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Use of a Leaching Assessment Framework for Evaluation of the Impacts of Coal Type and Facility Configuration on Beneficial Use Scenarios for Coal Combustion Residues

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ABSTRACT

An integrated leaching assessment framework and evaluation of a range of coal combustion residues (CCRs) provides a foundation for screening environmental compatibility of beneficial use and disposal scenarios and simplified testing for CCR quality control during production. Detailed characterization includes measurement of leaching as a function of pH and liquid-to-solid ratio using batch and column testing for percolation-based applications, and diffusion controlled release testing for low permeability materials. Approximately 70 samples of coal combustion residues (CCRs) have been evaluated for leaching characteristics as part of analysis of potential environmental impacts from CCR use and disposal, considering the coal type and air pollution control processes used by coal-fired power plants. The resulting information provides the basis for establishing classes of CCRs based on characteristic leaching behavior for constituents of potential concern (COPCs) that then can be used for comparative evaluation of CCRs from other facilities and quality control for beneficial use. This paper summarizes application of the leaching assessment framework for evaluating beneficial use scenarios and provides examples concerning the impacts of facility configuration and coal type on CCR leaching.

INTRODUCTION

More wide-spread implementation of multi-pollutant controls is occurring at U.S. coal-fired power plants. Although much research has occurred to characterize high-volume coal combustion residues [i.e., fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) solids] extending back to the 1970s, previous research has not considered the wide range of field conditions that occur for coal combustion residues (CCRs) during land disposal and use in agricultural, commercial, and engineering applications. Thus, USEPA is supporting a research program to characterize the total composition and constituent release potential (i.e., leaching) for CCRs resulting from wider use of multi-pollutant controls at U.S. coal-fired power plants. This characterization includes detailed analysis of CCRs in relationship to differences in air pollution control configurations and coal rank. CCRs evaluated include fly ash, gypsum, scrubber residues and combined residues (as managed for disposal) from facilities with different air pollution control configurations including particulate capture (electrostatic precipitators, fabric filters), sorbent injection for mercury control (powdered activated carbon, brominated activated carbon), nitrogen oxide controls (selective catalytic reaction, and selective non-catalytic reaction), and scrubber type (inhibited, natural and forced oxidation). Coal types included bituminous, sub-bituminous and lignite coals typically combusted in the United States. The characterization included evaluating the leaching potential of COPCs across the range of plausible management conditions that CCRs are likely to encounter during land disposal or use in agricultural, commercial, and engineering applications. Results of the CCR characterization have been provided in a series of three reports [Kosson et al, 2009; Sanchez et al, 2008; Sanchez et al, 2006] and a fourth report focusing on release under CCR use and disposal scenarios is under development. This research is part of an on-going effort by EPA to use an integrated, comprehensive approach to account for the fate of mercury and other metals in coal throughout the life-cycle stages of CCR management [Thorneloe et al., 2009; Thorneloe et al., 2008].

LEACHING ENVIRONMENTAL ASSESSMENT FRAMEWORK (LEAF)

LEAF is an integrated framework for evaluating leaching behavior of materials using a tiered approach that considers pH, liquid-to-solid ratio (L/S), and waste form across a range of field conditions [Kosson et al, 2002]. Implementation of LEAF includes leaching test methods, data management, assessment in the context of prior information and using scenario-based mass transfer models [van der Sloot et al, 2010; van der Sloot et al, 2006; van der Sloot et al, 2007; Dijkstra et al, 2008; Sanchez et al, 2002; Garrabrants et al. 2003], and statistical quality control [van der Sloot et al, 2009]. The LEAF leaching test methods are being adapted and are currently undergoing inter-laboratory precision and repeatability testing for inclusion into SW-846, a compendium of EPA methods to evaluate the physical and chemical properties of wastes and secondary materials. The methods being adapted for inclusion into SW-846 are:

- Method 1313 - liquid-solid partitioning as a function of eluate pH using a parallel batch extraction test,
- Method 1314 - liquid-solid partitioning as a function of liquid-solid ratio using a parallel batch test,
- Method 1315 - liquid-solid partitioning as a function of liquid-solid ratio using an up-flow column test, and
- Method 1316 - mass transfer in monolithic or compacted granular materials using a semi-dynamic tank leach test.

For the latest copy of the LEAF test methods, please refer to downloads at: www.vanderbilt.edu/leaching Microsoft Excel® templates are provided along with the test methods to facilitate leaching test method calculations and data entry. LeachXS Lite™ (see below) also is provided for data viewing and analysis.

Figure 1 provides an overview of the types of data generated and applications in assessment for use and disposal scenarios. Leaching test eluate concentrations provide a basis for comparison of materials and initial screening of potential risk, while use of leaching test results to parameterize scenario-based mass transfer models that include appropriate consideration of leaching chemistry, water flux and attenuation processes provides a source term for detailed impact assessment. In addition, results from detailed impact assessment can be used to back-calculate threshold values from leaching tests to use for subsequent decisions and on-going quality control as CCRs are produced for beneficial use applications. However, it should be recognized that the many factors controlling leaching and changes in CCR characteristics in response to environmental conditions result in non-linear responses in observed leaching behavior.

