 0.02 m³ was sampled during a curing interval of 21 ± 1 h for the set of experiments. On the basis of these data and the initial mercury content of each concrete, the mercury release and mercury release rate were determined. Each release rate was corrected for the average (*n* = 2) mercury contribution from the sampling chamber, referred to as the "system blank". Uncertainties associated with average release rate values are expressed as one standard deviation for three separate curing-sampling experiments.

Average mercury releases (Table 2) during steam curing for

FA50 and FA100 concrete were 1.9 ± 0.4 and 5.8 ± 1.3 ng/kg, respectively. In comparing the HgPAC concrete to FA50 concrete, the mass release of mercury from HgPAC concrete was 2.5 ± 1.1 ng/kg, which is somewhat higher than the mass release of mercury from FA50 concrete. The control concrete (OSCC) had the lowest mass release of mercury (0.4 ± 0.6 ng/kg). As mentioned previously, all mercury releases from the initial 3 h curing at ambient temperature were at or below the limit of detection for CVAFS, and thus, the mercury releases discussed here are solely from the steam-curing interval.

The percent release of mercury for each concrete is also shown in Table 2. The percent releases for mercury from the OSCC control and FA100 were higher than those from the FA50 and HgPAC concretes. The average percent mercury releases from OSCC and FA100 concrete are approximately twice those from FA50 and HgPAC. The HgPAC concrete had the lowest percent release of all of the concretes examined.

The data in Tables 1 and 2, plotted as a function of initial mercury content in Figure 2, indicate that the average mercury released from steam-curing concrete correlated with the initial concentrations of mercury in the concretes. Application of analysis of variance (one-sided ANOVA) to the mean mercury release data sets for the four concretes, followed by Dunnett's
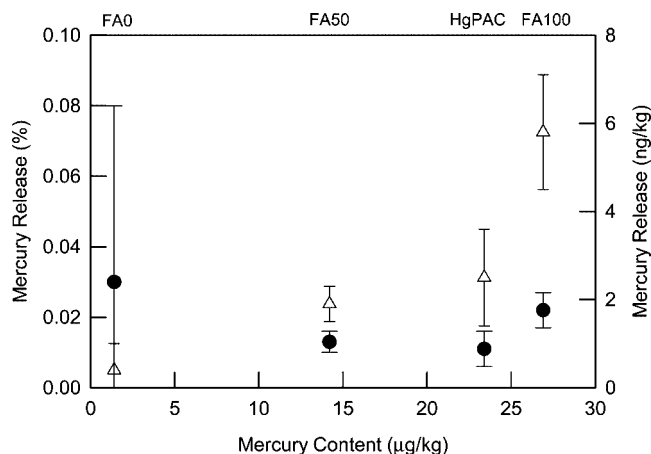

Figure 2. Mercury release from steam-curing aerated concretes as a function of initial total mercury content from all ingredients [Average percent releases (left y axis) are depicted by filled circular points, and average mass releases (right y axis; ng of Hg/kg of concrete) are represented by open triangles. Error bars show 1 standard deviation for *n* = 3].

(20) U.S. Environmental Protection Agency (EPA). Wastes from the combustion of coal by electric utility power plants, EPA/530-SW-88-002, Report to Congress, U.S. EPA, Washington, D.C., 1988.

(21) U.S. Environmental Protection Agency (EPA). Characterization of mercury-enriched coal combustion residues from electric utilities using enhanced sorbents for mercury control, EPA/600/R-6/008, U.S. EPA, Washington, D.C., 2006.

multiple comparison test of treatments versus the control (α = 0.1), revealed that the mean release for FA100 was significantly greater than that for the OSCC (OSCC < FA100). Mean releases for FA50 and HgPAC appeared similar and bordered on being statistically different from the mean release for OSCC. Thus, from a practical perspective, the relationship between mean releases of mercury was summarized: OSCC ≤ FA50 ≤ HgPAC < FA100.

