Health and Safety Risks of Fly Ash Cement Mixtures

Antoinette "Toni" Stein, PhD
(Environmental Engineering –Air Quality Control.)

Coal fly ash contains Mercury and poses a potential health and safety risk.
Coal ash intrinsically contains specified amounts of mercury, and other heavy metals. Numerous studies and datasets show that coal fly ash contains quantities of mercury and other toxic compounds[1]. US EPA documents that mercury is emitted from coal burning power plants at a rate of 1.600E-5 Lb per Million BTUs Heat Input[2], [3]. In the US many studies have been funded through the Coal Ash Research Center (CARC) at the University of North Dakota[4] studying the mercury content of coal fly ash. The Canadian Electricity Association (CAE) data indicates mercury concentrations ranging from <0.002 to 1.221 ppm in fly ash[5]. Hassett et al. reported mercury concentrations ranging from <0.01 to 2.41 ppm in samples of fly ash from full-scale coal-fired power plants from all ranks of U.S. coal[6], [7] , [8].
Because coal fly ash is exempt from hazardous waste regulations it is not required to be labeled or to undergo any formal toxicity characteristic testing for its mercury or other toxic content. Mercury concentrations in fly ash vary due to the variations in mercury

---

[1] XAFS investigation of Hg sorption on fly-ash , Hutton et al.
http://www.flyash.org/1999/ashpdf/hugg1.pdf ,
http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/emissions.html
For those unfamiliar, the toxics come from the coal itself and from the combustion process where they are contained or entrained in the particulate fly ash that is captured in flue gas air pollution control devices.

[2] See US EPA's WebFire database of emission factors,
http://cfpub.epa.gov/oarweb/index.cfm?action=fire.main

[3] http://www.energyjustice.net/coal/wastecoal/epa-icrdata.html
[4]See the University of North Dakota's website on Hg in CFA at,
http://www.undeerc.org/carrc/html/Mercury.html.
[5] http://www.ceamercuryprogram.ca/EN/Program%20Overview/Mercury_revised.pdf

[6] Hassett, D.J.; Pflughoeft-Hassett, D.F.; Laudal, D.L.; Pavlish, J.H. Mercury Release from Coal Combustion By-Products to the Environment. In Proceedings of the Specialty Conference on Mercury in the Environment: Minneapolis, MN, Sept. 15–17, 1999; Air and Waste Management Association: Pittsburgh, PA, 1999; pp 485–493.
6. Hassett, D.J.; Heebink, L.V.; Pflughoeft-Hassett, D.F. Potential for Mercury Release from Coal Combustion By-Products. In Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference; Arlington, VA, Sept 9–12, 2002; Paper A2-02.
7. Pflughoeft-Hassett, D.F. Overview of EERC Studies in Evaluating CCR Products and Identification of Major Data Gaps. Agenda for Coal Combustion Residues Workshop; Research Triangle Park, New Jersey, January 10–11, 2001.
8. Zhenglong, L.; Hwang, J.Y. Mercury Distribution in Fly Ash Components. In Proceedings of the Air and Waste Management Association 90th Annual Meeting and Exhibition; Toronto, Ontario, Canada, June 8–13, 1997.
[7] http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html
[8] http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html

found in the geological coal deposits and due to the different types of air pollution control systems installed at each coal burning power plant in the US which absorb varying quantities of mercury from the coal combustion.

Mercury (Hg) is a toxic compound that in its elemental inorganic form is a liquid at room temperature and is readily volatilized due to its vapor pressure. As a result it represents a significant inhalation exposure risk. Mercury is listed as a persistent bio-accumulative toxic (PBT) compound and poses significant risk to human health for exposures that exceed daily regulatory limits. Mercury and mercury compounds are on the list of chemicals known to the state of CA to cause reproductive toxicity. OEHHA lists inorganic Hg and its compounds on CA's chronic toxic compound list and has a very low inhalation reference exposure level 0.09 mg/m^3 and it is listed on OEHHA's acute REL list with a Severe severity effect rating and is listed as having a reproductive/developmental toxicity endpoint[9]. Coal fly ash also contains other heavy metals and significant quantities of crystalline silica, a human carcinogen.