LeachXS Lite

LeachXS Lite is a leaching environmental assessment framework (LEAF) tool that allows the user to evaluate and characterize the leaching of constituents in materials under various conditions based on comparisons derived from leaching test results. LeachXS Lite is a simplified version of full software package LeachXS™ [van der Sloot et al, 2008], which facilitates data comparison with field results and a range of scenarios based using either empirical relationships or mass transfer and geochemical speciation models to provide a source term for constituent leaching. Licenses for LeachXS Lite are available free of charge and LeachXS Lite can be downloaded from www.Vanderbilt.edu/leaching; user registration is required. Development of LeachXS Lite is on-going with additional functionality and data intended to be added subsequent versions over the next several months. Updated versions will also be available for downloading from the above cited website. LeachXS and LeachXS Lite have been developed jointly by The Energy Research Centre of The Netherlands (Petten, The Netherlands), Vanderbilt University (Nashville, TN, USA) and DHI (Hørsholm, Denmark).

LeachXS Lite is supplied currently with a database of leaching test results generated under the USEPA program for characterization of coal combustion residues (CCRs) discussed earlier. Leaching test results included in the published reports was for more than 70 CCRs but was limited to 13 constituents while the supplied LeachXS Lite database provides further data for approximately 40 constituents in most cases. All data contained in the LeachXS Lite database has been subject to quality assurance processes as part of the USEPA program. Additional data will be provided from on-going testing and evaluation of CCRs as produced and “as used” under selected material use scenarios (e.g., incorporation into cementitious materials, blended with other materials to meet construction requirements).

LeachXS Lite can be used for data management and analysis for results from leaching tests carried out on a wide range of materials and waste types (e.g., secondary or recycled materials, stabilized waste and construction materials).