Extended Sampling. Mercury release from a single batch of FA100 concrete was monitored at ambient laboratory temperatures over 10 days immediately following steam curing. Only 1.45 ng of mercury was collected in the outlet IC trap for 5.0 m^3 of air sampled. The calculated mercury release over this extended sampling period was 0.073 ng/kg (0.005% of initial mercury content). Therefore, the release over this extended time period was an order of magnitude less than the release observed during steam curing, indicating that the majority of the low mercury release occurred during the steam-curing interval.

Mercury−Concrete Interactions. Mercury is collected on the surface of fly ash from flue gas during coal combustion. A portion of the mercury originating from coal is elemental and a portion is oxidized to Hg^{II}.[3] Both Hg^0 and Hg^{II} interact with ash particulate surfaces where reactive chemical species, oxidation catalysts, and activated sorption sites are available in the postcombustion process. 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.[3] In general, physisorption is a weak, dipole-induced dipole interaction, while chemisorption involves the formation of a specific chemical bond between mercury and the sorption surface. Hall et al.[22] tested the adsorption mechanisms of mercury on fly ash between 20 and 400 °C and found both physical and chemical sorption mechanisms are significant at the lower range of temperature. These previous studies suggest that physically sorbed mercury may be released from fly ash concrete under conditions in our experiments (20−80 °C), which would explain an increase in the mercury emission rate as the amount of added fly ash increased.

Although the initial concentration of mercury in the concrete containing Hg-loaded PAC was higher than the FA50 concrete, the release of mercury was statistically similar (α = 0.1) as that released from the FA50 concrete. This observation may indicate a stronger adsorption of mercury on PAC than on fly ash, which is consistent with our previous work examining air-cured concretes.[7] Similar to the situation for fly ash, adsorption of mercury by activated carbon at ambient temperatures has been suggested to be a combination of chemisorption and physisorption, where chemisorption is prevalent at higher temperatures.[23] With increasing temperatures, physisorption of mercury is decreased because of the reduction of intermolecular forces between carbon and adsorbed mercury molecules. Krishnan et al.[24] suggested that the activated sites causing Hg^0 adsorption in the activated carbon may include oxygenated organic species and functional groups containing inorganic elements, such as chlorine or sulfur.

The sulfur content of PAC used in our experiments was 1.8%. Sulfur impregnated in PAC is known to bind mercury by

forming chemical bonds.[25] For the conditions to which our curing concretes were subjected, that is, 80 °C and a 0.35 L/min flow of purified steam−air, some of the mercury physically adsorbed by other components of the concrete may be released and subsequently form chemical bonds with carbon surface functional groups (chemisorption). Thus, some of the physically adsorbed mercury may be released, but mercury chemisorbed onto activated carbon is much less likely to be released.

Water is adsorbed onto activated carbon surfaces by means of hydrogen bonding.[26] Adsorbed H_2O molecules become secondary adsorption centers as the H_2O vapor pressure increases and begins to compete with the oxygen complexes on carbon surfaces that form the primary adsorption centers. Chemisorption of Hg^0, that is, bonding at reactive surface sites associated with oxygen, perhaps lactone and carbonyl groups,[6] is a dominant process at ~27 °C for moisture-containing activated carbon.[23] In addition, unburned carbon in fly ash is expected to chemisorb Hg^0 similarly. Thus, Hg^0 emitted from other physisorbed sites in the steam-curing concrete process may be adsorbed onto these secondary adsorption centers. Further, as the hydration of cement and lime proceeds, a buildup of gel membrane outside the carbon pores has been postulated. Once in the solidified form, activated carbon particles will retain most of the adsorbed mercury by forming a barrier outside of the activated carbon particles.[27] Chemisorption of Hg^0 to carbon in the presence of H_2O and formation of a gel membrane outside carbon pores may account for an overall low release rate of mercury in our experiments.