Mercury content in Coal fly ash is increasing due to phase in of new clean air rules.

US EPA acknowledges that coal fly ash contains mercury and other quantities of toxics and that the mercury can be potentially released into the air. During rulemaking of the new Clean Air Mercury Rule (CAMR) US EPA acknowledged that their Rule was expected to result in significant reductions in mercury emissions from coal-fired power plants and might affect the quantity of mercury in fly ash and may require further assessment of mercury content in ash and the issue[10]. –Today CAMR is now in its implementation phase and we are waiting for the US EPA report and reassessment of this issue. As air emissions are made cleaner by injection technologies, the ash as a consequence gets more concentrated with toxics-conservation of mass.

New air rules have changed what is in fly ash.

Many power plants have air pollution control devices installed. Some use injection of dry flue gas desulfurization (FGD) sorbents and chemicals to capture SO_2 and NO_x gas pollutants to maintain compliance with the NAAQS. These powder sorbents are captured and mixed in with fly ash and included within compounds called fly ash. Fly ash with FGD sorbents and chemicals are not marked or labeled to distinguish them from other fly ash.

EERC reports that calcium-based FGD systems are expected to remove oxidized mercury from flue gas at varying efficiency levels. Mercury has been found to be in fly ash FGD mixtures in concentrations of 39 and 70 ppm in sorbent materials that are mixed together in coal fly ash as reported by DeVito and Rosenhoover[11] and DeVito[12] for two FGD materials. Recently, the EERC reported that the mercury content of fly ash and FGD

[9] http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html

[10] http://www.epa.gov/epaoswer/osw/conserve/c2p2/use/concerns.htm#mercury

[11] DeVito, M.S.; Rosenhoover, W.A. Flue Gas Hg Measurements from Coal-Fired Boilers Equipped with Wet Scrubbers. In Proceedings of the Air and Waste Management Association 92nd Annual Meeting and Exhibition; St. Louis, MO, June 20–24, 1999.

[12] DeVito, M.S. The Effect of Low-NOx Burner Operation on Mercury Emissions, Speciation, and Removal at a Coal-Fired Boiler Equipped with Wet FGD. Presented at the 17th Annual Pittsburgh Coal Conference, Pittsburgh, PA, Sept 11–14, 2000.

collected during tests of mercury control technologies are significantly increased; samples containing a total mercury concentration as high as 120 ppm were reported.

FGD in fly ash is reported to adversely affect cement's structural properties.
"Fly ash" is a catch phrase. In truth fly ash includes more than coal combustion ash. It also includes any chemical or sorbent injected into the gas stream for pollution control of coal combustion. In a recent article discussing how the new air pollution rules are affecting fly ash, it is revealed that injection of chemicals used to capture airborne pollutants to comply with new air pollution rules cause changes in the composition of fly ash that result in interactions with concrete inhibiting it from hardening properly.[13] Dave Goss, executive director of the American Coal Ash Association is quoted there as saying "If in exchange for clean air they have to dispose of material -- that's the challenge. The only option may be putting it in a landfill." and Bruce Dockter, a research engineer with the Energy and Environmental Research Center (EERC) at the University of North Dakota acknowledges that "You're replacing an air problem with a land problem…" this new hardening problem raises a new structural issue that could significantly result in a safety risk. Because there is no labeling or characterization requirements it is difficult or impossible to know if fly ash quantities being used contain the chemicals that result in hardening problems. Quality control, labeling, and specific characterization must be instituted prior to CARB promoting or promulgating any measures to add fly ash to cement.

