

Characterization of Coal Combustion Residues II

2.3.8. X-Ray Fluorescence (XRF)

XRF analysis was performed on each CCR to provide additional information on each CCR total elemental composition. For each CCR two pellets were prepared as follows. 3000 mg of material was weighed and mixed with 1.5 mL (100 mg dry solids) of liquid binder to give a 32 mm diameter pellet weighing 3150 mg with a material-to-diluent ratio of 0.05. For high carbon content samples 3.0 mL (100 mg dry solids) of liquid binder was used to give a 32 mm diameter pellet weighing 3300 mg with a material to diluent ratio of 0.1. XRF intensities were collected on each side of each pellet using Philips SuperQ data collection software and evaluated using Omega Data System's UniQuant 4 XRF "standardless" data analysis software. The UQ/Fly ash calibration was used to analyze the samples. The pellets were evaluated as oxides. Known fly ash Standard Reference Materials (SRMs) were also run to assess the accuracy of the analysis. This information is useful in supplementing CVAA and ICP results.

2.3.9. MDL and ML for Analytical Results

The MDL is defined by 40 CFR Part 136, Appendix B, July 1, 1995, Revision 1.11 as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte."

The MDL was determined statistically from data generated by the analysis of seven or more aliquots of a spiked reagent matrix¹⁴ and verified by the analysis of calibration standards near the calculated MDL according to EPA (2003). The MDL then was determined by multiplying the standard deviation of the replicate measurements by the appropriate Students t value for a 99% confidence level (two tailed) and n-1 (six) degrees of freedom and also multiplying by the minimum dilution factor required for matrix preservation and analysis.

The ML is defined by 40 CFR Part 136, 1994 as "the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte." According to EPA (2003), the ML is intended to be the nearest integer value (i.e., 1, 2 or 5×10^n , where n is an integer) to 10 times the standard deviation observed for determination of the MDL. This value is also multiplied by the minimum dilution factor required for preservation and analysis of the sample matrix to obtain the ML reported here.

Mercury, as measured by CVAA, required modification of the calculation of the MDL and ML because very consistent replication resulted in calculation of a MDL lower than the instrument detection limit. For this case, the standard deviation of seven replicate analyses of 0.025 µg/L was 0.00069. Therefore, the MDL was set equal to the instrument detection limit of 0.001 µg/L times the minimum dilution factor from sample preparation (3.59) to result in an MDL of 0.0036 µg/L. The ML was set to 10 times the instrument detection limit and rounded to the nearest integer value as above. The resulting ML was 0.01 µg/L.

¹⁴ Establishing spikes in an actual leaching extract matrix is not possible because the sample being extracted dictates the matrix composition by virtue of the constituents that partition into the resulting aqueous extract, which varies by test position and material being tested. However, the extract aliquots are diluted at least 10:1 with 1% nitric acid (prepared from Optima grade nitric acid, Fisher Scientific), and the COPCs are dilute in the resulting analytical sample. Therefore, the 1% nitric acid solution was used as the matrix for MDL and ML determinations.

2.4. QUALITY ASSURANCE ASSESSMENT

2.4.1. Homogenization of Individual CCR Samples and Aliquots for Analyses

To ensure sample homogeneity the fly ashes were mixed using a Morse single can tumbler model 1-305 as described in Sanchez et al. (2006). Scrubber sludges that were flowable slurries were mixed using a paddle mixer. Gypsum and fixated scrubber sludge samples were mixed by repetitively coning¹⁵ and quartering while passing through a mesh screen. After mixing, ten Subsamples were taken from FSSL sample MAD and analyzed by XRF to evaluate the homogeneity of the resultant material; Figure 9 presents the coefficient of variation for the XRF results. These results indicate that total content variability for primary and most trace constituents is less than 20% for this set of samples.

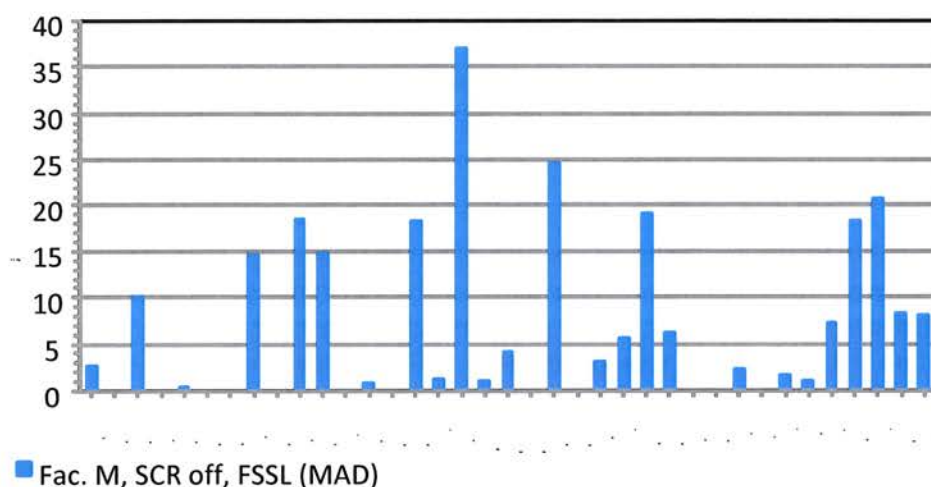


Figure 9. Coefficient of variation (C.V.) from XRF elemental analysis of 10 subsamples of FSSL sample MAD after mixing by coning and quartering.

2.4.2. Leaching Test Methods and Analytical QA/QC

One of the requirements of this project was to establish a QA/QC framework for the leaching assessment approach developed by Kosson et al. (2002). The developed QA/QC framework incorporates the use of blanks, spiked samples, and replicates. Appendix A provides the complete Quality Assurance Project Plan, as updated for this phase of the study. For each designated leaching test condition (i.e., acid or base addition to establish end-point pH values and LS value), triplicate leaching test extractions were completed (i.e., three separate aliquots of CCR were each extracted at the designated test condition) for early samples, while duplicate extractions were used after evaluation of initial results. The three types of method blanks were the deionized water case, the most concentrated nitric acid addition case, and the most

¹⁵ "Coning and quartering" is a term used to describe how the material is mixed. The approach is to pass the material through a screen so that a "cone" forms in the collection container. Then the cone is bisected twice into quarters (quarter sections of the cone) and each section then is passed sequentially through the screen again to form a new cone. This sequence is repeated several times to achieve desired mixing.

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concentrated potassium hydroxide addition case. Each method blank was carried through the entire protocol, including tumbling and filtration, except an aliquot of CCR was not added.

During analysis for mercury and elemental species by ICP-MS, analytical spikes for the constituents of interest were carried out for one replicate of each test case to assess analytical recoveries over the complete range of pH and liquid matrix conditions. Multipoint calibration curves using at least seven standards and an initial calibration verification (ICV) using a standard obtained from a different source than the calibration standards were completed daily or after every 50 samples, whichever was more frequent. In addition, instrument blanks and continuing calibration verification (CCV) standards were analyzed after every 10 analytical samples and required to be within 10 percent of the expected value. Samples are rerun if they are not within 10 percent of the expected value. CCV standards and instrument blanks also were run at the end of each batch of samples.

For both ICP-MS and CVAA analyses, each sample was analyzed along with a matrix spike, which is an aliquot of the sample plus a known spike concentration of the element of interest. The “spike recovery” was required to be within 80 – 120% of the expected value for an acceptable analytical result.

2.4.3. Improving QA/QC efficiency

Throughout the study, the approach to QA/QC was regularly reviewed to seek out opportunities for increased evaluation efficiency without unacceptable degradation of precision or accuracy in results. Based on evaluation of results from the first several facilities (Sanchez et al, 2006), the number of replicates for Method SR002.1 (solubility as a function of pH) and Method SR003.1 (solubility as a function of liquid/solid ratio) was reduced from three to two. Results from this study (Sanchez et al., 2006 and this report) show that the precision between duplicate analyses is acceptable and that the triplicate set does not significantly increase the quality of the data set. This finding follows from recognition that (i) the data sets generated by Method SR002.1 and SR003.1 must provide both consistency between replicate extractions and analyses, and internal consistency between results at different pH and LS ratio, and (ii) precision is controlled primarily by the degree of homogeneity of the CCR under evaluation and representative sub-sampling, rather than by the intrinsic variability of the leaching test methods. There were a total of 11,743 observations for the 14 parameters evaluated in detail in this report (pH and 13 constituents of interest). Review of the resulting data sets indicated 15 outlier pH values of 846 measurements¹⁶ and an additional 19 outliers out of 10,897 measurements of specific constituents. Thus, the overall error rate was less than 2%. Implementation of a reduction in the number of replicates has greatly improved laboratory efficiency without compromising data quality.

Data were screened for outliers based on comparison of individual data points (i) relative to replicate extractions (i.e., parallel extractions of aliquots of the same material under the same extraction conditions), and (ii) relative to the other data points in the extraction series (i.e., parallel extractions of aliquots of the same material at different pH (SR02) and LS conditions

¹⁶ When a pH measurement is determined to be an outlier, then all constituent measurements associated with the particular extract sample are also considered outliers because they would be incorrectly evaluated as release as a function of pH. This resulted in excluding $(15) \times (13) = 195$ individual constituent measurements.

(SR03)) because of the expected systematic response behavior. The pH was considered an outlier when the final pH of the extract deviated from the other replicates by more than 0.5 pH units and corresponding constituent analyses did not follow systematic behavior indicated by other extracts across multiple constituents. Individual constituents were considered outliers when results of constituent analyses deviated from the systematic behavior indicated by results in the extraction series (as a function of pH or as a function of LS) by more than one-half to one order of magnitude. Results were screened through inspection of the appropriately plotted results.

Data quality indicators (DQIs) were measured for all parameters continuously during the leaching experiments and during analytical tasks. Chemical (ICP, CVAA, XRF, IC, EC/OC) and physical (surface area, pore size distribution and density) characterization data were reduced and reports were generated automatically by the instrument software. The primary analyst reviewed 100% of the report data for completeness to ensure that quality control checks met established criteria. Sample analysis was repeated for any results not meeting acceptance criteria. A secondary review was performed by the Inorganic Laboratory Manager to validate the analytical report. A data quality report for the CCR leach testing results will be provided in the fourth and final report of this research. The data quality report will cover the leach test results documented in Report 1 (Sanchez et al., 2006), Report 2 (this report), and a third report (in preparation). The fourth report summarizes the data from the first three reports and provides probabilistic assessment of the potential release rates of mercury and other metals based on plausible management practices.

2.5. INTERPRETATION AND PRESENTATION OF LABORATORY LEACHING DATA

Complete laboratory leaching results for each CCR type and test method are presented in Appendices D and E. Appendix D presents results for Solubility and Release as a Function of pH (SR002.1). Appendix E presents results for Solubility and Release as a Function of LS ratio (SR003.1). Results are organized by CCR type (fly ash, gypsum, scrubber sludge, fixated scrubber sludge), with pH results followed by mercury and then other constituents of interest (aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, selenium and thallium). For SR002.1, pH results are a titration curve of pH as a function of milliequivalents of acid or base, with acid additions considered positive (+) and base additions considered negative (-). For SR003.1, pH results are a curve of pH as a function of LS ratio.

For Solubility and Release as a Function of pH (SR002.1), results for each CCR type are grouped as described in Figure 5 through Figure 8. Results are presented as extract concentrations as a function of pH. The “natural” pH¹⁷ of the system is indicated as a vertical line to the average pH and a horizontal line to the y-axis indicating the corresponding extract concentration. Included with each figure are horizontal lines at the drinking water maximum concentration level (MCL) or drinking water equivalent level (DWEL)¹⁸, and analytical limits (ML and MDL) to provide a frame of reference for the results. Also included with each figure are the 5 and 95 percentile for pH (vertical lines) from field observations of leachate from landfills and surface impoundments

¹⁷ “Natural pH” or “own pH” of a material refers to the equilibrium pH when the material is placed in deionized water at a ratio of 10 g CCR per 100 mL of water.

¹⁸ MCL and DWEL values used are as reported in (EPA, 2006).

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for combustion residues (see Section 2.5.1). An annotated example of the results is provided as Figure 10.

For Solubility and Release as a Function of LS ratio (SR003.1), results are presented as extract concentrations as a function of LS ratio. Also indicated are the relevant MCL, ML and MDL or DWEL.