The potential for release of mercury from curing concrete appears to be controlled by (a) porosity of cement pastes, which is dependent upon microstructural features that change during hydration[28,29] and (b) the relatively weak bonding responsible for attachment of mercury species to diverse sites on the carbonaceous phases in fly ash. In newly prepared conventional concretes, a pathway for transport of gas- and aqueous-phase chemical species is the macropores, which are wide tubular pores between cement grains. As the initial setting of cement paste continues, exothermic hydration of calcium aluminates, in the presence of gypsum, produce colloidal hydrated sulfoaluminates that give rise to interhydrate porosity generally known as mesoporosity. Further progression of hydration produces the calcium silicate hydrates (C−S−H) that form rigid gels common to microporosity. These gels consist of very small particles that tend to aggregate into layer formations of a few micrometers thickness. Distances between layers are less than 2 nm, and surface areas of the layers range from 100 to 700 m^2/g. Each of these tubular interconnected pores change and diminish the transport pathway, as hardening of the cement progresses to form fully hydrated mineral phases (approaching the composition $C_3S_2H_3$) within the paste.[7] Prior to the setting time, when cement forms a rigid structure having low compressive strength, only curing temperatures above 80 °C affect the pore size distribution.[28] For cement cured for 24 h at 84 °C, Parcevaux[28] reported 0% macroporosity, 39% mesoporosity, and 61%

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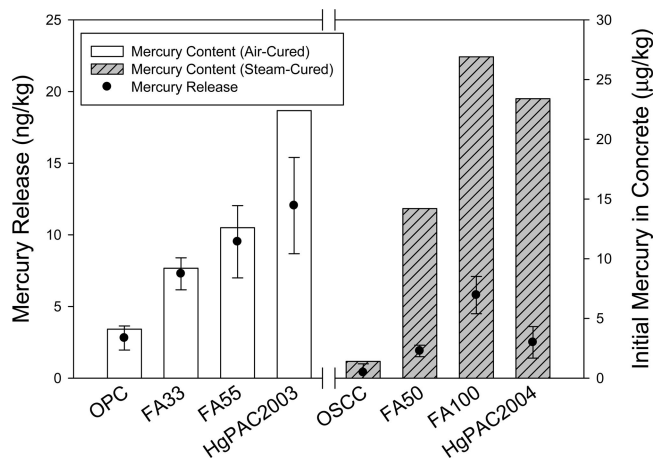
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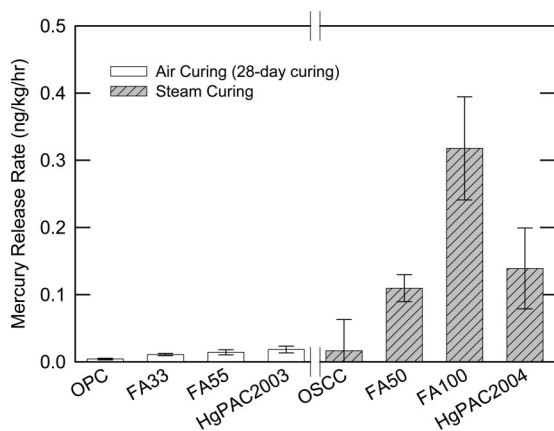**Figure 3.** Mass release of mercury (ng/kg) from air- and steam-cured concretes and initial mercury content (μg/kg).

Figure 4. Mass release rate (ng kg^{-1} h^{-1}) of mercury from air- and steam-cured concretes.

microporosity, where the percentages are based on total porosity, that is, free plus trapped. This lack of macroporosity, therefore, may explain the reduction in mercury release during the extended sampling period after steam-curing measured for the FA100.

Comparison of Mercury Release from Steam- and Air-Cured Concrete. The release of mercury from steam-cured concrete was compared to the release from air-cured conventional fly ash concrete from a previous study (Figure 3).[7] In our previous work, we examined mercury release during air-curing of ordinary portland cement concrete (OPC) and portland cement concrete in which 33% (FA33) and 55% (FA55) of the cement was replaced with fly ash. A concrete in which 33% of cement was replaced with fly ash containing mercury-laden powdered activated carbon (HgPAC 2003) was also investigated. As shown in Figure 3, the mass mercury release was generally lower for the steam-cured concrete as compared to the air-cured samples.

It should be noted, however, that the total curing time for the steam-cured samples was considerably less (∼24 h) than for the air-cured experiments (28 days). The mercury release rates for steam- and air-cured concretes are shown in Figure 4. These data demonstrate that the mercury release rates (ng kg^{-1} h^{-1}) are significantly higher for the steam-cured concretes containing fly ash and mercury-loaded PAC. The steam-cured concrete without fly ash had a mercury release rate similar to those observed for the air-cured concrete samples. Importantly though, the data in Figures 3 and 4 indicate that both the mass

release and release rates of mercury from all of these concretes were low, with the majority of mercury being retained in the concrete.