Leach tests do not assess the comprehensive risk of exposures outside of landfills.
Leaching in aqueous solutions is the primary area where testing has been conducted because it has been required by the Water Board to comply with some land discharge requirements for its land disposal. Leach testing is designed to show that toxic compounds will not leach out of a landfill and pose threat to waterways, or drinking water sources. It is not the appropriate test to determine if mercury will be emitted into air when it is placed in a school use scenario or other indoor building applications. Leach tests do not comprehensively screen and check the health and safety risks that may be encountered in the use of cement fly ash mixtures outside of lined landfills in schools, homes, and offices. Prior to promulgating or promoting any measures to use or add fly ash in cement these mixtures and all of their foreseeable uses should be carefully assessed for their health and safety risks.

Mercury emissions from fly ash cement mixtures into air in their foreseeable uses such as in foundations, floors, walls, ceilings, in buildings and other products made with these mixtures such as swimming pools, baths, tubs, docks, countertops needs to be properly assessed. Tests need to be conducted and assess fugitive dust issues during handling for production of these mixtures and the mobility of mercury in the cement matrix under conditions of salt water, chlorine, contact with moisture and mastics, full range of temperatures, erosion, wind, sun etc. The State of California should not be required to fund these studies but instead the State should propose necessary testing required by fly ash generators to ensure that their product is safe. The producers should be responsible for all of the safety testing not the State of California.

[13] http://biz.yahoo.com/ap/070826/clean_air_dirty_land.html?.v=3

Leach tests do not directly address volatilization and mobility of mercury from concrete-ash mixtures into indoor air. Leach tests are not air emission tests and are designed only to look at aqueous leaching under landfill scenario and not classroom scenarios. The mercury leach tests do not consider scenarios where there may be thin surface layers of moisture on concrete-ash mixtures nor do they consider chemical interactions from the case where concrete ash mixtures are used in combination with flooring adhesives for applications with resilient or carpet flooring. What is missing from published literature is indoor air chamber test data to verify that there is are no toxic mercury emissions under the conditions of heat, moisture and combination contact with mastics coming off of the concrete/ash products? Without this data there is no sound argument that these building materials are mercury emission free and safe for use.

On going statistical leach testing and air emission testing for the full range of mercury coal fly ash quantities is needed to properly assess the risks of coal fly ash. There presently is no voluntary screening testing conducted for quantification of mercury in coal ash to certify that it poses no threat of being released into the air or leached out. Additionally, California has more stringent hazardous waste toxicity test leach tests called (STLC). There is limited data available on the leaching of mercury under STLC testing

Mercury may be released to into air from fly ash cement mixtures.

The DOE/NETL in a memo dated April 2006 discusses some of the issues of mercury in coal fly ash. DOE/NETL clearly recognizes that there are multiple means for mercury to be released from coal fly ash. The research shows that mercury may be transported via aqueous transport via direct leaching, 2) vapor-phase release at ambient and elevated temperatures, and 3) biologically induced leaching. Their research includes different testing protocols for each of these modes. On page 4 it is confirmed that the environmental impact studies are not yet complete. The 2005 memo states, "DOE/NETL is carrying out research directed at evaluating the fate of mercury in coal combustion by-products and developing ways to ensure that the mercury is not released." [14]

Release mechanisms of mercury from coal fly ash is complicated by the different mercury species that are inherent in coal fly ash and by chemical interactions that may occur within concrete -coal fly ash mixtures.

Energy and Environmental Research Center at the University of North Dakota has studied the mercury content of a large number of coal combustion fly ash samples submitted by industry representing various types from different coal mining areas in the US.[15] Mercury has been found to be released from coal fly ash into air at room and at

---

[14] DOE Memo found at: http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/pubs/NETL%20Clarification%20on%20Mercury%20FINAL%200406.pdf also see their website for their Hg program, http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/index.html

[15] Information http://www.undeerc.org/carrc/html/Mercury.html

elevated temperatures. Specifically, EERC studies have reported mercury releases from fly ash[16].