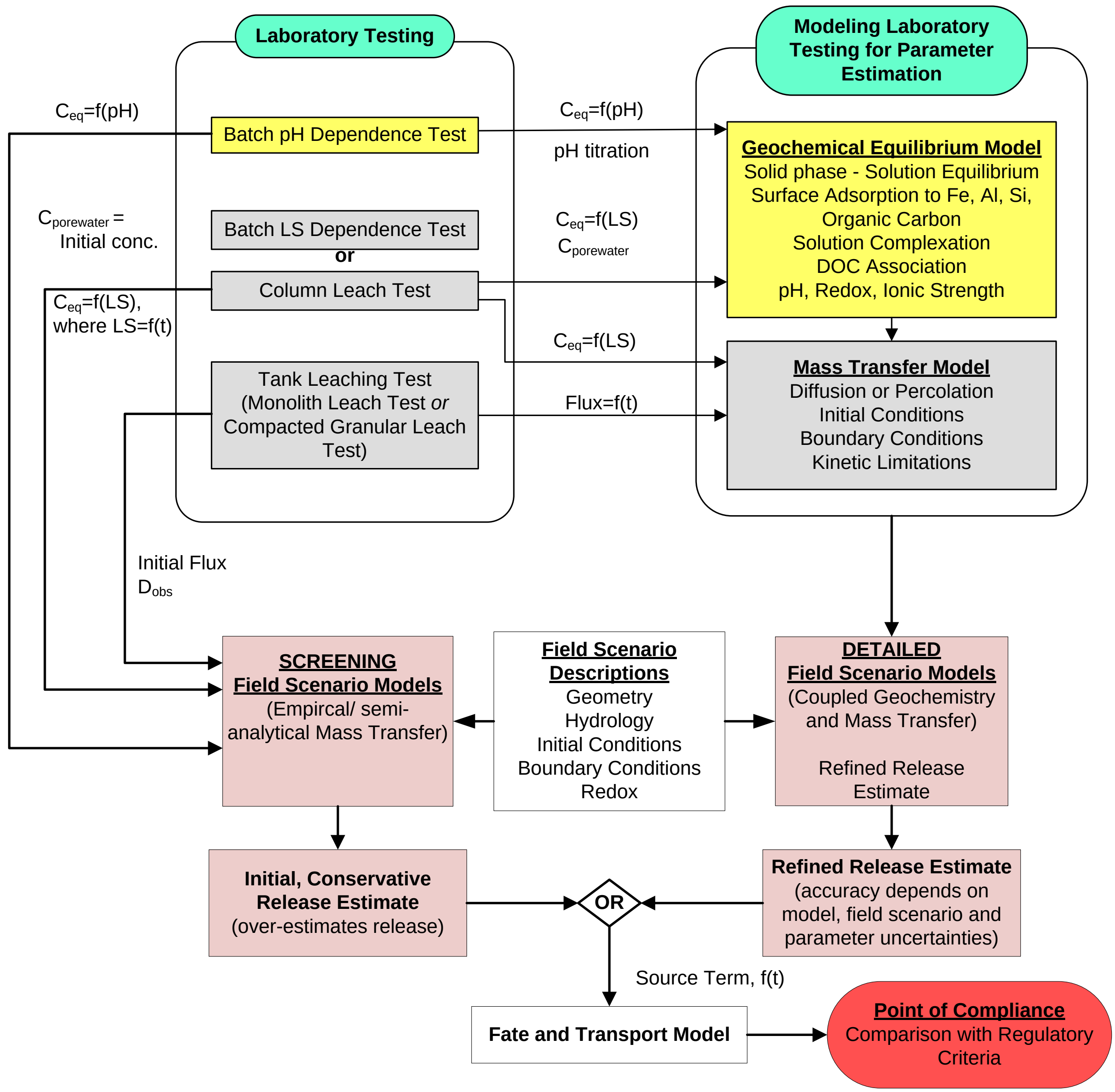

Figure 1. Information Flow for Using Laboratory Leaching Test Results for Assessing Use and Disposal Scenarios Based on either Empirical Results or Geochemical Speciation with Reactive Transport Modeling.

LeachXS Lite provides facilitated data management and leaching data comparison:

- Direct import of leaching data from Excel data templates (Methods 1313-1316),
- Comparison of leaching from different materials or leaching tests, allowing inferences about leaching mechanisms and material characteristics and behavior under different conditions,
- Comparison of leaching to reference values (e.g., method detection limits, applicable pH domain, water quality indicators; either preloaded or user defined) for individual constituents,
- Comparison of leaching from a specific material to statistical representation of a class or sub-class of materials, and
- Uniform data presentation and graphic output to Excel spreadsheets.

RESULTS AND DISCUSSION

The EPA Risk Report [EPA, 2007] identified the following COPCs based on the potential for either human health or ecological impacts using a screening risk assessment: aluminum (Al), arsenic (As), antimony (Sb), barium (Ba), boron (B), cadmium (Cd), cobalt (Co), chromium (Cr), lead (Pb), mercury (Hg), molybdenum (Mo), selenium (Se), and thallium (Tl).[1] Thus, the evaluation provided as part of the current research program focuses on the same thirteen constituents.

Figure 2 illustrates the diversity in the characteristic leaching behavior as a function of pH from different fly ash samples; the facility configuration for each fly ash sample is provided in Table 1. The pH domain of 5.4-12.4 is indicated on each graph by vertical red lines to delineate the 5th to 95th percentile of leachate pH observed under field disposal conditions. The “own pH”, defined as the end-point pH when extracted with deionized water at L/S of 10 mL/g, is indicated for each fly as a circled data point. In general, the own pH is correlated with the calcium content of the fly ash, with alkali pH associated with high calcium fly ash. For many COPCs, the leaching behavior is fairly consistent within a bandwidth for a given coal rank with notable differentiation between low and high calcium content for leaching of arsenic, boron and antimony, as well as the likely impact of residual ammonium content (injected for NOx control) on the leaching of arsenic and mercury between pH 7-9 (see GAB and AaFA, respectively). In addition, leachability of chromium is highly variable between facilities, with hexavalent chromium being the predominant species leaching at near-neutral pH.

Figures 3 and 4 illustrate the relationships between results from laboratory tests characterizing two fly ash samples for arsenic and chromium leaching, respectively. Resulting data is presented as a function of pH (Methods 1313, 1314, 1316) and as a function of L/S (Methods 1314, 1316), on a concentration basis (mg/L) and a mass basis (mg leached/kg material) to facilitate comparisons. When results of the column test (1314) and the batch L/S dependence test (1316) are plotted as a function of pH along with pH dependence results (1313), and interpreted in the context of results from other constituents,

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[1] The database used in the EPA Risk Report [EPA, 2007] for the assessment was based on both measurements of field samples (e.g., leachate, pore water) and single point laboratory leaching tests (e.g., TCLP, SPLP).

