

Characterization of Coal Combustion Residues III

EXECUTIVE SUMMARY

This report is the third in a series to evaluate changes in composition and constituent release by leaching that may occur to fly ash and other coal combustion residues (CCRs) in response to changes in air pollution control technology at coal-fired power plants. The addition of flue-gas desulfurization (FGD) systems, selective catalytic reduction, and activated carbon injection to capture mercury and other pollutants will shift mercury and other pollutants from the stack gas to fly ash, FGD gypsum, and other air pollution control residues. The Air Pollution Prevention and Control Division (APPCD) of EPA's Office of Research and Development (ORD) is conducting research to evaluate potential leaching and other cross media transfers of mercury and other constituents of potential concern (COPCs) resulting from the management of CCRs resulting from wider use of state-of-the-art air pollution control technology. This research was cited as a priority in EPA's Mercury Roadmap¹ to ensure that one environmental problem is not being traded for another. The objective is to understand the fate of mercury and other COPCs in air pollution control residues and support EPA's broader goal of ensuring that emissions being controlled in the flue gas at power plants are not later being released to other environmental media.

Approximately 40% of the 126 million tons of CCRs produced in the U.S. as of 2006 were utilized in agricultural, commercial, and engineering applications. The remainder (i.e., 75 million tons) was managed in either landfills or impoundments. The physical and chemical characteristics of CCRs make them potentially suitable as replacements for materials used in a wide range of products including cement, concrete, road base, and wallboard. Use of CCRs as an alternative to virgin materials helps conserve natural resources and energy, as well as decrease the amount of CCRs being land disposed.

In developing data to characterize the leaching potential of COPCs from the range of likely CCRs resulting from use of state-of-the-art air pollution control technology, improved leaching test methods have been used². The principle advantage of these methods is that they consider the impact on leaching of management conditions. These methods address concerns raised by National Academy of Science and EPA's Science Advisory Board with the use of single-point pH tests. Because of the range of field conditions that CCRs are managed during disposal or use as secondary (or alternative) materials, it is important to understand the leaching behavior of materials over the range of plausible field conditions that can include acid mine drainage and co-disposal of fly ash and other CCRs with pyrites or high-sulfur coal rejects^{3, 4}. The methods have

¹ EPA (2006). EPA's Roadmap for Mercury, EPA-HQ-OPPT-2005-0013. U.S. Environmental Protection Agency, <http://www.epa.gov/mercury/pdfs/FINAL-Mercury-Roadmap-6-29.pdf> (accessed August 21, 2009).

² Improved leaching test methods described in (Kosson et al., 2002) have been developed as draft SW-846 protocols. These methods consider the effect of varying environmental conditions on waste constituent leaching.

³ National Academy of Sciences (2006). Managing Coal Combustion Residues in Mines, Washington, D.C.

⁴ Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; <http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf>.

Characterization of Coal Combustion Residues III

also been developed into draft protocols for inclusion in EPA's waste testing guidance document, SW-846, which would make them available for more routine use.

(<http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm>).

The selected testing approach was chosen for use because it evaluates leaching over a range of values for two key variables [pH and liquid-to-solid ratio (LS)] that both vary in the environment and affect the rate of constituent release from waste. The range of values used in the laboratory testing encompasses the range of values expected to be found in the environment for these parameters. Because the effect of these variables on leaching is evaluated in the laboratory, prediction of leaching from the waste in the field is expected to be done with much greater reliability.

The categories into which samples have been grouped are fly ash, flue gas desulfurization (FGD) gypsum, "other" FGD residues (such as from spray drier absorbers), blended CCRs "as managed" (mixtures of fly ash and scrubber residues with and without added lime or mixture of fly ash and gypsum), and wastewater filter cake. In the first report from this research⁵, results of leaching from fly ash were reported for mercury, arsenic, and selenium. Report 2 provided leaching results for an expanded list of materials and COPCs to include mercury, aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, selenium and thallium⁶. In the current report (Report 3), analyses of eluates from CCR samples presented in Report 1 have been included for the expanded list of COPCs. Report 3 also includes the data previously reported in Report 2, and leach test results for an additional 38 CCRs. A total of 73 samples were evaluated, and all results are presented in the current report to facilitate comparisons (Table ES-1).

⁵ Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; <http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf>.

⁶ Sanchez, F.; Kosson, D.; Keeney, R.; Delapp, R.; Turner, L.; Kariher, P.; Thorneloe, S. Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; <http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf>.

Characterization of Coal Combustion Residues III

Table ES-1. Identification of CCRs evaluated and included in this Report.

