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Improved Leach Testing for Evaluating Fate of Mercury and Other Metals from Management of Coal Combustion Residues

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ABSTRACT

Coal-fired power plants, the largest domestic source of atmospheric mercury emissions in the U.S., are also a major emission source of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and particulate matter (PM). In response to the U.S. Environmental Protection Agency's (EPA's) Clean Air Interstate Rule (CAIR) and concern for mercury emissions, multi-pollutant control technologies are being installed at U.S. coal-fired power plants to reduce emissions of concern. Multi-pollutant control technologies include the use of fabric filters, electrostatic precipitators (ESPs), oxidizing chemicals, sorbents, and wet scrubbers. Pollutants of concern are being transferred from the flue gas to the fly ash and other air pollution control residues. The properties of fly ash, scrubber residues, and other coal combustion residues (CCRs) may change as a result of implementation of multi-pollutant control technologies. The characteristics of these residues and how they are managed will influence whether mercury and other pollutants being controlled at the power plant are being released later through cross media transfer.

In 2006, EPA issued the Mercury Roadmap, which describes progress to date in addressing mercury sources and identifies priority activities for addressing remaining mercury risks. A key scientific question to be addressed is: What is the fate of mercury and other metals from the management of residues resulting from the implementation of multi-pollutant control technologies at coal-fired power plants? Meeting the commitment made in the Mercury Roadmap is challenging due to a wide range of CCR management practices and lack of data that allows comparison between CCR materials and these management practices. This paper provides an overview of ongoing research to evaluate the fate of mercury and other metals from the management of CCRs through either beneficial use or land disposal.

INTRODUCTION

A survey by the American Coal Ash Association (ACAA) reported that 125 million tons of CCRs were produced in 2006 with about 43% used in commercial and engineering applications (ACAA, 2007). EPA's Coal Combustion Products Partnership (C^2P^2) and the ACAA have a goal of reaching 50% utilization by 2011.

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Fly ash, flue gas desulfurization (FGD) gypsum, and other air pollution control residues are targeted for reuse because of their wide range of applications (Figure 1).