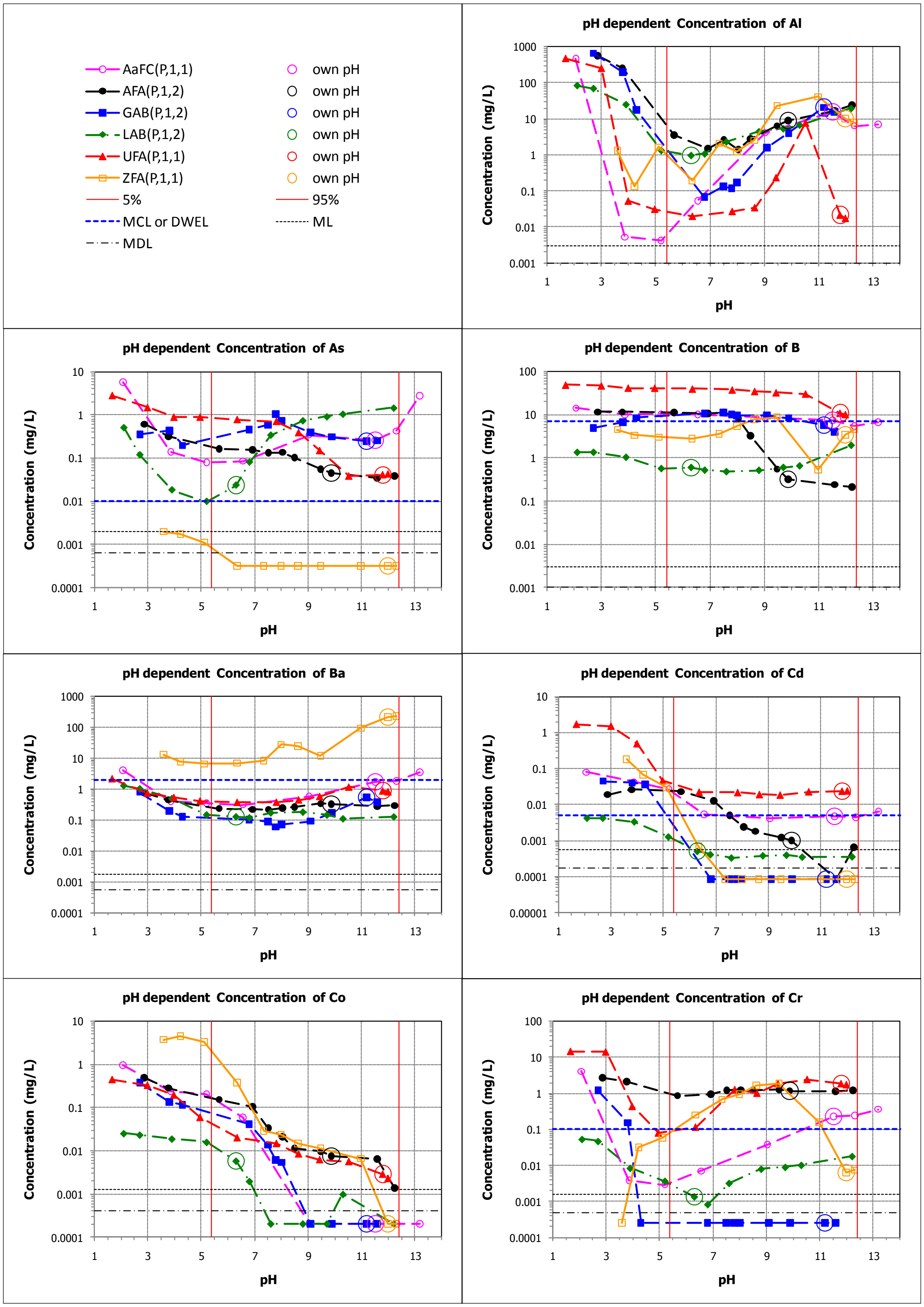

Figure 2. pH Dependent Leaching Results to Illustrate Variety in Characteristic Leaching Behavior.