Normalizing the release over the curing time (Table 2) shows a higher release rate for steam curing over ordinary curing. The higher release rate is consistent with our hypothesis that the higher curing temperatures and greater porosity of the steam-cured concrete would facilitate more mercury release. However, because curing occurs more rapidly with steam curing, entrapment of mercury happens faster. In addition, the higher curing temperature favors chemisorption onto secondary sorption sites over physisorption of mercury released from initial sorption sites. Therefore, although the release rate is higher for steam curing, the total amount of mercury released during the curing period is less than for ordinary curing.

Mercury Flux from Steam-Cured Concrete. To better understand the significance of these results with respect to atmospheric levels of mercury, it is useful to compare the flux of mercury from steam-cured concrete to the fluxes from natural soils. Zehner and Gustin extensively characterized the flux of mercury from a variety of Nevada soils and serves as a basis for comparison. The average flux of mercury from Nevada soils was reported to be 4.2 ± 1.4 ng m^{-2} h^{-1}.[30] For the steam-cured concrete examined in the current study, the mercury flux from exposed surfaces (0.496 m^2) during the steam-curing interval ranged from 0.77 ng m^{-2} h^{-1} for the ordinary steam-cured concrete (not containing fly ash or PAC) to 11.1 ng m^{-2} h^{-1} for FA100. These represent fluxes from steam-cured concrete to mercury-free air, while flux measurements from natural soils typically examine the flux to ambient air. Therefore, the mercury fluxes for steam-cured concrete presented here should be considered as upper-limit values rather than typical values representative of field conditions. These data indicate that fluxes of mercury from steam-cured concrete to mercury-free air are comparable to natural fluxes of mercury from soils to ambient air. Field measurements at industrial sites that routinely perform steam-curing of concretes containing either fly ash or fly ash–sorbent mixtures are needed for practical information on the release of mercury for this widespread approach to accelerated curing.

The global use of fly ash in the production of aerated blocks was estimated as 6.5 million tons per year,[31] which translates into global mercury emissions of approximately 0.1 kg or less per year. Few data are available on the quantity of fly ash used in the production of steam-cured aerated concrete in the United States. A preliminary survey of the industry suggests the use of fly ash for this application in the United States is low at the current time. However, as an upper limit estimate, if the 66 million tons of fly ash produced in the United States in 2006 were to be used entirely in aerated concrete, the results from this study suggest the total release of mercury during steam curing would be 1 kg/year or less. Our longer term data suggest that substantially lower mercury emissions would be realized during the service life of the concrete block. It should be noted, however, that these

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calculations do not consider potential mercury release upon disposal of the crushed block in landfill environments.

Conclusions

The results presented here demonstrate that the release of mercury during steam curing of aerated concretes containing fly ash and mercury-laden activated carbon was less than 0.022% of the total quantity from all sources in the concrete. The majority of the low release of mercury occurred during steam curing, with substantially less release observed following the curing interval. The presence of PAC in the concrete appears to more tightly bind the mercury or act as a sink for released mercury from other components of the cellular concrete, reducing the total amount released. While low, the rate of release of mercury during steam curing of aerated concrete was greater than the rate of release observed during air curing of ordinary portland cement concretes containing fly ash and PAC, presumably because of the higher temperature during the steam-curing process and greater porosity of the aerated concrete. However, the total release of mercury from aerated concretes was less than from ordinary portland cement concretes because of the shortened curing time. The low release rates of mercury from aerated concretes were similar to those observed from natural sources. These results indicate that nearly all of the mercury incorporated into aerated concretes upon addition of fly ash and mercury-laden PAC sorbent is retained in the aerated concrete upon steam curing.

Supporting Information Available: Table S1, concrete formulations for 20 kg batches of steam-cured aerated concrete; Figure S1, temperatures of FA100 concrete block and steam chamber during curing of concrete. This material is available free of charge via the Internet at http://pubs.acs.org.

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