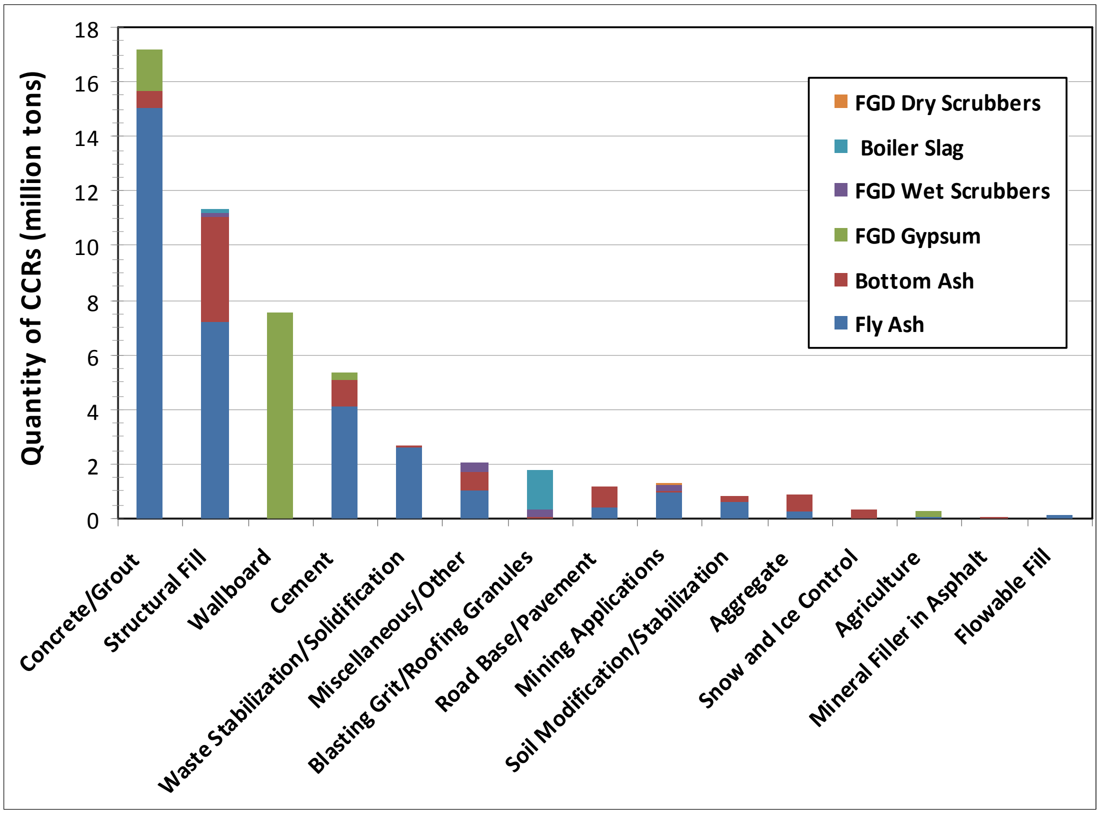

Figure 1. Uses of CCRs based on 2006 Industry Statistics (ACAA, 2007).

The properties of fly ash and other CCRs can make them suitable as replacements for materials used in a wide range of products including cement, concrete, road base, toothpaste, and wallboard. Recycling CCRs helps conserve natural resources and energy, as well as decreases the amount of CCRs being land disposed. However, as changes occur in control technologies at coal-fired power plants, the effects on CCR composition and its ability to be used in commercial applications are uncertain. With the use of controls to reduce emissions of mercury and other pollutants from the flue gas, these pollutants will be found in the air pollution control residues primarily the fly ash and scrubber residues.

The types and combinations of multi-pollutant controls are important in understanding how the characteristics and behavior of CCRs are impacted. Existing coal-fired power plants will retrofit to meet changing air pollution control requirements. Typical air pollution control configurations for NO_x, PM, and SO_2 control include selective catalytic reduction (SCR), followed by ESPs and wet scrubbers, respectively (Figure 2). These technologies are also capable of removing mercury from the flue gas.

A major change in air pollution control at coal-fired power plants will require wider use of wet scrubbers in response to EPA's CAIR. (EPA, 2005a) Most of the material produced will be in the form of gypsum. Currently, 80% of the 12 million tons of gypsum being made at power plants is utilized (ACAA, 2007). Of the FGD gypsum that is utilized (i.e., 9.6 million tons), 80% (or 7.6 million tons) is used in the production of wall board and 19% (1.8 million tons) in production of cement and concrete (ACAA, 2007). Industry experts indicate that the amount of FGD gypsum being produced may double (and some say triple). The gypsum market for making wall board has been reported to be at saturation. Therefore, other uses of FGD gypsum are needed to prevent landfilling of this material.

One of the major interests for utilizing FGD gypsum is as a soil amendment. Gypsum has been found to improve crop production and to reclaim sodic soil. The chemical composition of gypsum ($CaSO_4 \bullet 2H_2O$) is reported to improve soil quality and plant nutrition by supplying calcium and sulfur, two main elements found in gypsum. The properties of wet scrubber residues can differ depending upon the type of sorbent or catalyst being used (e.g., lime or limestone, various Mg compounds, and ammonia).