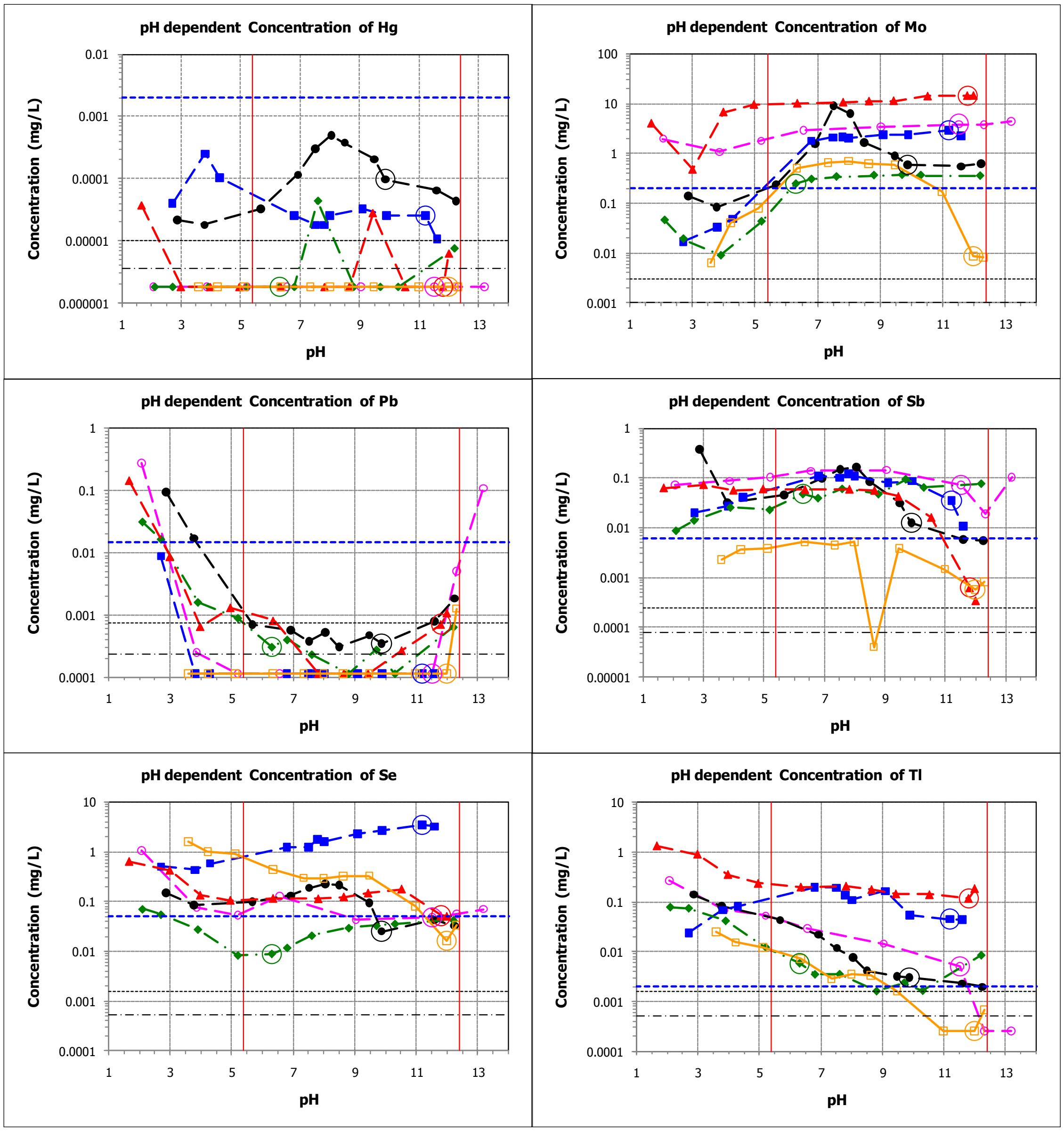

Figure 2 (continued). pH Dependent Leaching Results to Illustrate Variety in Characteristic Leaching Behavior.

inter-related leaching behavior can be discerned. Samples AaFA and UFA have similar total contents for arsenic (31 and 42 mg/kg) and chromium (214 and 141 mg/kg). For arsenic, AaFA (low calcium fly ash) indicates own pH at 4.36 and similar leaching concentrations from Methods 1313 and 1316, while eluate concentrations during column percolation (Method 1314) are significantly lower. UFA (high calcium fly ash) indicates own pH at 11.81 with lower eluate concentrations at low L/S from Method 1314 and 1316 than indicated by Method 1313. This observed behavior is explained by a decrease in sorption to iron at pH<4 and eluted concentrations of dissolved organic carbon and calcium. For chromium, AaFA eluate concentrations follow a similar relative pattern as for arsenic and cationic behavior coupled with adsorption and dissolved organic carbon interaction indicated.

Table 1. Process Characteristics for Fly Ash Samples Indicated in Figures 2 through 4.

Material Code	FGD Scrubber additive	NOx Control	Scrubber type	Particulate Capture	Coal type	Region
AaFC	Limestone	SCR	Wet - Forced Oxidation	Hot-side ESP	Bituminous (Med S)	Eastern Bituminous
AFA	Limestone	SNCR	Wet - Natural Oxidation	Fabric Filter	Bituminous (Low S)	Eastern Bituminous
GAB	None	None	None	Hot-side ESP w/COHPAC	Bituminous (Low S)	Eastern Bituminous
LAB	None	SOFA	None	Hot-side ESP	Bituminous (Low S)	Southern Appalachian
UFA	Limestone	SCR	Wet - Forced Oxidation	Cold-side ESP	Bituminous (Low S)	Southern Appalachian
ZFA	None	None	None	Cold-side ESP	Sub-bituminous	Powder River Basin

ESP – electrostatic precipitator
COHPAC – injection of powdered activated carbon after ESP then collected on fabric filter
SCR – selective catalytic oxidation
SNCR – selective non-catalytic oxidation
SOFA – supplemental over fire air

At the alkali pH of UFA batch (Method 1316) and column (Method 1314) tests, elution of highly soluble chromate anion is indicated. These examples further illustrate the complex chemistry occurring as a function of CCR characteristics and leaching conditions, indicating the need for understanding of geochemical speciation to evaluation release under a range of potential use or disposal scenarios.

Figure 5 illustrates the minimum dilution and attenuation factor necessary to reduce the maximum leaching concentration of all COPCs from eluates between pH 5.4-12.4 to less than the drinking water standard for each CCR tested. The COPC that would need to be attenuated the most for each CCR is also indicated. These results suggest an approach to defining the performance requirements for the management scenario. For example, a management scenario for sample BPB (the first sample indicated at the left in Figure 5) would need to result in a dilution and attenuation factor (DAF) of greater than 600 to reduce anticipated porewater leaching concentrations of selenium to less than the maximum contaminant level (MCL; commonly referred to as the drinking water standard). For many CCRs tested, the analogous DAF would be less than 10 while for several CCRs the DAF would be greater than 1000. Dilution and attenuation factors for metals (DAFs) have been estimated to be potentially as low as 2 to 10 on a national basis or as high as 8,000 at a particular site with hydrogeology that indicated low transport potential.[2] Clearly, there is a

[2] See 60 FR 66372, Dec. 21, 1995, for a discussion of model parameters leading to low DAFs, particularly the assumption of a continuous source landfill. Implied DAFs for the metals of interest here can be found at 60 FR 66432-66438 in Table C-2. Site specific high-end DAFs are discussed at 65 FR 55703, September 14, 2000.