2.5.1. Interpretation of Mechanisms Controlling Constituent Leaching

Constituent (e.g., mercury, arsenic, and selenium) concentrations observed in laboratory leach test extracts and in field leachate samples may be the result of several mechanisms and factors. The discussion presented here focuses on constituent leaching and source term modeling approaches. Source term is defined here as the flux or amount of constituent released from the waste or secondary material (e.g., CCRs). Factors controlling constituent release and transport in and within the near field of the CCRs are often distinctly different from the factors and mechanisms which are important for subsequent vadose zone or groundwater transport outside of the near field area.

In general, constituents are present in the waste or secondary material either as adsorbed species, co-precipitated as amorphous or crystalline solid phases, or incorporated as trace components in solid phases. If chemical equilibrium conditions are approached (as is the approximate case for the laboratory and field sample conditions discussed in this report), then the functional behavior of the aqueous solution concentration reflects the nature of the constituent species in the waste or secondary material, the presence of any co-constituents in the aqueous phase influencing aqueous solution speciation (e.g., effects of high ionic strength, chelating or complexing constituents), and the presence of species in the solution that may compete for adsorption sites if adsorption is the controlling solid phase mechanism. If the constituent is present in the waste or secondary material as an adsorbed species, many different adsorption/desorption characteristic patterns are possible (Ruthven, 1984; Duong, 1998).

The simplest case is when the constituent of interest is present at very low concentration in the waste or secondary material, relatively weakly adsorbed, and the presence of complexing and, or, competing species in solution is at a constant concentration. For this case, leaching test results will indicate a constant concentration as a function of pH at a fixed LS ratio, and linearly increasing concentration as LS ratio decreases at constant pH. This case is represented mathematically as a linear equilibrium partitioning function, where the critical constant of proportionality is the partitioning coefficient, commonly known as K_d . Linear partitioning and use of K_d values is a common approach for mathematically modeling contaminant transport at low contaminant concentrations in soils. Assumption of linear partitioning is a valid and useful approach when the necessary conditions (discussed above) are fulfilled¹⁹.

For mercury adsorbed on activated carbon or char particles in fly ash, a complex combination of adsorption mechanisms is indicated. During laboratory leaching tests, mercury concentrations in the leaching test extracts are relatively constant over the pH range and LS ratio of interest, and

¹⁹ Often specific K_d values are a function of pH because of competition for adsorption sites by hydrogen ions. However, often a single K_d or range of K_d values are used in contaminant fate and transport models, without specific relationship between pH and K_d which can result in misrepresentation of actual contaminant behavior.

independent of total mercury content in the CCR. In addition, the total mercury content in the CCR is very low. These results are indicative of adsorption phenomena where, in the adsorbed state, interactions between adsorbed mercury species are stronger (thermodynamically) than the interactions between the adsorbed mercury species and carbon surface²⁰. This observation has been supported by the observation of mercury dimer formation during sorption (Munro et al, 2001) and the occurrence of chemisorption as the dominant adsorption mechanism at temperatures above 75 °C (consistent with conditions in air pollution control devices; Vidic, 2002). In other studies, this phenomenon has been observed as the formation of molecular clusters on the adsorbent surface (Ruthven, 1984; Duong, 1998; Rudzinski et al., 1997). For this case, use of a K_d approach would underestimate release because desorption is best represented as a constant aqueous concentration until depletion occurs.

A third case is encountered when the constituent of interest is present in the waste or secondary material (e.g., CCR) as a primary or trace constituent in either an amorphous or crystalline solid phase and there may be complexing or chelating co-constituents in the aqueous phase. Observed aqueous concentrations are a non-linear function of pH and LS ratio, and reflect aqueous saturation with respect to the species of interest under the given conditions (pH, co-constituents). For these cases, an approximation of field conditions can be made empirically based on laboratory testing and observed saturation over the relevant domain (as applied in this report) or geochemical speciation modeling coupled with mass transfer modeling can be used to assess release under specific field scenarios (the subject of a future report). Use of a K_d approach would not be appropriate for these cases because constituent concentrations will remain relatively constant at a given pH until the controlling solid phase is depleted and control is shifted to a new solid phase or mechanism.

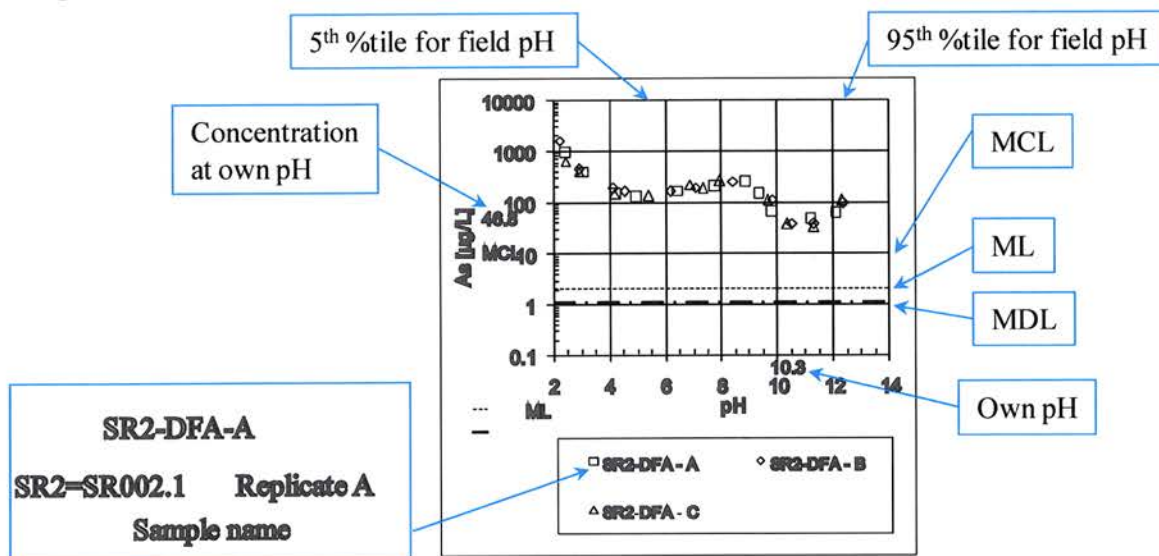


Figure 10. An example of extract concentrations as a function of pH from SR002.1.

²⁰ For this case, the first mercury molecule is adsorbed more weakly than subsequent mercury molecules because the adsorbed mercury-mercury interaction is stronger than the adsorbed mercury-carbon surface interaction [see Sanchez et al. (2006) for further discussion].

2.6. FIELD pH PROBABILITY DISTRIBUTION

A probability distribution of field leachate pH values from coal combustion waste landfills was derived, as described below, from the set of field pH observations included in the EPA Risk Report (EPA, 2007). The pH probability distribution used in this report considers additional data beyond the pH probability distribution used in Report 1 (Sanchez et al, 2006), which was based solely on relevant data from the EPA Office of Solid Waste database (EPA, 2000) and included 158 observations from six CCR disposal facilities. The data set developed for the EPA Risk Report included (i) observations from the comprehensive database of landfill leachate characteristics developed by the EPA's Office of Solid Waste (EPA, 2000), (ii) field observations from literature, primarily from EPRI reports, (iii) additional data reported to EPA, and (vi) pH observations from laboratory leaching tests. Only pH measurements from field samples (i.e., leachate, pore water) were selected for use in development of the resulting pH probability distribution. The resulting data set included 580 observations from 42 CCR landfill disposal facilities and was highly unbalanced, with some sites having only a few (e.g., less than five) observations and some sites having many observations (e.g., greater than 20). To prevent the unbalanced data from skewing the resulting probability distribution, the minimum, 25th, 50th, 75th percentile, and maximum values of observations for each individual facility were compiled into a single data set. For facilities with fewer than five observations, all observations for that facility were included. This data set then served as the basis for fitting a statistical distribution function. For each data set, different distribution functions were used to fit the data and the one providing the best data fit based on the chi-square test was selected. The resulting field pH probability distribution was truncated and normalized to the pH range of the field data.

The resulting pH probability distribution developed in this report is compared in Figure 11 and Table 7 to the pH probability distribution used in Report 1. The new pH probability distribution reflects a similar range of pH, but has a more alkaline median value, and in general, has greater weighting in the pH range between 8 and 12. The probability distribution used in this report is considered more representative than what was used in Report 1 because of a larger dataset using results from recent studies by EPA and EPRI. (EPA, 2006; EPRI, 2006)

Field pH observations were also evaluated for surface impoundments receiving CCRs from coal combustion facilities with FGD scrubbers in use. Pore water pH values measured in samples obtained from within the settled CCRs were selected from the EPRI database. Resulting pH observations were across the same range as the landfill field pH observations, but were insufficient to develop an independent pH probability distribution. Therefore, the same pH probability distribution was used for landfill and surface impoundment facilities in this report.

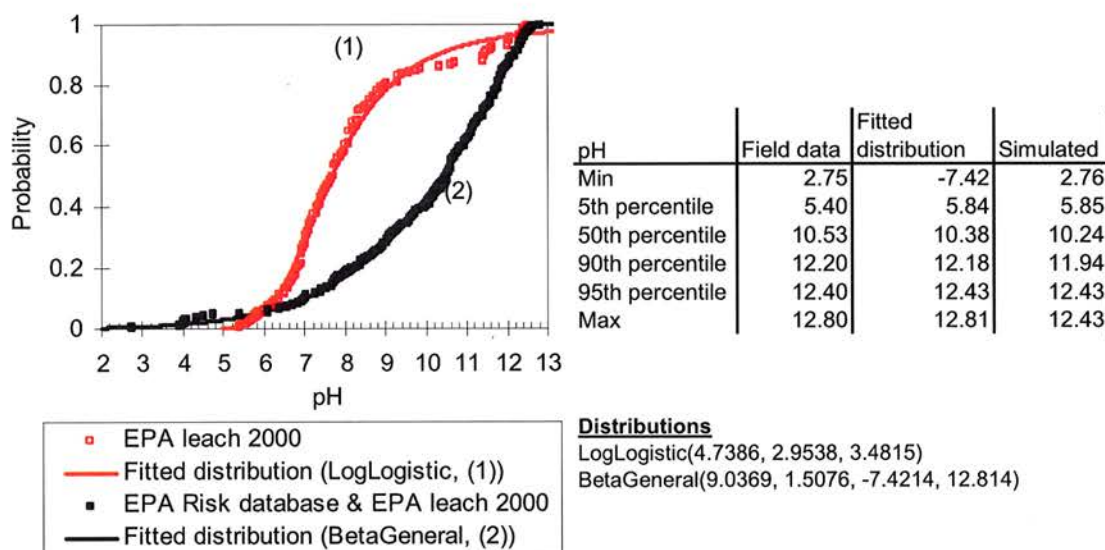


Figure 11. Probability distributions for field pH used in Report 1 (LogLogistic) and this report (BetaGeneral). Summary statistics for the field data and the probability distribution used in this report (BetaGeneral) are provided to the right of the graph..

Table 7. Comparison of summary statistics for field pH data and pH probability distributions used in Report 1 and this report.

	Field Data		Distribution Used in Release Estimates	
	Report 1	This Report	Report 1	This Report
Minimum	5.40	2.75	4.92	2.76
5 th percentile	5.80	5.40	5.97	5.85
50 th percentile	7.70	10.53	7.63	10.24
90 th percentile	NR	12.20	NR	11.94
95 th percentile	12.09	12.40	10.63	12.43
Maximum	12.80	12.80	12.50	12.43

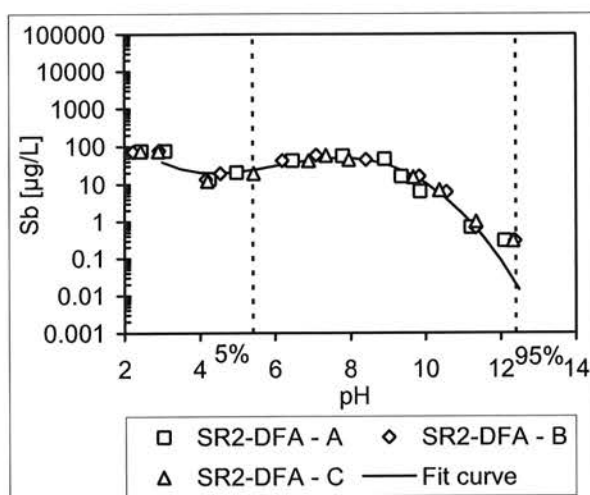
NR=not reported.