Samples Evaluated	Report 1*	Report 2**	Additional Samples Collected	Total in Report 3
Fly Ash	12	5	17	34
FGD Gypsum	-	6	14	20
"Other" FGD Residues	-	5	2	7
Blended CCRs "as managed"	-	7	1	8
Wastewater Treatment Filter Cake	-		4	4

* Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; <http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf>.

** Sanchez, F.; Kosson, D.; Keeney, R.; Delapp, R.; Turner, L.; Kariher, P.; Thorneloe, S. Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; <http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf>.

Each of the CCRs sampled has been analyzed for a range of physical properties, total elemental content, and leaching characteristics. Laboratory leach data are compared to field observations from industry and EPA data from sampling of impoundments and landfills. The laboratory leach results are also compared to reference indicators to provide context for the data including:

- The toxicity characteristic (TC), which is a threshold for hazardous waste determinations;
- The maximum concentration limit (MCL), which is used for protecting drinking water; and,
- The drinking water equivalent level (DWEL), which is used to be protective for non carcinogenic endpoints of toxicity over a lifetime of exposure⁷.

These comparisons to reference indicators do not consider dilution and attenuation factors (collectively referred to in this report as attenuation factors) that arise as a consequence of disposal or beneficial use designs and transport from the point of release to the potential receptor. Minimum attenuation factors needed to reduce maximum leach concentrations (based on laboratory test results) to less than MCL or DWEL values are provided to illustrate the importance of consideration of attenuation factors during evaluation of management options.

The intended use for the data in this report is to support future risk and environmental assessments of the CCRs. A follow-up report is planned which will use these data in conducting a probabilistic assessment of mercury and other COPCs release rates based on the range of plausible management scenarios for these materials in either disposal or beneficial use situations.

The data summarized in this report will be made available electronically through a leaching assessment tool that can be used to develop source-term inputs needed for using groundwater

⁷DWEL was developed for chemicals that have a significant carcinogenic potential and provides risk managers with evaluation on non-cancer endpoints, but infers that carcinogenicity should be considered the toxic effect of greatest concern (<http://www.epa.gov/safewater/pubs/gloss2.html#D>).

Characterization of Coal Combustion Residues III

transport and fate models⁸. The leaching assessment tool will provide easier access to the leach data for a range of CCRs and potential field conditions. The tool can be used to develop more detailed leach data as input to more refined assessments of CCRs and support environmental decision-making that will ensure protection of human health and the environment.

Summary of Conclusions

In Table ES-2 and Table ES-3, the total metals content of the fly ash and FGD gypsum samples evaluated is provided along with the leach test results. Reference indicators (i.e., TC, MCL, and DWEL) are also provided to provide some context in understanding the leach results. It is critical to bear in mind that the leach test results represent a distribution of potential constituent release concentrations from the material as disposed or used on the land. The data presented do not include any attempt to estimate the amount of constituent that may reach an aquifer or drinking water well. Leachate leaving a landfill is invariably diluted in ground water to some degree when it reaches the water table, or constituent concentrations are attenuated by sorption and other chemical reactions in groundwater and sediment. Also, groundwater pH may be different from the pH at the site of contaminant release, and so the solubility and mobility of leached contaminants may change when they reach groundwater. None of these dilution or attenuation processes is incorporated into the leaching values presented. Thus, comparisons with regulatory health values, particularly drinking water values, must be done with caution. Groundwater transport and fate modeling would be needed to generate an assessment of the likely risk that may result from the CCRs represented by these data.

In reviewing the data and keeping these caveats in mind, conclusions to date from the research include:

1. Review of the fly ash and FGD gypsum (Table ES-2 and Table ES-3) show a range of total constituent concentration values, but a much broader range (by orders of magnitude) of leaching values, in nearly all cases. This much greater range of leaching values only partially illustrates what more detailed review of the data shows: that for CCRs, the rate of constituent release to the environment is affected by leaching conditions (in some cases dramatically so), and that leaching evaluation under a single set of conditions may, to the degree that single point leach tests fail to consider actual management conditions, lead to inaccurate conclusions about expected leaching in the field.
2. Comparison of the ranges of totals values and leachate data from the complete data set supports earlier conclusions^{9, 10, 11} that the rate of constituent leaching cannot be reliably estimated based on total constituent concentration.

⁸ The leaching assessment tool, LeachXS Lite®, will be available for inclusion in the CCR docket (December 2009).

⁹ Senior, C; Thorneloe, S.; Khan, B.; Goss, D. Fate of Mercury Collected from Air Pollution Control Devices; Environmental Management, July 2009, 15-21.

¹⁰ U.S. EPA, Characterization of Mercury-Enriched Coal Combustion Residuals from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; <http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf>.