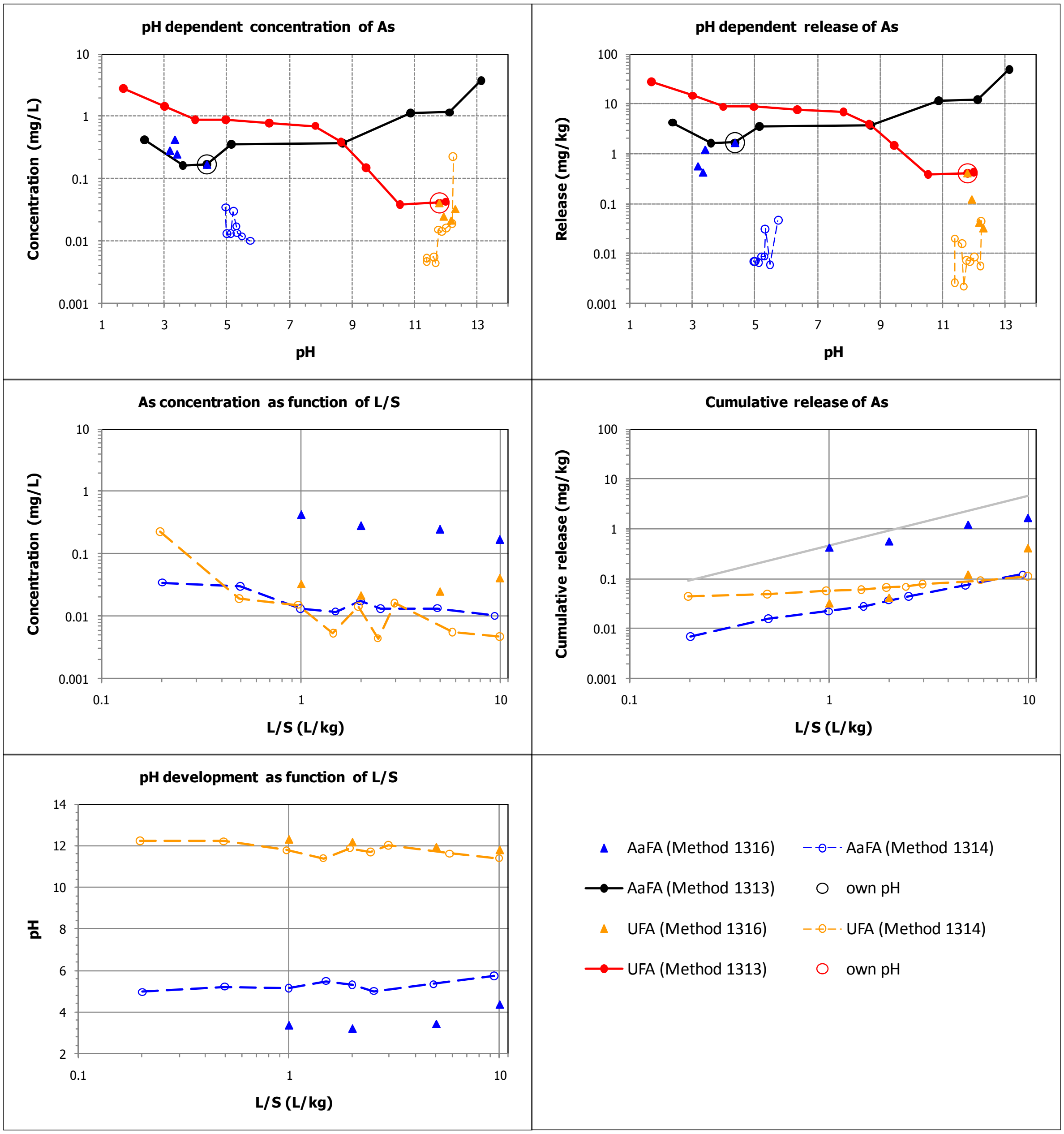

Figure 3. Comparison of Method Results for Arsenic [Methods 1313 (pH dependence), 1314 (column), 1316 (batch LS dependence)].