2.7. ESTIMATED LEACHATE CONCENTRATION AS A FUNCTION OF pH

For each CCR tested, results from SR002.1 (Alkalinity, Solubility and Release as a Function of pH) were used to develop an empirical functional relationship between solution pH and expected concentration for each constituent of interest. For each constituent within each CCR case, a polynomial function was regressed to the results from SR002.1 (Alkalinity, Solubility and

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Release as a Function of pH) to provide the expected leachate concentration as a function of solution pH. Up to a fifth order polynomial was used for the regression. An example of a regression fit and corresponding equation for solubility and release as a function of pH is presented in Figure 12. The coefficients provided in the table reflect the order of the polynomial used. For all cases, the lowest order polynomial possible based on the R-square (no further increase for higher order) was used. Also included with each figure of regression fit is the 5th and 95th percentile for pH (vertical line) from field observations of leachate from landfills and surface impoundments for combustion residues. Regression fit results are provided in Appendix F for each case examined (i.e., for each constituent in each CCR tested).



Antimony		
log (µg/L)	Number of points	pH range of validity
0.0000 pH ⁵	33	2.2-12.4
0.0008 pH ⁴		
-0.0399 pH ³		
0.5519 pH ²		
-2.7978 pH		
6.031866 pH ⁰		
0.97 R ²		

Figure 12. Example of regression fit and corresponding coefficients for a 5th order polynomial equation used to represent solubility and release as a function of pH (antimony for fly ash from Facility B with SCR bypassed (DFA)).

3. 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).²¹ Thus, the evaluation provided here focuses on the same thirteen constituents and can be used in future risk and environmental assessments.

3.1. TOTAL ELEMENTAL CONTENT BY DIGESTION

Total elemental compositions using digestion²², on a dry weight basis, for COPCs for the CCRs evaluated are compared by constituent in Figures 13 through 24; tabular results are provided in Appendix B. Boron was not analyzed because it is used in the digestion process and therefore analysis would not yield meaningful results.

Mercury. Mercury content exhibited a similar range (0.01 to 1.0 µg/g) for all CCR types. Use of SNCR (Facility A) resulted in increased mercury content in the fly ash and decreased mercury content in the scrubber sludge, compared to when the SNCR was not in use. In contrast, use of SCR (Facility B) resulted in decreased mercury content in the fly ash and increased mercury content in the scrubber sludge, compared to when the SCR was bypassed. For all three comparative cases (Facilities A, B and M) use of the NO_x control increased the total mercury content in the fixated scrubber sludge. Mercury content in gypsum was significantly lower in the washed gypsum than in the unwashed gypsum for comparative cases (Facilities N and O).

Aluminum. Aluminum content was approximately an order of magnitude greater in the fly ash samples than in the scrubber sludge samples from facilities without SCR and than in gypsum samples with and without SCR. Facilities with SCR operating (samples BGD, KGD) had greater aluminum content in scrubber sludge than the other scrubber sludges, likely because of the addition of aluminum with the SCR catalyst. Fixated scrubber sludge samples had intermediate Al content, reflective of the blending of fly ash with scrubber sludge.

Antimony. Antimony content ranged over similar levels for fly ash, scrubber sludge and fixated scrubber sludge; gypsum had lower antimony content except for the sample from Facility Q. Samples from both Facilities K and Q had greater antimony content than comparative FGD residues from other facilities (scrubber sludges and fixated scrubber sludges for Facility K, gypsum for Facility Q) perhaps as a consequence of greater antimony content in sub-bituminous coal burned by these facilities than bituminous coal burned by the other facilities. The SNCR samples had higher antimony contents in the fly ash, scrubber sludge and fixated scrubber sludge for Facility A than the samples collected with SNCR off. The SCR samples had higher antimony contents in the fly ash from Facility B and the fixated scrubber sludges from Facilities A, B and

²¹ 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). The database was sparse with respect to measurements of field samples for many constituents.

²² Digestion Method 3052 and ICP-MS analysis by Method 6020; see Section 2.3.7.

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M, although the reason for the high level of antimony in sample BCC cannot be explained by the relative antimony content in samples BFA and BGD.

Arsenic. Gypsum had very low arsenic content ($<5 \mu\text{g/g}$) compared to the other residue types. Arsenic content in scrubber sludge was significantly less than in fly ash for residue from the same facility. Use of NO_x controls resulted in decreased arsenic content in the fly ash, increased content in the scrubber sludge (Facilities A and B) and decreased content in the fixated scrubber sludge (Facilities A, B and M; reflecting the relative contributions of fly ash and scrubber sludge in fixated scrubber sludge) for comparative samples.

Barium. Barium content was similar in scrubber sludge and gypsum for all facilities except for sample BGD (unexplained), and lower than barium content in fly ash by approximately an order of magnitude. The relatively low barium content in unwashed gypsum from Facility O is also unexplained.

Cadmium. Cadmium content was low in the gypsum ($<0.69 \text{ ng/g}$) and scrubber sludges ($<1.72 \mu\text{g/g}$) and generally total content of the gypsum was half that in fly ash ($<1.51 \text{ ng/g}$). The greater cadmium content in sample BGD relative to sample DGD may be a consequence of the use of post-combustion NO_x control using SCR.

Chromium. Chromium content in gypsum ($<19.3 \text{ ng/g}$) and scrubber sludges ($<139 \text{ ng/g}$) was low and approximately an order of magnitude less than in fly ash samples (<194). Scrubber sludge samples without SCR in operation also had chromium content similar to that of gypsum. Scrubber sludge samples without SCR in use also had chromium content similar to that of gypsum. Elevated chromium content in scrubber sludge samples BGD and KGD may be associated with the use of post-combustion NO_x control using SCR.

Cobalt. Cobalt content in gypsum was low and approximately an order of magnitude less than in fly ash samples. Scrubber sludge samples without SCR in operation also had cobalt content similar to that of gypsum. Elevated cobalt content in scrubber sludge samples BGD and KGD may be associated with SCR catalyst addition. The relatively low cobalt content in fixated scrubber sludge samples BCC and KCC relative to corresponding fly ash and scrubber sludge samples is unexplained.

Lead. Lead content in gypsum was low and less than one third of the lead content in fly ash samples. Scrubber sludge samples without SCR in operation also had lead content similar to that of gypsum. The relatively low lead content in fixated scrubber sludge samples BCC and KCC in relationship to corresponding fly ash and scrubber sludge samples is unexplained.

Molybdenum. A similar range in molybdenum content was found in fly ash, scrubber sludge and fixated scrubber sludge samples, with lower content by approximately one third in gypsum samples, with the exception of gypsum sample QAU.

Selenium. All samples were less than $5 \mu\text{g/g}$, except for samples for fly ash and fixated scrubber sludge from Facility A and unwashed gypsum from Facilities P and Q. The upper bound for these samples was less than $30 \mu\text{g/g}$.

Thallium. All gypsum samples had thallium content less than $3 \mu\text{g/g}$. Fly ash, scrubber sludge, and fixated scrubber sludge samples all had a similar range of thallium content between 2 and $5 \mu\text{g/g}$, except scrubber sludge and fixated scrubber sludge from Facility B with SCR and fly ash and fixated scrubber sludge from Facility K. Both of these observations of greater thallium content (between 5 and $13 \mu\text{g/g}$) may result from the SCR catalyst addition.

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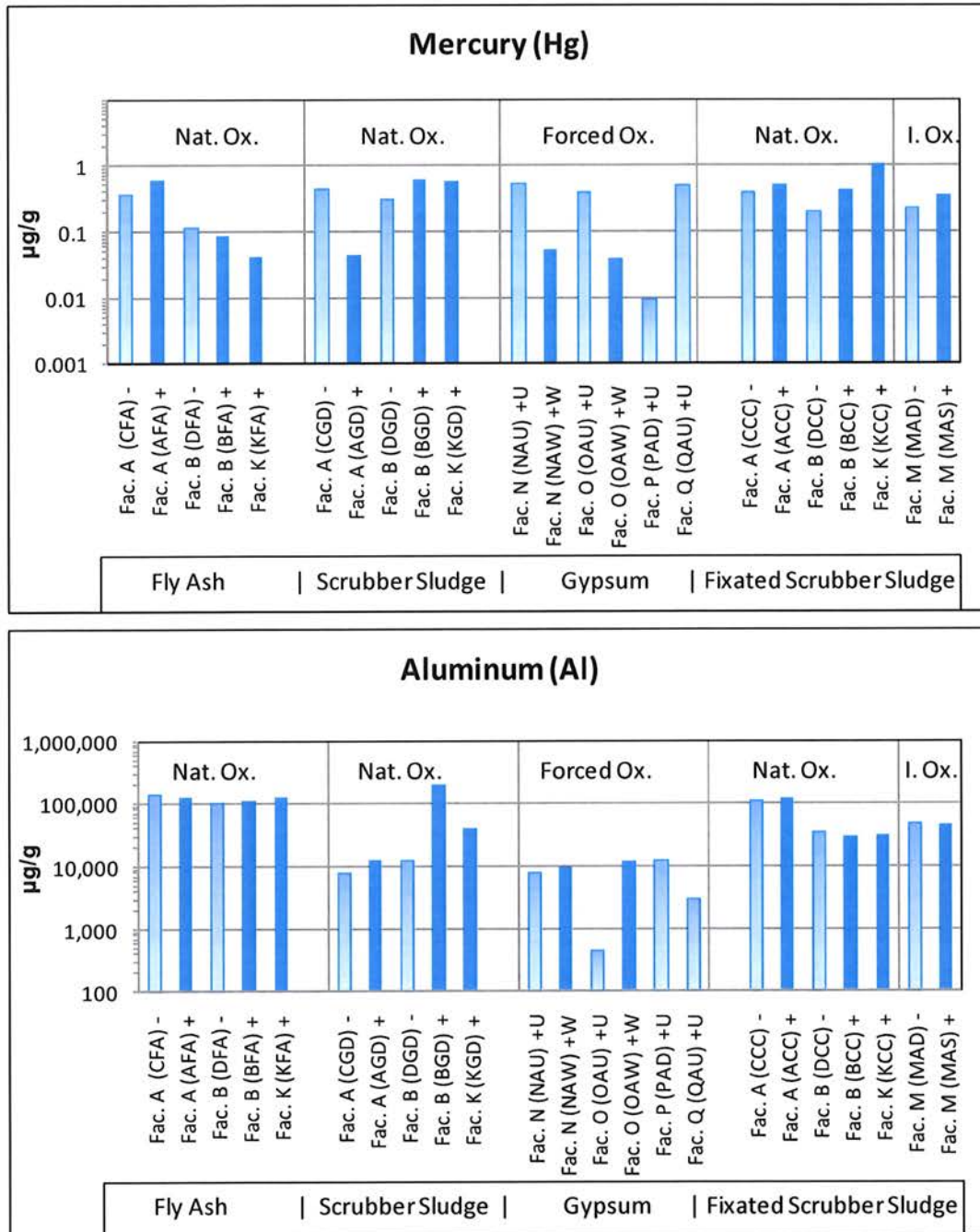