Importantly mercury was also found to be emitted into air from ash that is wet from water[17]. Experiments that included the addition of water to the samples exposed to air resulted in increases in the mercury flux.

The release of mercury from coal fly ash mixed with FGD has been evaluated on a limited basis. Results of thermal desorption tests indicate that mercury is thermally released from sorbents at temperatures considerably below the peak temperatures observed for fly ashes. Significant percentages of the mercury captured on the saturated sorbents were reported to be released upon heating above 135°C (275°F).

Pozzolonic concrete is NOT INERT: adhesives and mastics are reported to react
Documented studies showing that some adhesives used to secure carpet and flooring when in contact with concrete have resulted in concrete reactions and have facilitated migration of compounds in the concrete matrix despite claims that concrete is a pozzolonic inert material. These studies confirmed volatile emissions from concrete. Although theses studies do not provide any specific data about toxic emissions from concrete-ash mixtures or about mercury emissions they do provide important corollary information that concrete is NOT inert and has the potential to react with other substances and chemicals it comes in contact with and may emit toxics from its matrix into the air that may cause significant exposure risks to humans. There is no scientific data supporting claims that "pozzolonic" forces in concrete coal fly ash mixtures are adequate to bind mercury in the concrete matrix and prevent it from being emitted into the air during use. There is some data to substantiate that concrete-coal fly ash mixtures subjected to moisture, heat, and cracking may emit toxics including mercury into air.

Develop standards and require peer reviewed environmental tests.
The literature reveals that emissions of mercury ARE found for coal fly ash, and are potentially increasing due to the new CAMR requirements for mercury capture. Precaution therefore should be taken. Sufficient and adequate scientific information for concrete coal fly ash mixtures are needed to assure that its use in buildings and schools are safe. Actions are needed to partner with the fly ash centers and industry groups to develop emission and content standards for industry to use to conduct emission testing

---

[16] Hasset et al. report Mercury release from fly ash from their experiments documented in their MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION Final year Annual report for the U.S. Department of Energy National Energy Technology Laboratory , June 2005, http://www.undeerc.org/carrc/Assets/Yr2AnnualRpt.pdf

[17] Gustin, M.S.; Ladwig, K. An Assessment of the Significance of Mercury Release from Coal Fly Ash. *J. Air Waste Manage. Assoc*. **2004**, *54*, 320–330.

and provide data on the vapor phase mobility of mercury and other toxics from flyash under foreseeable use scenario conditions of moisture, heat and contact with mastics used in applications on slab. Cement fly ash mixtures have NOT to date been adequately and comprehensively screened and tested for their health and safety risks to humans. Although some cement fly ash mixtures containing mercury have been studied the scope of the past testing is limited and does not include the full range of proposed uses in the scope of this proposed measure.

Conduct a full independent peer and stakeholder reviewed LCA to look at GHG and H&S impacts.

True greenhouse gas (GHG) emission reductions have not yet been shown for "fly ash additions in cement" for California. Estimates indicate GHG emissions are in fact HIGHER when back to back comparisons are conducted that include emissions from cradle to shipping fly ash to CA. CARB should conduct independent peer and stakeholder reviewed LCA analysis to assess the GHG emissions and the health and safety impacts.

Prohibit fly ash cement mixtures uses in CA.

The use of concrete fly ash mixtures should be prohibited in schools, and on surfaces where there is direct contact with children's skin. (i.e. gyms, pools, playgrounds, kindergarten rooms as flooring); on surfaces where there may be food preparation in homes, kitchens; it should not be used in combination with phthalate or soy based mastics or carpet backings in regions where flooding may occur or other high water intrusion probabilities exist; It should not be used as an under floor or over floor surface where there is heating pipes where high local temperatures might be experienced in the concrete-coal ash mixture.

"Fly ash additions in cement" are not a sustainable measure they perpetuate and prolong coal burning activities and disadvantage the viability of emerging alternative energy developments.