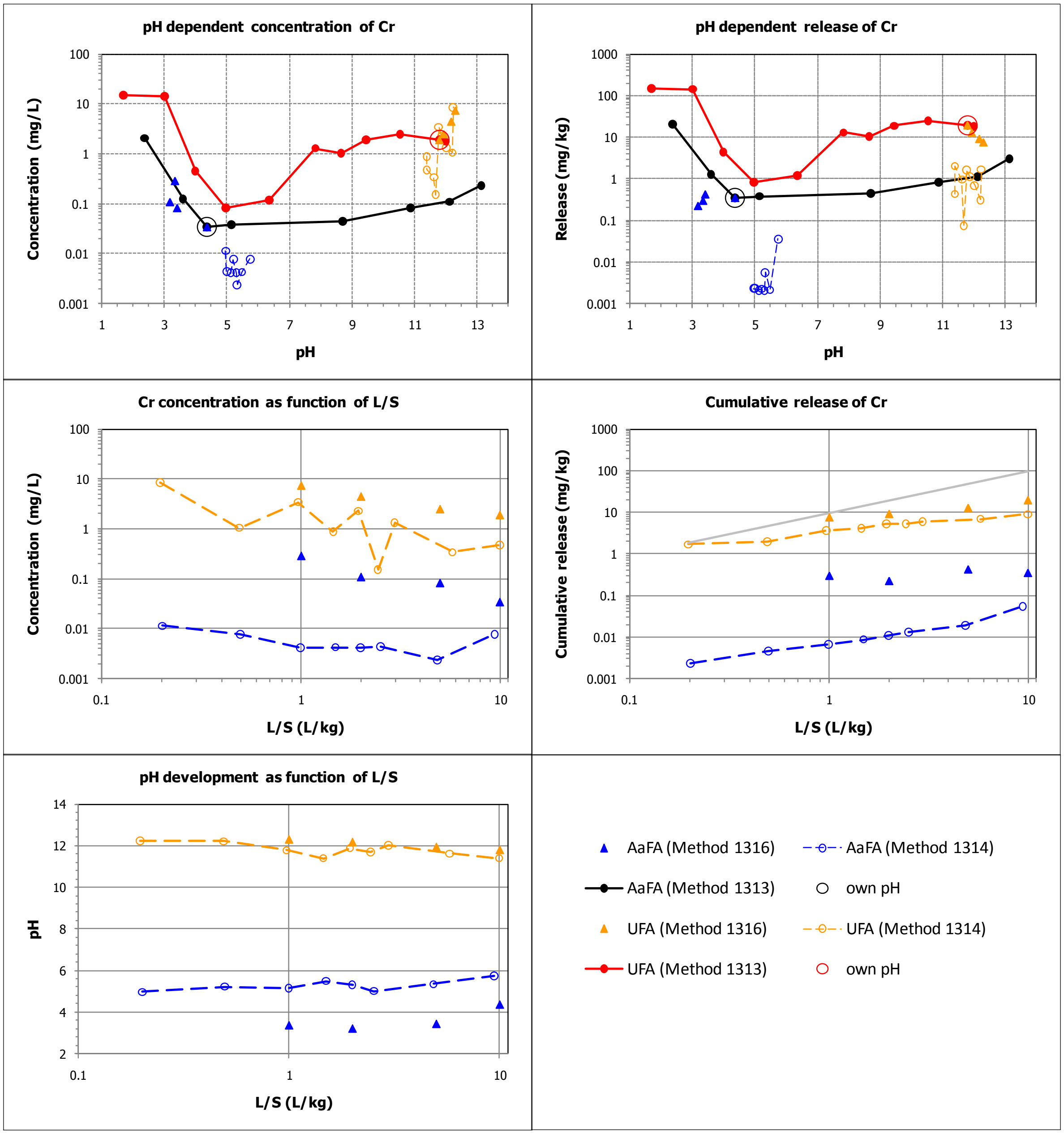

Figure 4. Comparison of Method Results for Chromium [Methods 1313 (pH dependence), 1314 (column), 1316 (batch LS dependence)].