Figure 13 and Figure 14. Mercury and Aluminum. Comparison of total elemental content by digestion (key: - = NO_x control off; + = NO_x control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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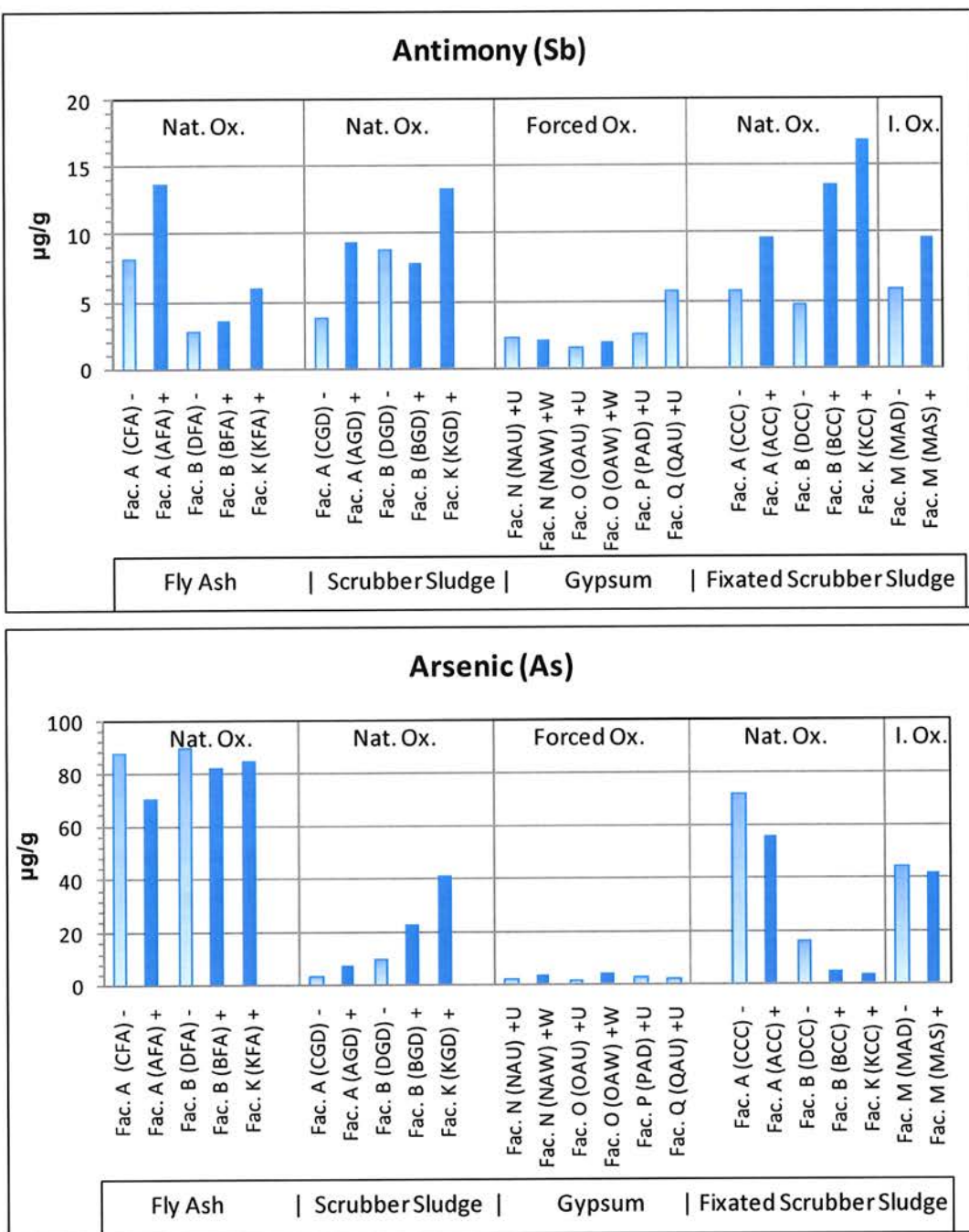


Figure 15 and Figure 16. Antimony and Arsenic. Comparison of total elemental content by digestion (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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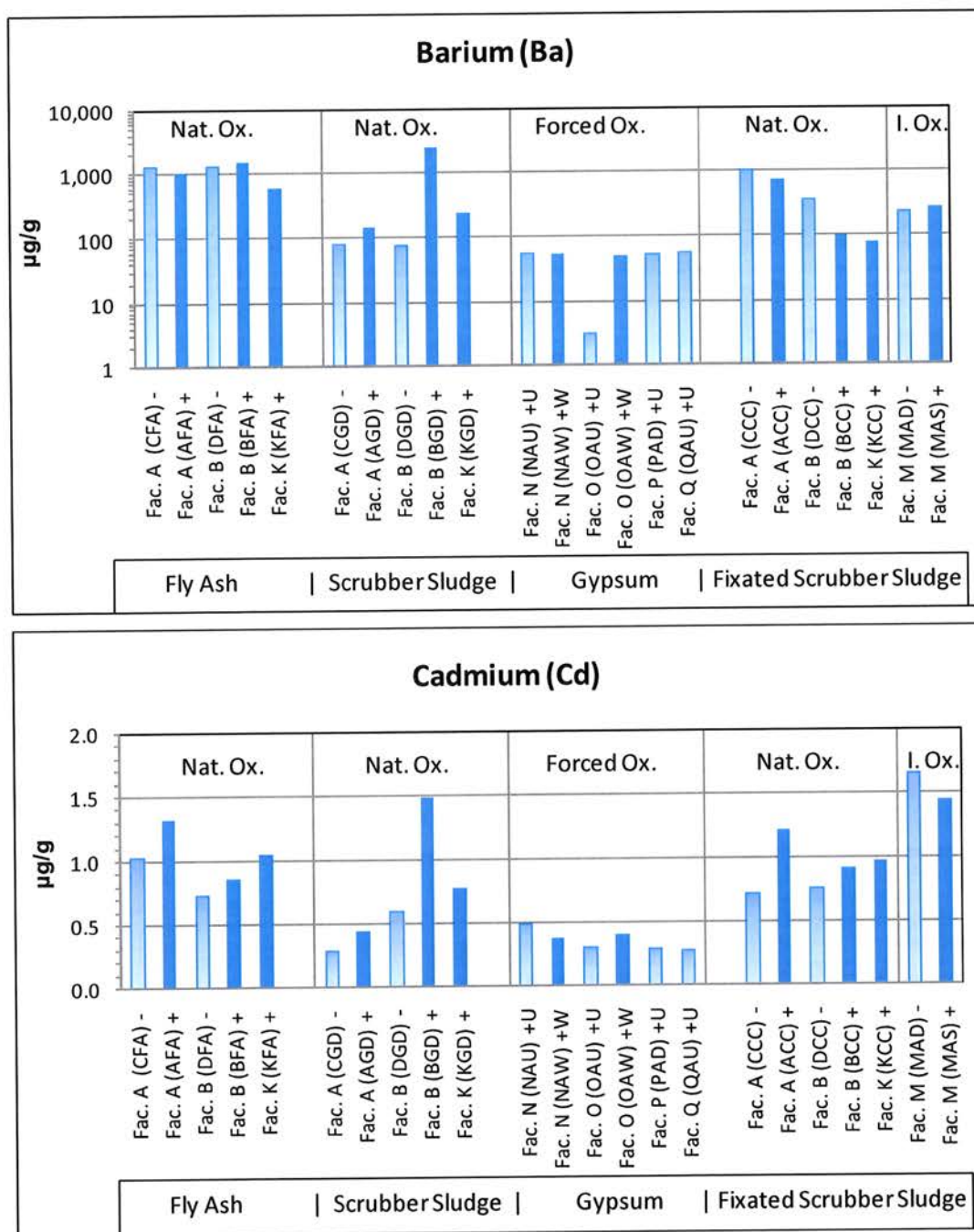


Figure 17 and Figure 18. Barium and Cadmium. Comparison of total elemental content by digestion (key: - = NO_x control off; + = NO_x control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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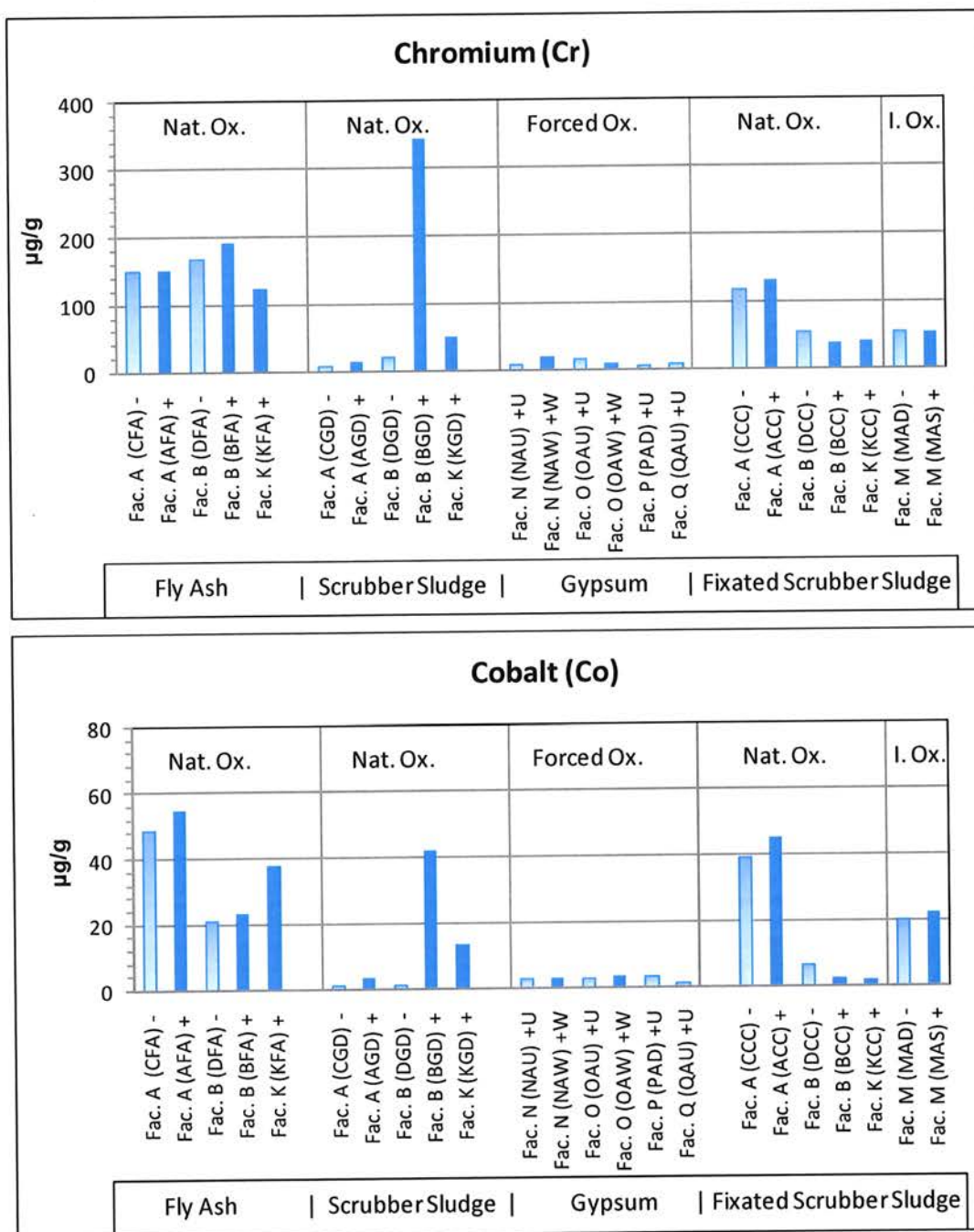


Figure 19 and Figure 20. Chromium and Cobalt. Comparison of total elemental content by digestion (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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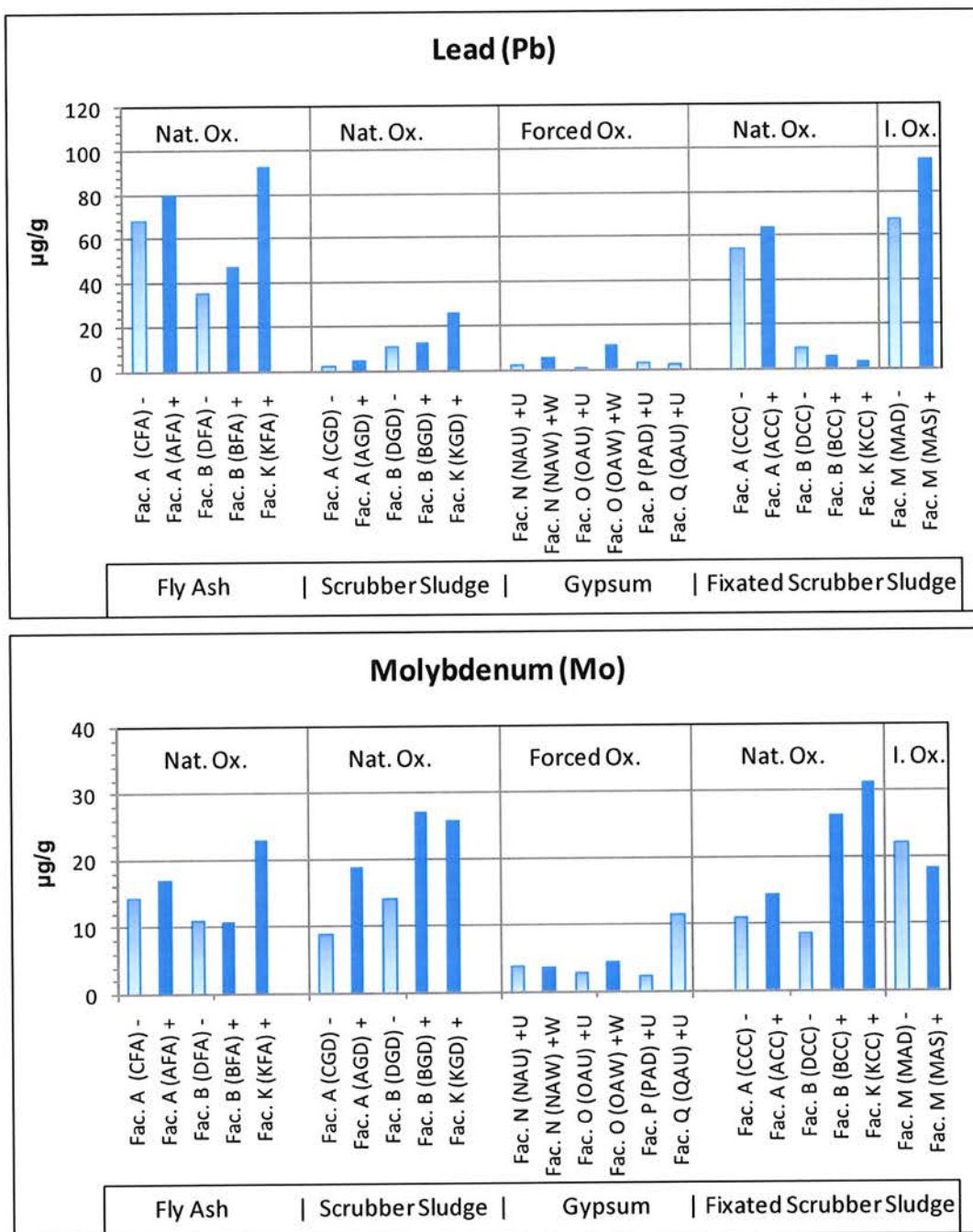