Characterization of Coal Combustion Residues III

3. The maximum eluate concentration from leaching test results varies over a wide range in pH and is different for different CCR types and elements. This indicates that there is not a single pH for which testing is likely to provide confidence in release estimates over a wide range of disposal and beneficial use options, emphasizing the benefit of multi-pH testing.
4. From the more complete data in this report, distinctive patterns in leaching behavior have been identified over the range of pH values that would plausibly be encountered for CCR disposal, depending on the type of material sampled and the element. This reinforces the above conclusions based on the summary data.
5. Summary data in Table ES-2 on the leach results from evaluation of 34 fly ash samples across the plausible management pH domain of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and ash source:
 - the leach results at the upper end of the concentration ranges exceeded the TC values for As, Ba, Cd, Cr, and Se.
 - the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, Ba, B, Cd, Cr, Pb, Mo, Se, and Tl.
6. Summary data in Table ES-3 on the leach results from evaluation of 20 FGD gypsum samples across the plausible management pH domain of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and FGD gypsum source:
 - the leach results at the upper end of the concentration ranges exceeded the TC values for Cd and Se.
 - the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, B, Cd, Cr, Mo, Se, and Tl.
7. The variability in total content and the leaching of constituents within a material type (e.g., fly ash, gypsum) is such that, while leaching of many samples exceeds one or more of the available reference indicators, many of the other samples within the material type may be lower than the available regulatory or reference indicators. Additional or more refined assessment of the dataset may allow some distinctions regarding release potential to be made among particular sources of some CCRs, which may be particularly useful in evaluating CCRs in reuse applications.

Work is underway to develop a fourth report that presents such additional analysis of the leaching data to provide more insight into constituent release potential for a wider range of scenarios, including beneficial use applications. This will include calculating potential release

¹¹U.S. EPA, Characterization of Coal Combustion Residuals from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; <http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf>.

Characterization of Coal Combustion Residues III

rates over a specified time for a range of management scenarios including use in engineering and commercial applications using probabilistic assessment modeling¹².

In interpreting the results provided in this report, please note that the CCRs analyzed in this report are not considered to be a representative sample of all CCRs produced in the U.S. For many of the observations, only a few data points were available. It is hoped that through broader use of the improved leach test methods (as used in this report), that additional data from CCR characterization will become available. That will help better define trends associated with changes in air pollution control at coal-fired power plants.

¹² Sanchez, F. and D. S. Kosson, 2005. Probabilistic approach for estimating the release of contaminants under field management scenarios. *Waste Management* 25(5), 643-472 (2005).

Characterization of Coal Combustion Residues III

Table ES-2. Leach results for $5.4 \leq \text{pH} \leq 12.4$ and at "own pH"¹³ from evaluation of thirty-four fly ashes.

	<u>Hg</u>	<u>Sb</u>	<u>As</u>	<u>Ba</u>	<u>B</u>	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Pb</u>	<u>Mo</u>	<u>Se</u>	<u>TI</u>
Total in Material (mg/kg)	0.01 – 1.5	3 – 14	17 – 510	590 – 7,000	NA	0.3 – 1.8	66 – 210	16 – 66	24 – 120	6.9 – 77	1.1 – 210	0.72 – 13
Leach results (µg/L)	<0.01 – 0.50	<0.3 – 11,000	0.32 – 18,000	50 – 670,000	210 – 270,000	<0.1 – 320	<0.3 – 7,300	<0.3 – 500	<0.2 – 35	<0.5 – 130,000	5.7 – 29,000	<0.3 – 790
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

Table ES-3. Leach results for $5.4 \leq \text{pH} \leq 12.4$ and at "own pH" from evaluation of twenty FGD gypsums.

	<u>Hg</u>	<u>Sb</u>	<u>As</u>	<u>Ba</u>	<u>B</u>	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Pb</u>	<u>Mo</u>	<u>Se</u>	<u>TI</u>
Total in Material (mg/kg)	0.01 – 3.1	0.14 – 8.2	0.95 – 10	2.4 – 67	NA	0.11 – 0.61	1.2 – 20	0.77 – 4.4	0.51 – 12	1.1 – 12	2.3 – 46	0.24 – 2.3
Leach results (µg/L)	<0.01 – 0.66	<0.3 – 330	0.32 – 1,200	30 – 560	12 – 270,000	<0.2 – 370	<0.3 – 240	<0.2 – 1,100	<0.2 – 12	0.36 – 1,900	3.6 – 16,000	<0.3 – 1,100
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

¹³ "Own pH" is defined as the end-point (equilibrium) eluate pH when a CCR is extracted with DI water at liquid to solid ratio of 10 mL/g, and is measured as part of leach testing as a function of pH.