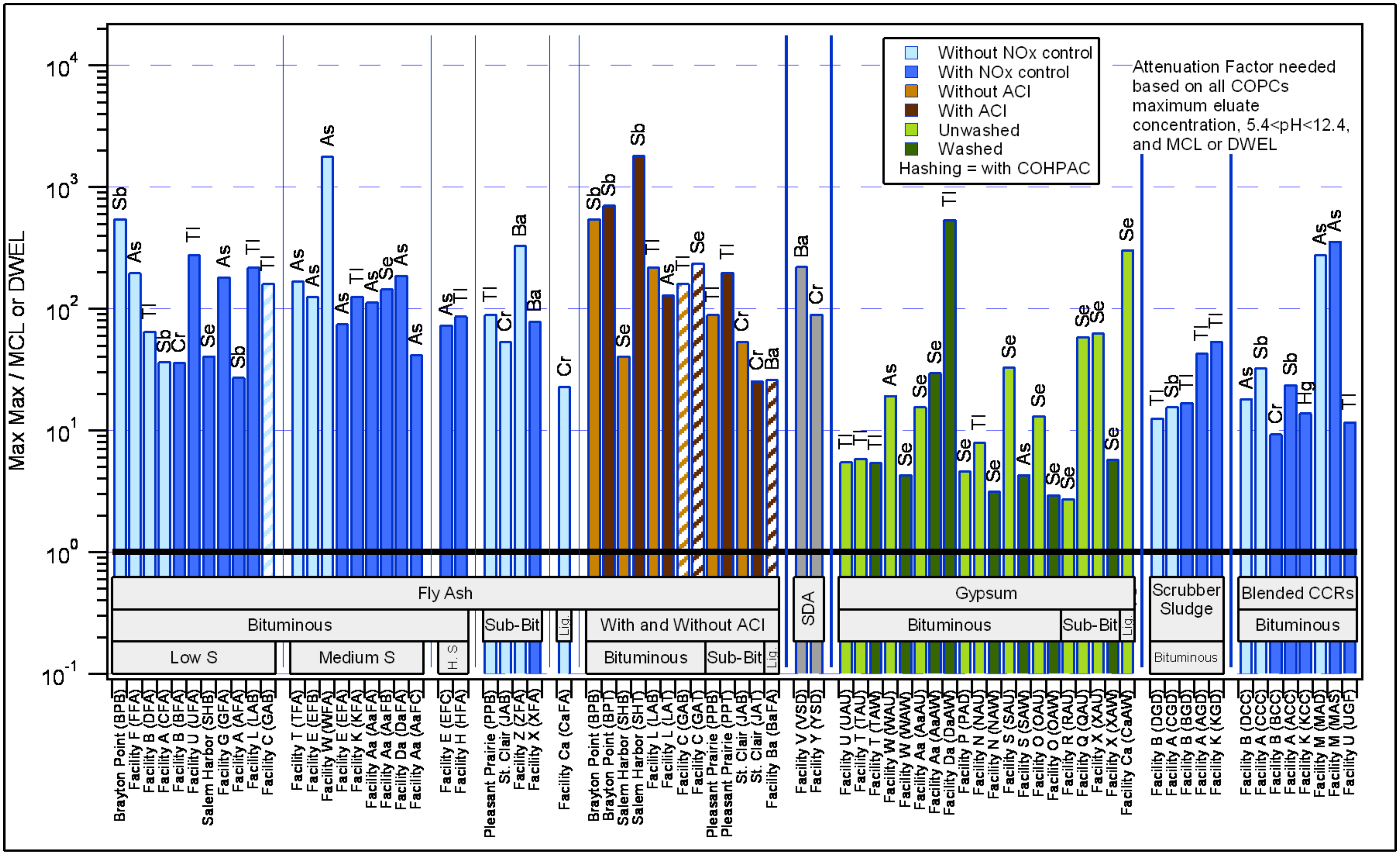

Figure 5. Minimum Attenuation Factor Needed for the Maximum Eluate Concentration (5.4 ≤ pH ≤ 12.4) to be Reduced Below the MCL or DWEL for all COPCs Considered in this Study. COPC Requiring the Greatest Attenuation Factor is Indicated for each CCR.

considerable range in the leachable concentrations of COPCs from CCRs of different types and from different sources, as well as a considerable range of DAFs resulting from different potential management scenarios. This suggests a need for developing DAF ranges for specific scenarios and evaluation in combination with CCR specific leaching test results. The effective dilution and attenuation achieved by the specific scenario can be further apportioned to the design of the engineered system (e.g., CCR compaction, blending with other materials, hydraulic controls) and the natural system (e.g., annual infiltration, attenuation during transport in the vadose zone or groundwater). Overall, a robust, flexible and practical evaluation system that distinguishes between environmentally acceptable and unacceptable management for specific CCRs is needed to facilitate safe beneficial use and ensure protection of water resources.

CONCLUSIONS

Changes to fly ash and other CCRs are expected to occur as a result of increased use and application of advanced air pollution control technologies in coal-fired power plants. These technologies include flue gas desulfurization systems for SO_2 control, selective catalytic reduction systems for NO_x control, and activated carbon injection systems for mercury control. These technologies are being or are expected to be installed in US coal-fired power plants in response to federal regulations, state regulations, legal consent decrees, and voluntary actions taken by industry to adopt more stringent air pollution control.

The primary conclusions from the evaluation are:

1. Fly ash and FGD gypsum, show a range of total concentration of constituents, 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 condition (such as by single-point leaching tests) will, in many cases, lead to inaccurate conclusions about expected leaching in the field.

2. Comparison of the ranges of total content values and leachate data also supports earlier conclusions that the rate of constituent leaching cannot be reliably estimated based on total constituent concentration alone or with use of linear K_d partitioning values.

3. The maximum eluate concentration from leaching test results varies over a wide range as a function of 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. Distinctive patterns are observed in leaching behavior as over the range of pH values that would plausibly be encountered on CCR disposal, depending upon the type of material and element.

5. There is considerable variability in total content and the leaching of constituents of potential within a material type (e.g., fly ash, gypsum) such that while leaching of many samples, without adjustment for dilution and attenuation, exceeds one or more of the available reference indicators, many of the other samples within the material type may be less than the available regulatory or reference indicators. This suggests that materials from certain facilities may be acceptable for particular disposal and

beneficial use scenarios while the same material type from a different facility or the same facility produced under different operating conditions (i.e., different air pollution controls) may not be acceptable for the same management scenario.

The CCRs analyzed in this study are not considered to be a representative sample of all CCRs produced in the U.S., and this should be considered in interpreting these results. 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, 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 and inform choices about environmentally compatible use and disposal practices for CCRs.

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