Figure 21 and Figure 22. Lead and Molybdenum. Comparison of total elemental content by digestion (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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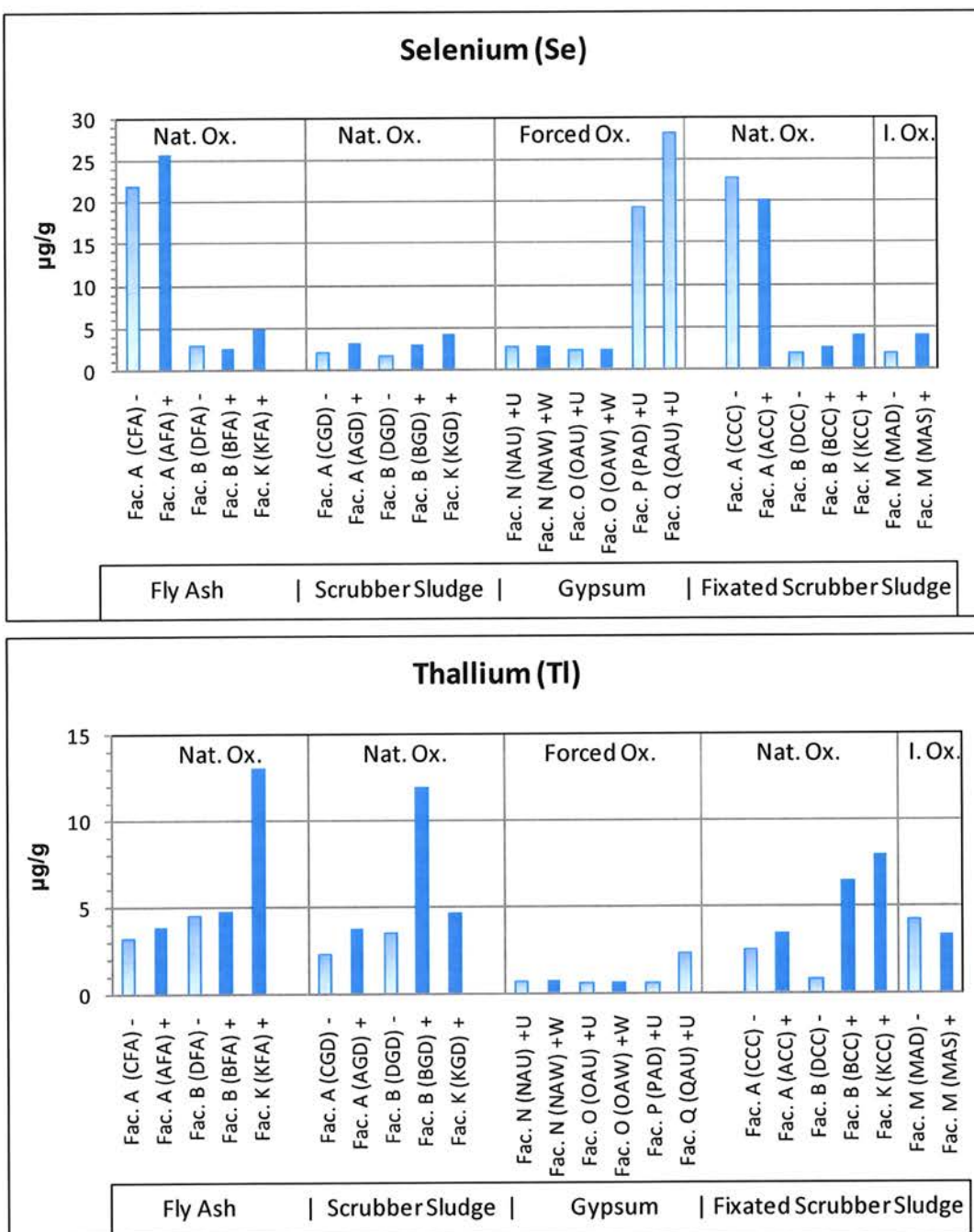


Figure 23 and Figure 24. Selenium and Thallium. Comparison of total elemental content by digestion (key: - = NO_x control off; + = NO_x control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

3.2. TOTAL ELEMENTAL CONTENT BY XRF

Total elemental compositions, on a dry weight basis, for major and some trace constituents in each of the CCRs evaluated are compared in grouping by CCR type (i.e., fly ash, gypsum, scrubber sludge, fixated scrubber sludge) in Figure 25 through Figure 29; tabular results are provided in Appendix C. Major elemental constituents present in CCRs but not detected by XRF analysis include oxygen and carbon. Elements that may be analyzed by XRF but were below the detection limit are indicated in the figures on the x-axis but without any reported value represented. Separate analyses were carried out for carbon and are also included in Appendix C.

Fly Ash. Elemental constituents typically present in fly ash at concentrations greater than 1 percent (10,000 mg/kg) are aluminum, calcium, iron, potassium, and silicon. Elemental constituents typically present at concentrations between 0.1 and 1 percent are barium, chloride, magnesium, sodium, phosphorus, strontium, sulfur, and titanium.

Gypsum. Elemental constituents typically present in gypsum at concentrations greater than 1 percent (10,000 mg/kg) are calcium and sulfur. Elemental constituents typically present at concentrations between 0.1 and 1 percent are chloride (unwashed gypsum), fluoride (unwashed gypsum), iron, magnesium, sodium (unwashed gypsum) and silicon.

Scrubber Residue. Elemental constituents typically present in scrubber residue at concentrations greater than 1 percent (10,000 mg/kg) are aluminum (SCR on), calcium, iron (SCR on), magnesium, silicon (SCR on) and sulfur. Elemental constituents typically present at concentrations between 0.1 and 1 percent are aluminum (except with SCR on), chloride, fluoride, iron (except with SCR on), potassium, sodium (SCR on), silicon (except with SCR on), and titanium (SCR on).

Fixated Scrubber Sludge. Elemental constituents typically present in fixated scrubber sludge at concentrations greater than 1 percent (10,000 mg/kg) are aluminum, calcium, iron, potassium, silicon and sulfur. Elemental constituents typically present at concentrations between 0.1 and 1 percent are barium, chloride, sodium, phosphorus and strontium.

Fixated Scrubber Sludge with Lime. Elemental constituents typically present in fixated scrubber sludge with lime at concentrations greater than 1 percent (10,000 mg/kg) are aluminum, calcium, iron, magnesium (Mg lime scrubbers), silicon, and sulfur. Elemental constituents typically present at concentrations between 0.1 and 1 percent are chloride, potassium, magnesium (non-Mg lime scrubbers), sodium, and titanium.

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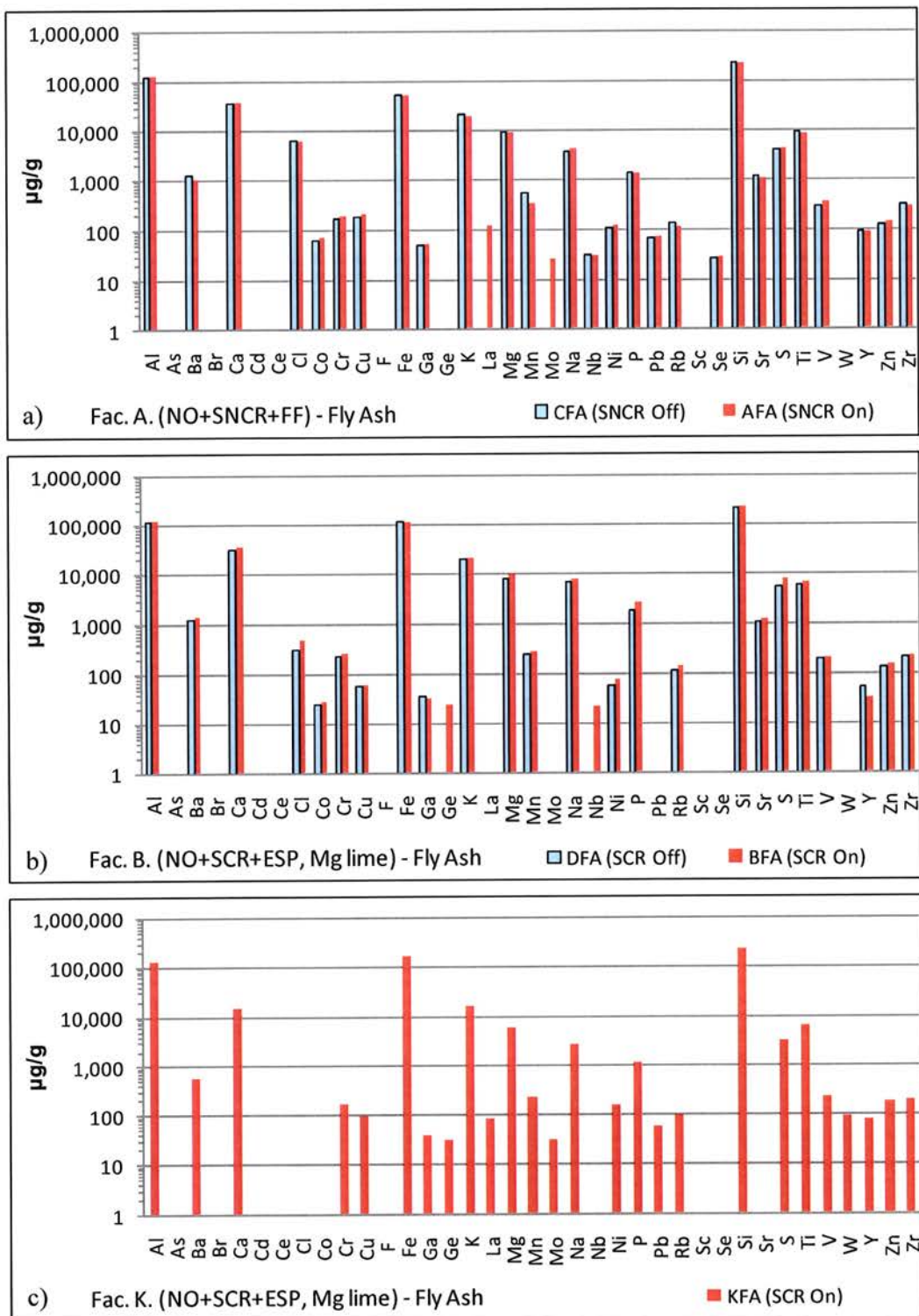


Figure 25. Fly Ash - Total content by XRF.