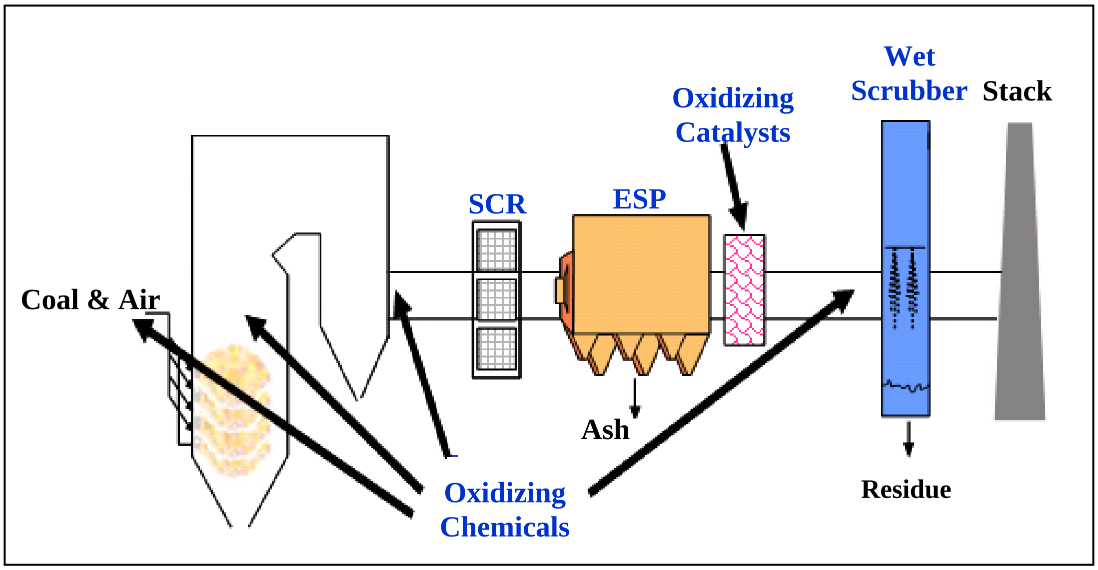

Figure 2. Multi-Pollutant Control Technologies at Coal-Fired Power Plants (EPA, 2002a; EPA 2005b).

Activated carbon is effective at capturing mercury but its use may alter the characteristics of the fly ash so that it is not suitable for some beneficial use applications (2002a, 2005b). The type of oxidizing catalyst used in reducing air pollutants can also change the characteristics of CCRs. The choice of technologies will vary from plant to plant and within a plant depending upon the coal rank, boiler configuration, existing controls in place, cost, and other considerations. Therefore, it is difficult to make generalizations without having the necessary data that encompass the range of CCRs produced due to the implementation of multi-pollutant control technologies.

A variety of environmental conditions are encountered in different beneficial use applications that range from mining applications, structural fill, road base, snow and ice control, soil modification/amendment, wallboard, and toothpaste (Ash at Work, 2008). The National Academy of Science (NAS) stated in the 2006 report on "*Managing Coal Combustion Residues (CCRs) in Mine*s" that variables affecting the behavior and potential impacts of CCR placement are attributed to the chemical and physical properties of CCRs (NAS, 2006). The NAS expressed concern about the use of single point pH tests on which most CCR management decisions are currently based because the single point pH test does not accurately reflect conditions under which the material is managed. The NAS cautioned that decisions regarding CCR placement should not be based on broad generalized tests that do not consider the potential for environmental release of metals under the field conditions where the material is managed. Although the main focus of the NAS report was mine applications, the concerns apply more broadly.

EPA released a risk assessment for coal combustion waste disposal in 2007 indicating that significant risk can occur if these CCRs are managed in unlined landfills or surface impoundments (EPA, 2007). In 2001, EPA determined that coal combustion waste does not warrant regulation as a hazardous waste. EPA also determined that coal combustion waste does warrant regulation under Subtitle D of the Resource Conservation and Recovery Act (RCRA). However, no rules have been proposed. Some states, however, are requiring liners for new land disposal units being permitted.

The need for more rigorous leach testing of CCRs has been recommended by EPA's Science Advisory Board (SAB) (SAB, 2003), as well as by the NAS (2006). For example, pH is known to influence leaching of metals. Use of sorbents such as ammonia, lime, or limestone can alter the pH of the residue. The amount of liquid infiltration occurring during management of the residues (either during land disposal or beneficial use) is an important consideration. The form of the material (such as particle size and homogeneity) is also of consequence when characterizing a material's leachability. Therefore, to ensure that management decisions are protective of human health and the environment, characteristics of CCRs (in response to changes in air pollution control technologies being implemented across the U.S.), as well as the field conditions under which CCRs are managed are important.

Leach Testing

As a first step in conducting this research, a review of available data was conducted to determine data gaps in characterization of leaching from the variety of management practices that occur (EPA, 2002b). Most of the available data predates changes in air pollution controls. Another major issue is the use of a variety of leach tests which prevents data comparison across management practices and materials. Also, many of the leach tests in use were not published or were not based on quality assurance practices that could withstand scrutiny. Another major concern was that the available leach test data were based on single-point pH tests which did not consider the conditions under which the material is actually managed.