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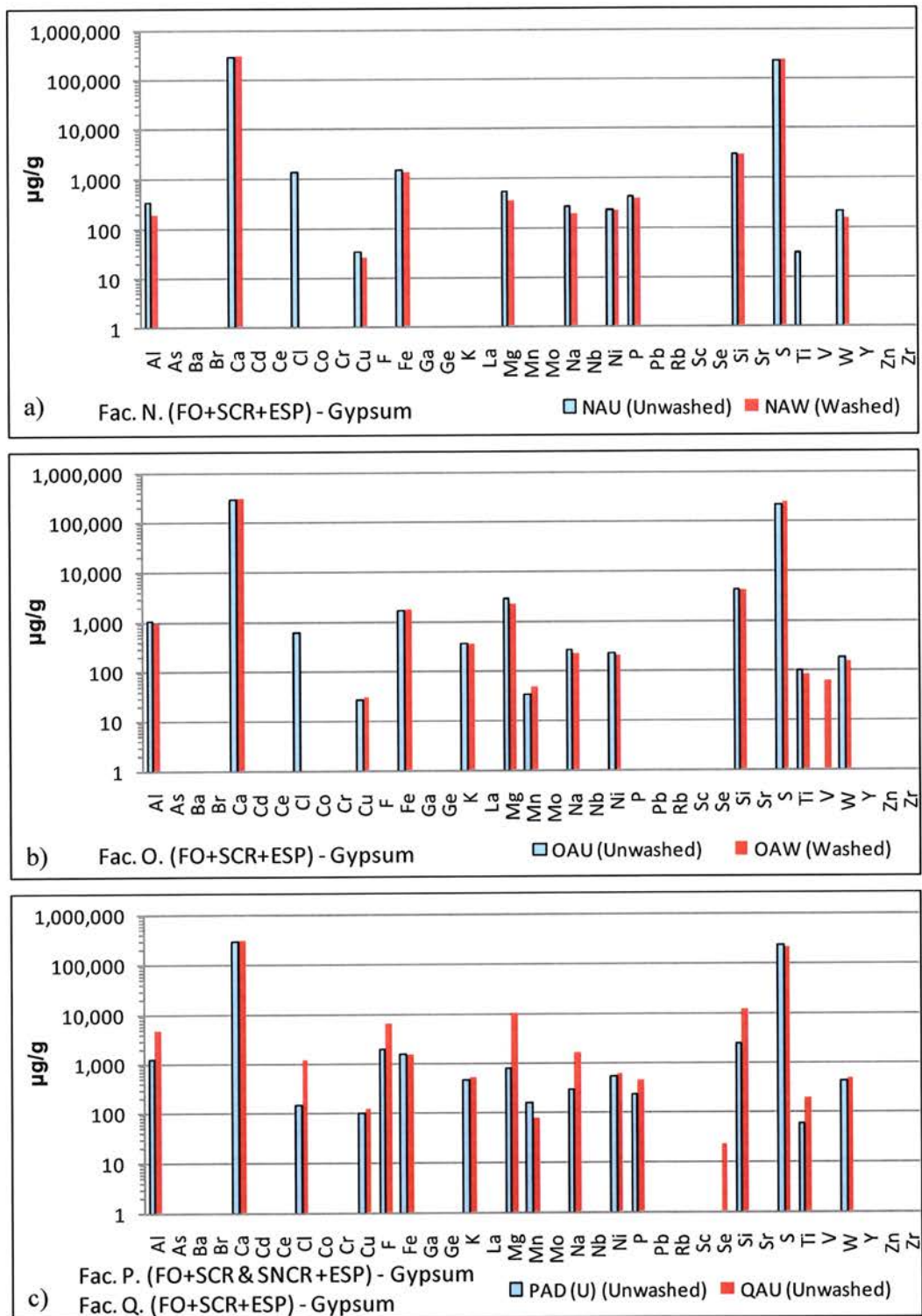


Figure 26. Gypsum – Total content by XRF.

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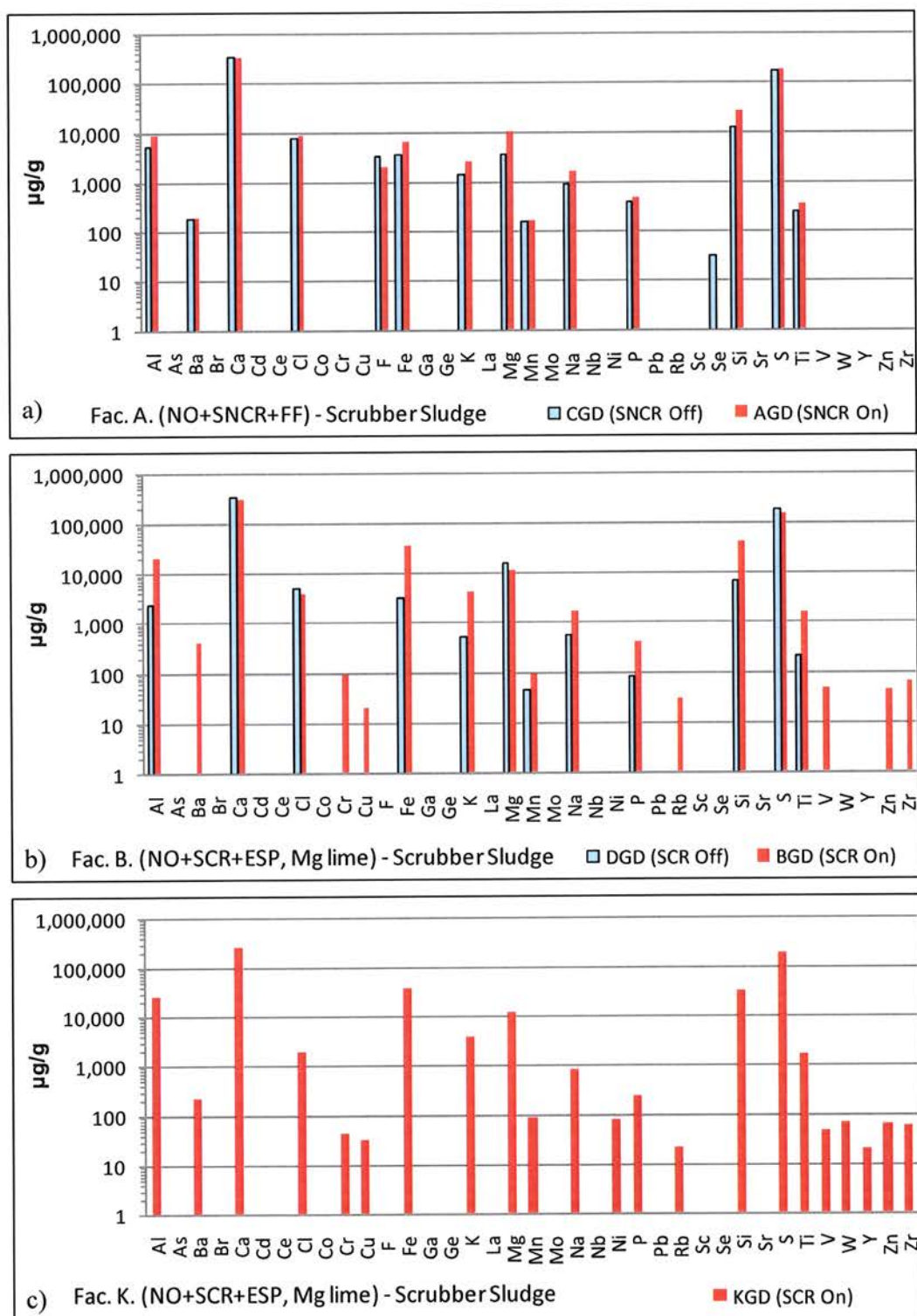


Figure 27. Scrubber Sludge – Total content by XRF.

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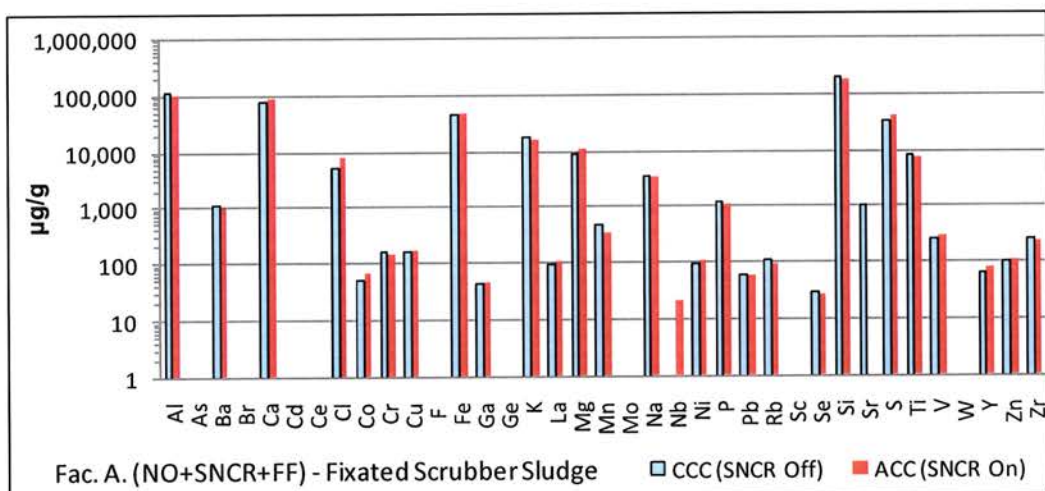


Figure 28. Fixated Scrubber Sludge – Total content by XRF.

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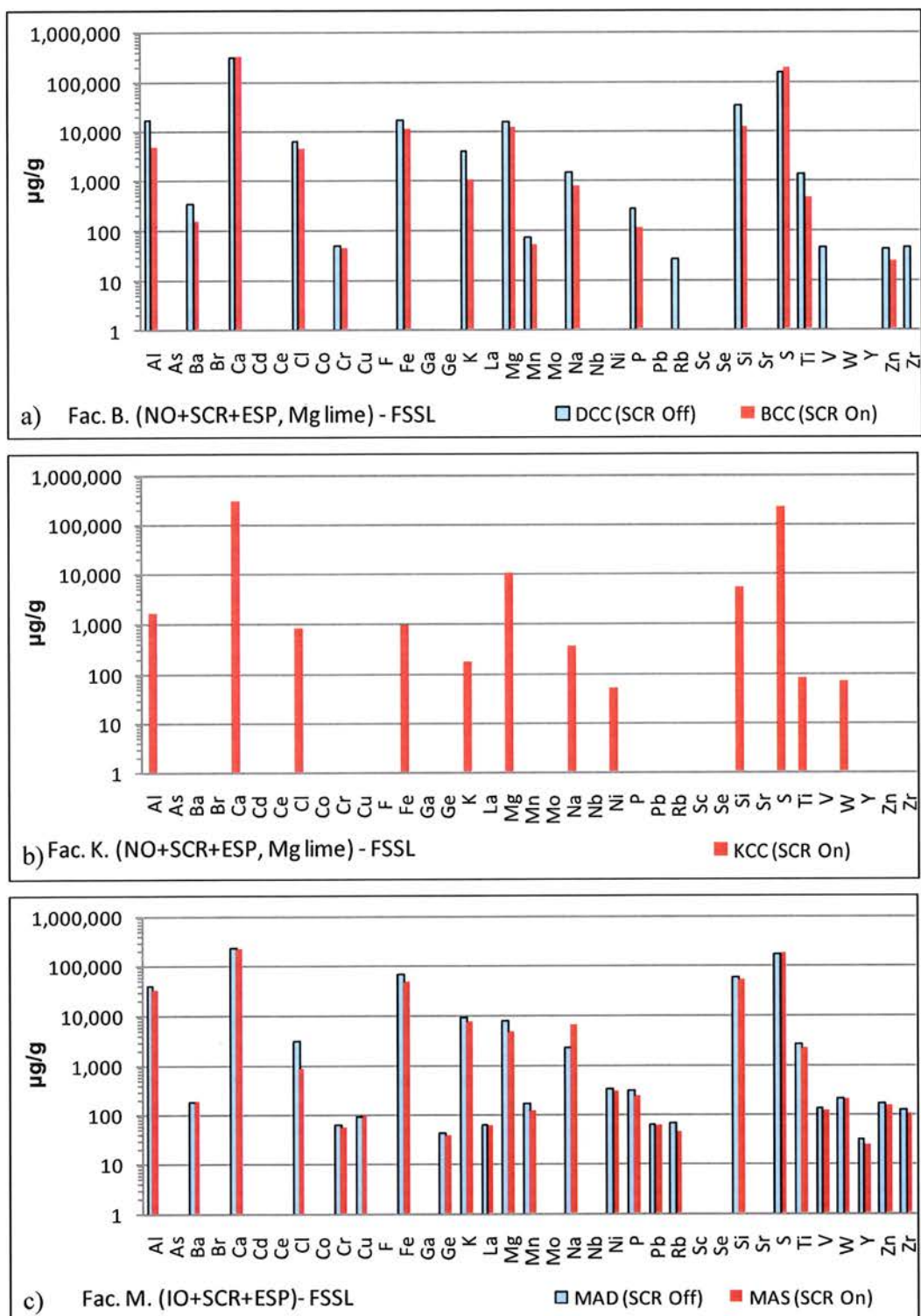


Figure 29. Fixated Scrubber Sludge with Lime – Total content by XRF.

3.3. LABORATORY LEACHING TEST RESULTS

Appendix D and Appendix E provide graphical presentation of the results of Solubility and Release as a Function of pH (SR002.1) and Solubility and Release as a Function of LS (SR003.1), respectively, for the 13 constituents of interest in this report. Within each appendix, results are grouped by CCR type (fly ash, gypsum, scrubber sludge, FSS, FSSL) and with each CCR type grouping, comparisons are made by constituent of interest. First discussed below are typical characteristic results for pH and each of the 13 constituents of interest (Section 3.3.1) followed by a discussion (Section 3.3.2) comparing the ranges of observed constituent concentrations (from both test methods) with measurements reported elsewhere on field leachate and pore water samples for CCR disposal sites and the database used in the EPA Risk Report (EPA, 2007). Complete data also have been developed for other constituents to facilitate evaluation of geochemical speciation of constituents of concern and provide more thorough evaluation of leaching under alternative management scenarios in the future if warranted.

For each CCR evaluated, results of the leaching tests provide the following information:

- Leachate concentrations for the constituents of interest as a function of pH over the range of reported field management conditions (from test method SR002.1);
- pH titration curves (from test method SR002.1). This information is useful in characterizing the CCR and assessing how it will respond to environmental stresses and material aging (e.g., carbon dioxide uptake, acid precipitation, co-disposal, mixing with other materials); and,
- Leachate concentrations for the constituents of interest, pH and electrical conductivity as a function of LS ratio when contacted with distilled water (from test method SR003.1). This information provides insight into the initial leachate concentrations expected during land disposal and effects of pH and ionic strength at low LS ratio. Often these concentrations can be either greater than or less than concentrations observed at higher LS ratio (i.e., LS=10 mL/g as used in SR002.1) because of ionic strength and co-constituent concentration effects.

The MCL is used as a reference threshold for the constituent of interest. However, releases identified here are estimates of concentrations potentially leaching from landfills. Any assessment of the environmental impact of these releases needs to consider the dilution and attenuation of these constituents in ground water, and the plausibility of drinking water well contamination resulting from the release. 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 potential²³. Therefore, comparison with thresholds greater than the MCL and developed for specific scenarios may be appropriate.

²³ 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 in 65 FR 55703, September 14, 2000.

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3.3.1. Typical Characteristic Leaching Behavior as a Function of pH and LS

Figure 30 through Figure 45 provide comparisons of typical leaching behavior as a function of pH for each constituent, as examples reproduced from Appendix D. These comparisons illustrate on an empirical basis some of the differences in leaching behavior for different CCRs that result from the combination of the coal rank combusted, combustion conditions and specific combustion facility design and operation. Also noted but not shown is the observed behavior for each constituent as a function of LS at the material's natural pH (see Appendix E). Elements with predominantly oxyanionic species (e.g., boron, molybdenum, selenium, etc.) typically exhibited non-linearly increasing extract concentrations as LS was decreased from 10 mL/g to 0.5 mL/g, in many cases increasing by a factor of 5 or 10 or greater.

These figures illustrate that for a particular constituent, the chemistry controlling release or aqueous-solid equilibrium may be similar within a material type (i.e., mercury behavior for fly ash or scrubber sludge) or across material types (i.e., the same behavior for aluminum in fly ash and fixated scrubber sludge) but that there are not necessarily generalized behaviors present for each constituent across all samples within a material type or between material types. The most robust groupings of leaching behavior will result from the development of geochemical speciation models of the materials that account for the underlying solid phase speciation (e.g., solid phases, adsorption behavior) and modifying solution characteristics (e.g., dissolved organic matter, pH, ionic strength, co-dissolved constituents). Development of the needed geochemical speciation models, and associated leaching behavior groupings as a function of coal rank, combustion facility design, and CCR type, will be the basis of a subsequent report. The resulting models and groupings, in turn, are expected to allow for more detailed constituent release predictions based on limited testing for a broader set of facilities.

Mercury. Figure 30 (a, b) compares the impact of SNCR usage (Facility A) on the release behavior of mercury from fly ash. The increased mercury release, reaching a maximum at pH~8, when SNCR is in use, is likely a consequence of additional ammonium present and consequent formation of an ammonium mercury complex in solution (Wang, 2007). For all fly ash samples except AFA (Facility A, SNCR[+]), the mercury release indicated apparently random scatter with solution concentrations ranging from 0.01 to 0.1 µg/L. This behavior is similar to that reported earlier in this study (Sanchez et al., 2006) and is indicative of adsorption of elemental mercury as the primary release mechanism. For gypsum samples, mercury release was either (i) similar to that observed for fly ash (Figure 30d, Facility P), (ii) at very low concentration near or below the MDL (Facility O, unwashed and washed; Facility N washed) potentially indicative of adsorption onto carbon char, or (iii) had increased release at pH<6 potentially indicative of adsorbed ionic mercury being displaced by hydrogen ions at acidic pH (Facility A, unwashed; Facility Q). For scrubber sludge, mercury release was either (i) similar to that observed for fly ash, (ii) had increasing release concurrent with decreasing pH at pH<8 (Facility B, Figure 30c), or (iii) had increased release at pH~8 (local peak, indicative of ammonium complexation) and then increasing release with decreasing pH at pH<6 (Facility K). For FSS, behavior was either (i) analogous to that observed for fly ash (Facility A), or (ii) analogous to that observed for scrubber sludge illustrated in Figure 30c (Facilities B, K, M). Mercury extract concentrations were not significantly affected by LS.

Aluminum. Figure 31 (a, b) compares the impact of SNCR usage (Facility A) on the release behavior of aluminum from fly ash and illustrates one of the three types of aluminum behavior observed across the CCR types. One type of observed aluminum behavior was amphoteric

behavior (minimum release at pH~6-8, with increasing release as pH decreases and increases outside of this range) with a local maximum of approximately 10,000 µg/L at pH~12 and a maximum of ca. 100,000 to 1,000,000 µg/L at pH~3. The concentration of the minimum at 6<pH<8 is typically influenced by the amount of DOC complexing aluminum in solution (increased complexation increases dissolved aluminum). This behavior was present for fly ash from Facilities A and K. Other samples exhibited increasing aluminum release with decreasing pH at pH<8 but without substantially increased release at pH>8 (fly ash from facility B; scrubber sludge from facilities B, K). Several samples exhibited increasing release with decreasing pH for pH<6 and a local maximum at pH~10 (Figure 31c, scrubber sludge from Facility A; FSS from Facility B). In addition, several samples exhibited relatively constant release (ca. 100 µg/L) at pH>8 with increasing release with decreasing pH at pH<8 (Figure 31d, scrubber sludge for facility B with SCR[-]; FSS from facilities A, B, K). Aluminum extract concentrations typically were either relatively constant or decreasing (salting out) with decreasing LS. The notable exception was the scrubber sludge from facility B with SCR off (DGD) and FSS from facility M with SCR on (MAS), where aluminum concentration increased with decreasing LS.

Antimony. Figure 32a illustrates antimony behavior with local maxima at pH~8 and pH<3, which was observed for fly ash from facilities A and B, and FSS from facility A. Figure 32b illustrates behavior that was observed for gypsum from Facility Q and scrubber sludge from Facility A. For gypsum samples other than from Facility Q, antimony release appeared random at concentrations of <MDL to 3 µg/L at pH>4 with a general slight increase in concentration at pH<4. Figure 32c and d illustrates behavior that was observed for the remaining CCR samples. For some samples, antimony concentrations in extracts increased by up to a factor of 5 with decreasing LS, while it remained constant or decreased for other samples.

Arsenic. Figure 33 illustrates the four typical release behaviors observed for arsenic release as a function of pH. Each of these four behaviors was observed for a least one of the samples from each material type (fly ash, gypsum, scrubber sludge, FSS). Leaching from gypsum generally was less than 10 µg/L for pH>6 and reached a maximum of approximately 30-100 µg/L at pH<5. Arsenic concentrations in extracts were either constant or increased by up to a factor of 2 with decreasing LS.

Barium. Figure 34 illustrates the four typical release behaviors observed for barium. For fly ash, barium was either relatively constant at approximately 100 µg/L as a function of pH or exhibited increases at pH<4 (Figure 34a) and pH>9 to approximately 1000 µg/L (i.e., facility K). For gypsum, Figure 35d illustrates the typical behavior. Behaviors illustrated by Figure 34b and c are typical of that observed for scrubber sludge and FSS, with both behaviors observed for both material types. Barium extract concentrations remained constant with decreasing LS, with the exception of fly ash from facility A, where barium concentrations increased by up to a factor of 5 with decreasing LS.

Boron. Figure 35 (a, b, c) illustrates the three typical release behaviors for boron: (i) decreasing concentration with increasing pH for pH>8 (Figure 35a, fly ash from facilities A, B; scrubber sludge from facility K; FSS from facilities A, M), (ii) relatively constant concentration with a slight decrease at 8<pH<10 (Figure 35b, scrubber sludge from facility B, FSS from facility K), (iii) relatively constant or with a slight increase at pH>10 (Figure 35d). Comparison of Figure 35c and d illustrates the reduction in leachable boron achieved through the washing step (facility N, unwashed and washed). Boron concentrations in extracts were either constant or increased by up to a factor of 10 with decreasing LS.

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Cadmium. Figure 36 illustrates typical release behavior for cadmium, which is similar for all cases. The maximum concentration at pH<4 reflects the total content in the sample, and the slope and pH shift in the increasing cadmium concentration with decreasing pH typically reflects the presence or absence of complexants in solution (e.g., chloride or DOC). Cadmium concentrations in extracts were either constant or increasing with decreasing LS.

Chromium. Figure 37 and Figure 38 illustrate typical release behavior for chromium. Comparison of the pairs Figure 37a and b, Figure 37c and d, and Figure 38a and b illustrate the effect of NO_x control on chromium release from fly ash, scrubber sludge, and FSS respectively for Facility B. Use of SCR at this facility appears to result in a larger fraction of the chromium in the residue being oxidized (Cr⁺⁶), forming chromate, which is more soluble at neutral pH. The SCR catalyst used for Facility B may have contributed to increased overall total chromium present in the CCRs from that facility when SCR was in use. Increased leachability of chromium as a consequence of NO_x control was also observed for Facility A (comparing results for SNCR[-] with SNCR[+]), even though total chromium content was similar for cases with and without NO_x control. Figure 38c and d illustrates the typical amphoteric behavior for reduced chromium (Cr⁺³), which was observed for gypsum samples. Chromium concentrations in extracts were either constant (for cases with low leachable chromium), or increasing by up to a factor of 10 (cases with Cr⁺⁶ as the apparently dominant chromium form) with decreasing LS.

Cobalt. Figure 39 illustrates typical release behavior for cobalt, which is similar for all CCRs tested. Cobalt release increases with decreasing pH at pH<8, with the maximum concentration reflecting the total leachable content and the slope and relative pH shift in the slope typically reflecting the presence or absence of complexants in solution. Cobalt concentrations in extracts (where greater than the MDL) were typically increasing by up to a factor of 5 with decreasing LS.

Lead. Figure 40 illustrates typical release behavior for lead, which generally is expected to be amphoteric (Figure 40a, c). However, many samples did not have sufficient lead content or complexants present in solution to produce amphoteric behavior at pH<12 (Figure 40b, d). Lead concentrations in extracts were not significantly changed at decreasing LS.

Molybdenum. Figure 41 and Figure 42 illustrate typical release behaviors for molybdenum. Figure 41a illustrates increased concentration peaking at pH~8 most likely from complexation with ammonium present from use of SNCR (Facility A). Note the similar release behavior observed for fly ash, FSS and gypsum illustrated by Figure 41b and Figure 42b, c, albeit at different orders of magnitude in concentration. Figure 41c, d and Figure 42b, d illustrate three additional observed behaviors, present across multiple CCR types. Molybdenum concentrations typically increased with decreasing LS, in some cases by a factor much greater than 10 (e.g., FSS from Facility A).