To comply with EPA's SAB and the NAS recommendations, efforts were made to identify a leach test that was suitable for evaluating CCRs so that the potential for leaching over a wide range of field conditions could be determined. Since the pathway of most concern for the release of mercury and other metals from CCR management is transfer to ground or surface waters, the method chosen to conduct leach tests on select CCRs was the "Leach Testing Framework" developed by Kosson et al. (2002). The Leach Testing Framework takes into consideration a number of factors (pH, liquid-solid ratio, waste form) known to influence metal leaching. If leaching is found to occur at levels of environmental concern, column testing can be conducted to consider the waste form, buffering capacity, and field conditions. EPA's Office of Solid Waste consulted the SAB on the proposed approach. The SAB was supportive but encouraged the collection of information that would allow comparison of laboratory and field leach data. This suggestion has been incorporated into this research through use of EPA and industry-supplied data.

CCRs were collected from multiple U.S facilities and subjected to the Kosson et al. (2002) leach test protocol. The CCRs being collected are fly ash and any residues from air pollution control equipment such as wet scrubbers. This research is ongoing and findings will be published in the form of four reports as data become available. These reports will be accessible for public use on the EPA website. Each research report is outlined below.

- *Report 1* (EPA, 2006b) has been completed and contains information on the leaching characteristics of metals from fly ash collected from six facilities that utilized powdered activated carbon (PAC) sorbents to increase mercury capture. Fly ash samples were collected at each facility with and without the use of sorbents to provide a baseline to compare the composition and leaching behavior of metals (Hg, As, and Se) with and without use of sorbents. A summary of the overall results is shown in Tables 1 and 2. Details for each facility comparing the leaching potential with and without sorbents in use are provided in the report and are being summarized for publication in a journal. The report and journal publication also provide comparisons of field and lab leach data. Based on the six facilities that were evaluated, findings include:
    - *Application of activated carbon injection substantially increased the total mercury content in the resulting CCRs for five of the six facilities.*
    - *Mercury is strongly retained by the resulting CCR and unlikely to be leached at levels of environmental concern.*
    - *Using a probabilistic assessment (Sanchez and Kosson, 2005) based on plausible field conditions for land disposal, results indicated that*

arsenic and selenium may be leached at levels of potential concern both with and without enhanced mercury control technology -

- *Highest As leach values at 20% of toxicity characteristic (TC)*[2]
- *Highest Se leach value is 10 times the TC*

- *Leachate concentrations and the potential release of mercury, arsenic, and selenium do not correlate with total content.*

- *Laboratory leach data (from the series of batch leach tests conducted using the Leach Testing Framework) compares very well to field leach data. The field leach data are from landfills containing CCRs.*

- *Report 2*, to be released in Fall 2008, will contain leaching information on CCR samples collected from eight facilities using wet scrubbers. The CCRs included are fly ash, FGD gypsum, and a combination of fly ash and scrubber sludge (which will be termed "as managed" material). Scrubber sludge (calcium sulfite, $CaSO_3$) is the residue produced when an oxidation process is not used to convert the FGD material to FGD gypsum ($CaSO_4 \cdot 2H_2O$). From five of these facilities, samples were collected with and without the use of NO_x controls. In addition to Hg, As, and Se, the list of metals for analysis was expanded to include Sb, Ba, B, Cd, Cr, Co, Pb, Mo, and Tl.

- *Report 3* is currently being drafted and will contain leaching data on fly ash samples collected from about 15 facilities. These samples were collected to fill the remaining data gaps that addressed coal rank [e.g., lignite and Powder River Basin (PRB) coal], air pollution control configurations (e.g., dry scrubbers, spray dryers, SO_3 controls), and fly ash class. The metals analyzed were the same ones included in Report 2.

- *Report 4* will focus on meeting the commitment to EPA's Mercury Roadmap in evaluating the fate of mercury and other metals from the management of CCRs resulting from implementation of multi-pollutant control. Data published in *Reports 1, 2,* and *3* will be used to conduct a probabilistic assessment of the plausible management scenarios – both for beneficial use applications and land disposal – to identify specific materials and management practices that may result in cross media transfer.

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[2] This observation does not agree with field data published from lysimeter tests to determine leaching of metals from use of CCRs in highway construction (Sauer et al., 2005). However, the characteristics of CCRs will be changing in light of new air pollution control requirements at power plants and previous data may not reflect these changes.

Table 1. Facilities included in *Report 1* where fly ash samples were evaluated with and without the use of sorbents for enhancing mercury capture.

Facility Code	Coal Rank	NO_x Control	PM Control	Hg Control
Brayton Point	Bituminous-Low Sulfur	None[1]	CS-ESP[2]	PAC
Pleasant Prairie	PRB-Sub-Bituminous	None[1]	CS-ESP	PAC
Salem Harbor	Bituminous-Low Sulfur	SNCR with urea[3]	CS-ESP	PAC
Facility C	Bituminous-Low Sulfur	None[1]	Hot Side-ESP	COHPAC[4]
St. Clair	PRB-Sub-Bituminous/ Low Sulfur Bituminous Blend	None[1]	CS-ESP	B-PAC[5]
Facility L	Bituminous-Low Sulfur	SCR	Hot Side-ESP	B-PAC

[1]NO_x controls were not in use during date of fly ash collection.
[2]CS-ESP – Cold side electrostatic precipitator.
[3]SNCR – Selective non-catalytic reduction.
[4]COHPAC uses additives such as carbon, sodium, or calcium to a baghouse downstream of ESP.
[5]B-PAC-Brominated powdered activated carbon.

Table 2. Results of leach testing analysis for coal fly ash from six facilities using sorbents for enhanced Hg capture (*Report 1*).

	Hg	As	Se
Total in CCR material (mg/kg)	0.1 -1	20 - 500	3 - 200
Leach results (µg/L)	Generally 0.1 or lower	<1 - 1000	5 – 10,000
MCL[1] (µg/L)	2	10	50
TC[2] (µg/L)	200	5,000	1,000
Variability relative to pH[3]	Low	Moderate to High	Moderate

[1]MCL is the maximum concentration limit for drinking water.
[2]TC is the toxicity characteristic and is a threshold for hazardous waste determinations.
[3] Variability defined as low is <1 order of magnitude difference; moderate is 1 to 2 orders of magnitude difference; and high is >2 orders of magnitude difference.

NEXT STEPS

Samples will continue to be collected to help span the range of coal rank and air pollution control configurations. Data collected through this research effort will be used to conduct a probabilistic assessment of plausible management scenarios. Results of the assessment will be reported in *Report 4*. Each CCR report upon completion will be available online through EPA's website. At the time of this writing, only *Report 1* is accessible. There appears to be much interest in the findings, particularly in regards to site-specific determinations. For example, a golf course is being constructed in Virginia using 1.5 million tons of fly ash. The surrounding homes are reported to be on well water. What was done to analyze this material to determine any potential leaching of metals in the fly ash? Were the conditions considered under which the material is actually managed? Are the data being produced through this research of help in evaluating site-specific determinations?

Interest exists in the development of a decision support tool that would assist end users in evaluating potential effects of using CCRs and CCR-made products. The objective of the decision support tool is to provide information for fate and transport models used in environmental and risk assessments. The end user could specify the material type and management approach to determine if there is a similar material that has already been evaluated. It could help identify what might be needed to assess any potential environmental impacts. The properties of fly ash and FGD gypsum are such that their use can help displace natural resources, reduce greenhouse gas emissions, and conserve energy. However, identifying the appropriate material and management practice is important to help facilitate informed decisions and minimize any adverse impacts.

SUMMARY

Air pollution control changes at coal-fired power plants may change the characteristics and leaching behavior of CCRs. There is much interest in potential beneficial use applications. As of 2006, 125 million tons of CCRs were generated with 43% used beneficially. Increasing coal consumption and air pollution control requirements will result in increasing the quantity of CCRs being generated. EPA's C^2P^2 and the ACAA have a goal of 50% utilization of CCRs by 2011. CCRs contain a host of trace elements originating from the burning of coal and the sorbents used for air pollution control. The concentrations of the elements in the CCRs are influenced by a variety of factors including coal rank, boiler configuration, existing controls in place, and other considerations. The leaching characteristics and the environmental impacts associated with the CCRs are generally unknown. This research evaluates the leaching characteristics of CCRs collected from a range of facility types using different coal ranks and air pollution control configurations. The results are being documented into a series of four reports. The fourth and final report is meeting a commitment of EPA's Mercury Roadmap to document what is known about the fate of mercury and other metals from the management of residues resulting from implementation of multi-pollutant control technologies at coal-fired power plants. Development of a decision support tool is being considered to help facilitate more informed decisions on CCR management by helping to identify any specific materials or management practices that might result in cross media transfer. The ultimate goal of this research is to ensure that effective environmental management is occurring through use of a more holistic approach that considers multiple pollutants, environmental conditions, and media.

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