Selenium. Figure 43 and Figure 44 illustrate typical selenium release behaviors observed for fly ash, scrubber sludge and FSS. For gypsum, selenium release was either constant as a function of pH (facilities O, P) or amphoteric (facilities N, Q). Selenium concentrations in extracts typically increased by up to a factor of 6 with decreasing LS.

Thallium. Figure 45 illustrates typical release behavior for thallium. Most cases were either analogous to Figure 45a or Figure 45c (increasing concentration with decreasing pH at pH<9) or Figure 45d (relatively constant as a function of pH). For gypsum, washing resulted in at least an

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order of magnitude reduction in the observed leaching concentrations (facilities N, O). Thallium concentrations typically increased by up to a factor of 5 with decreasing LS.

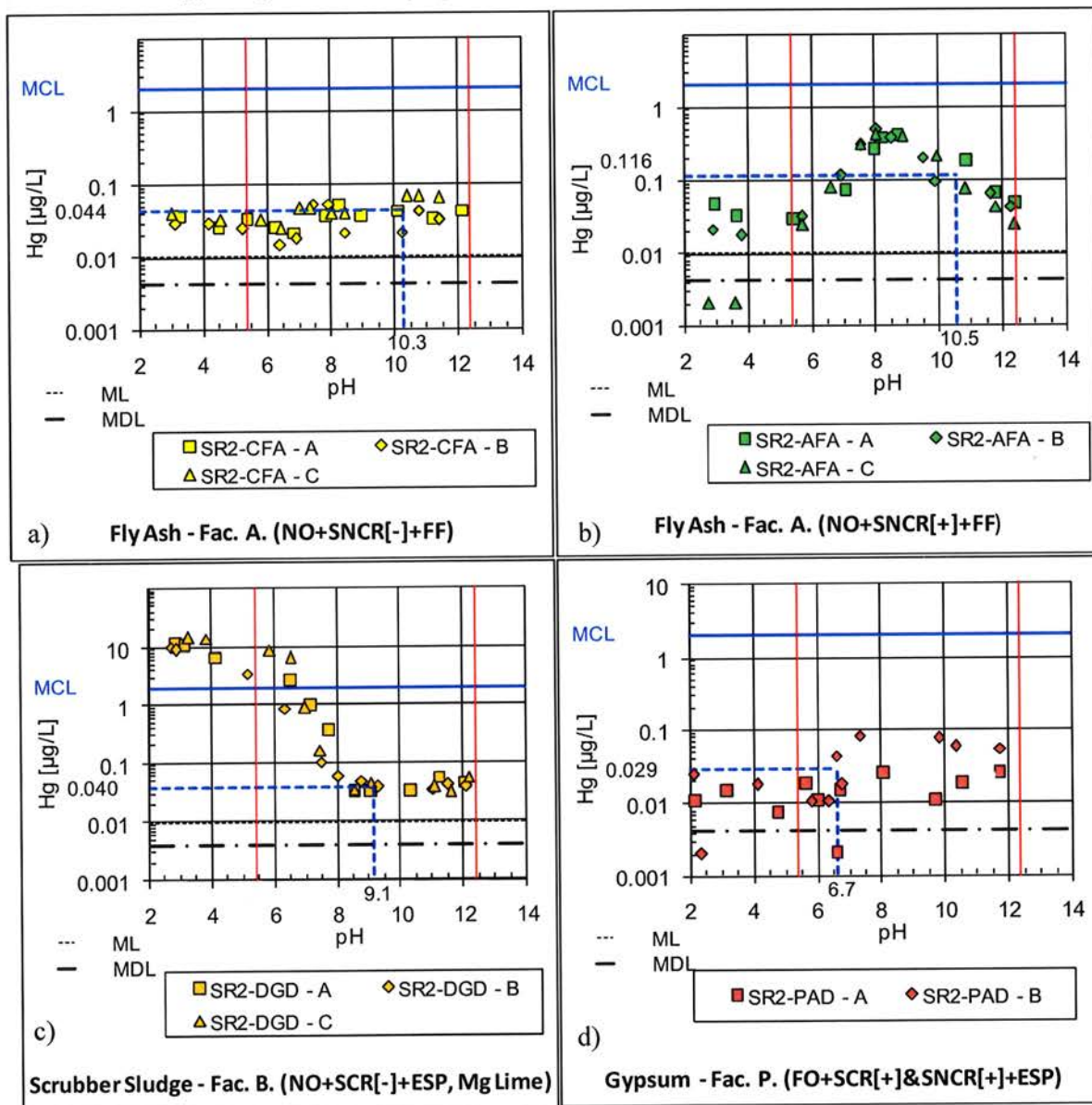


Figure 30. Mercury - Examples of characteristic leaching behavior as a function of pH (SR002.1 results).

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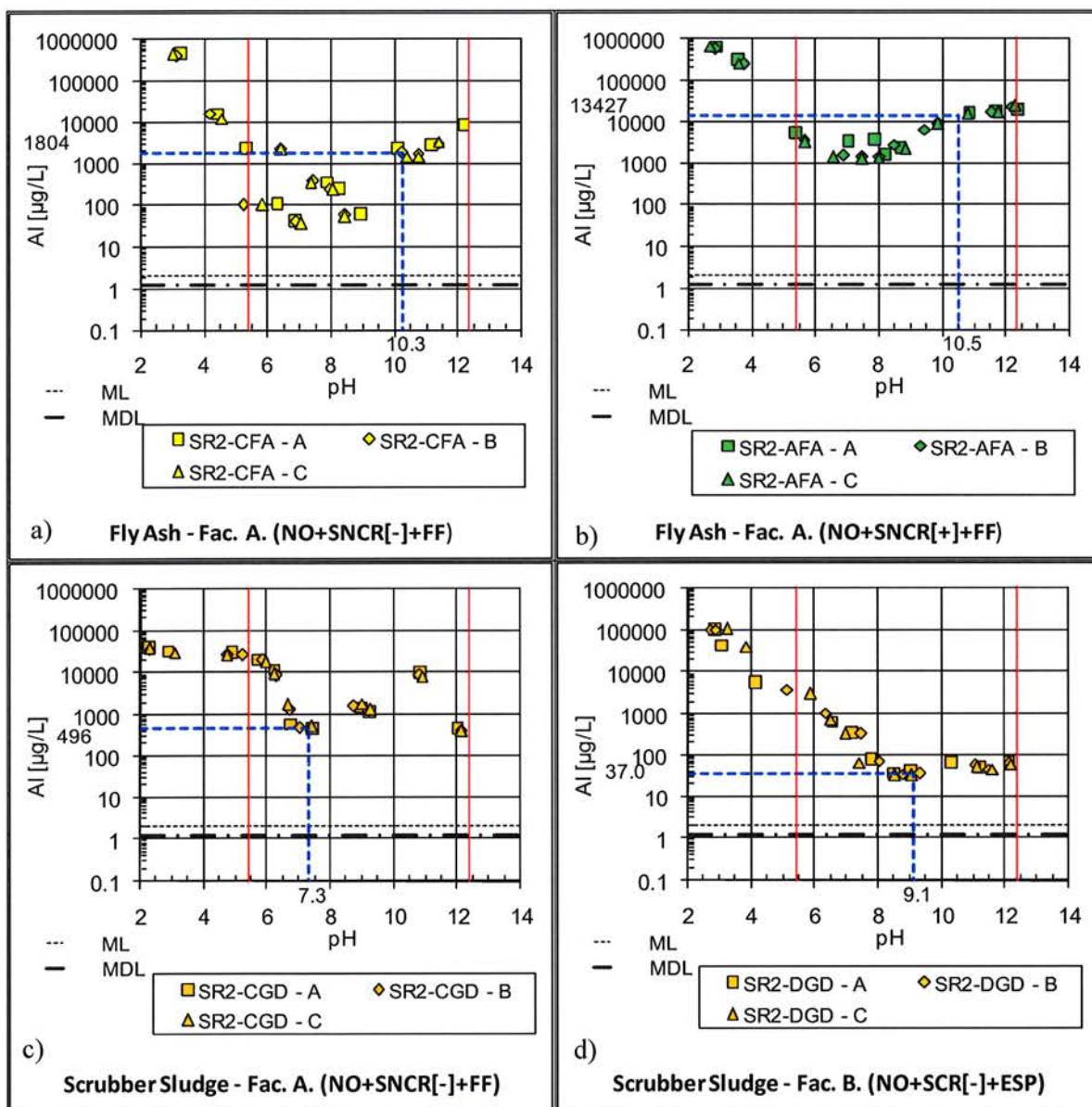


Figure 31. Aluminum. Examples of characteristic leaching behavior as a function of pH.

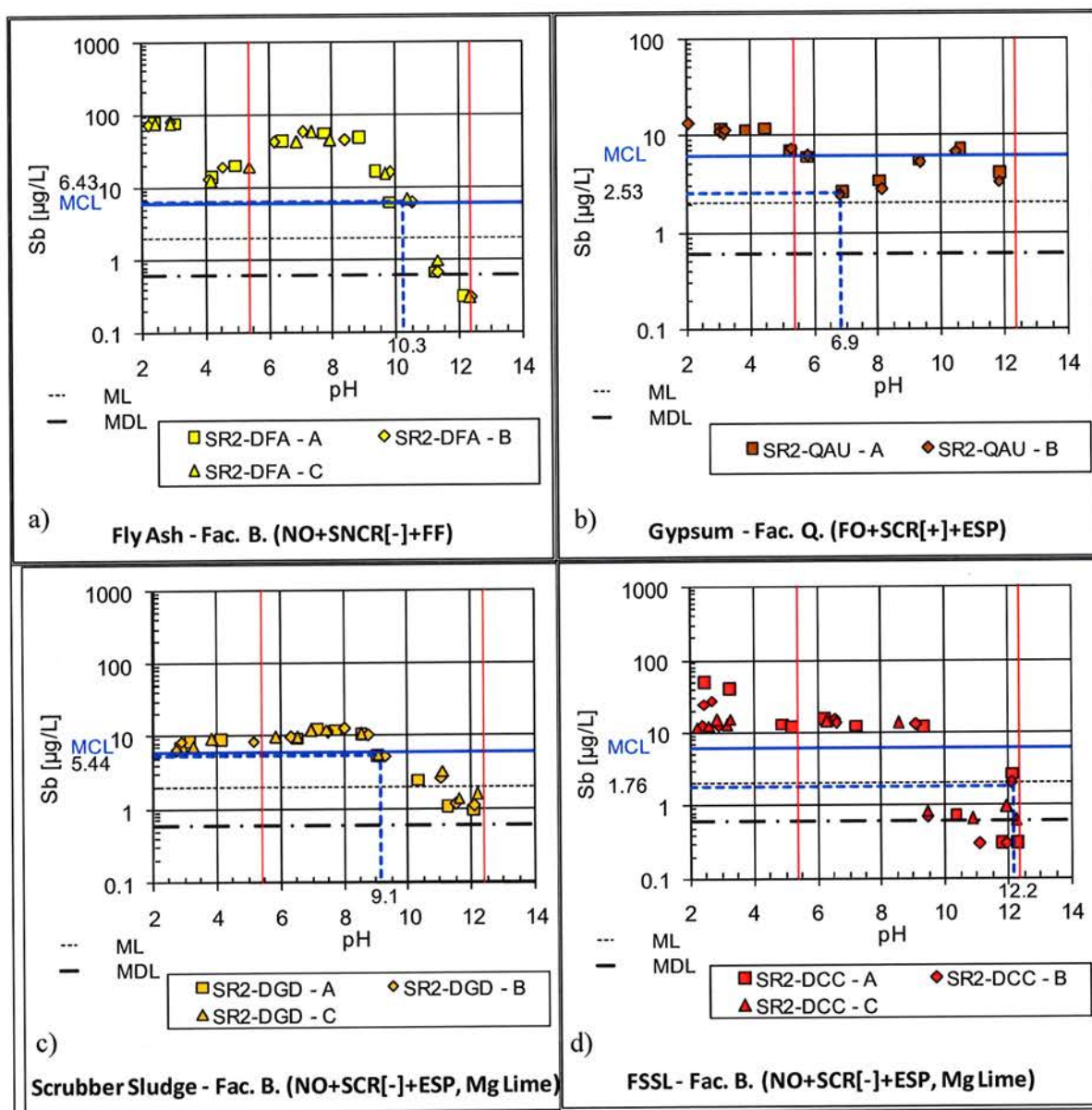


Figure 32. Antimony. Examples of characteristic leaching behavior as a function of pH.

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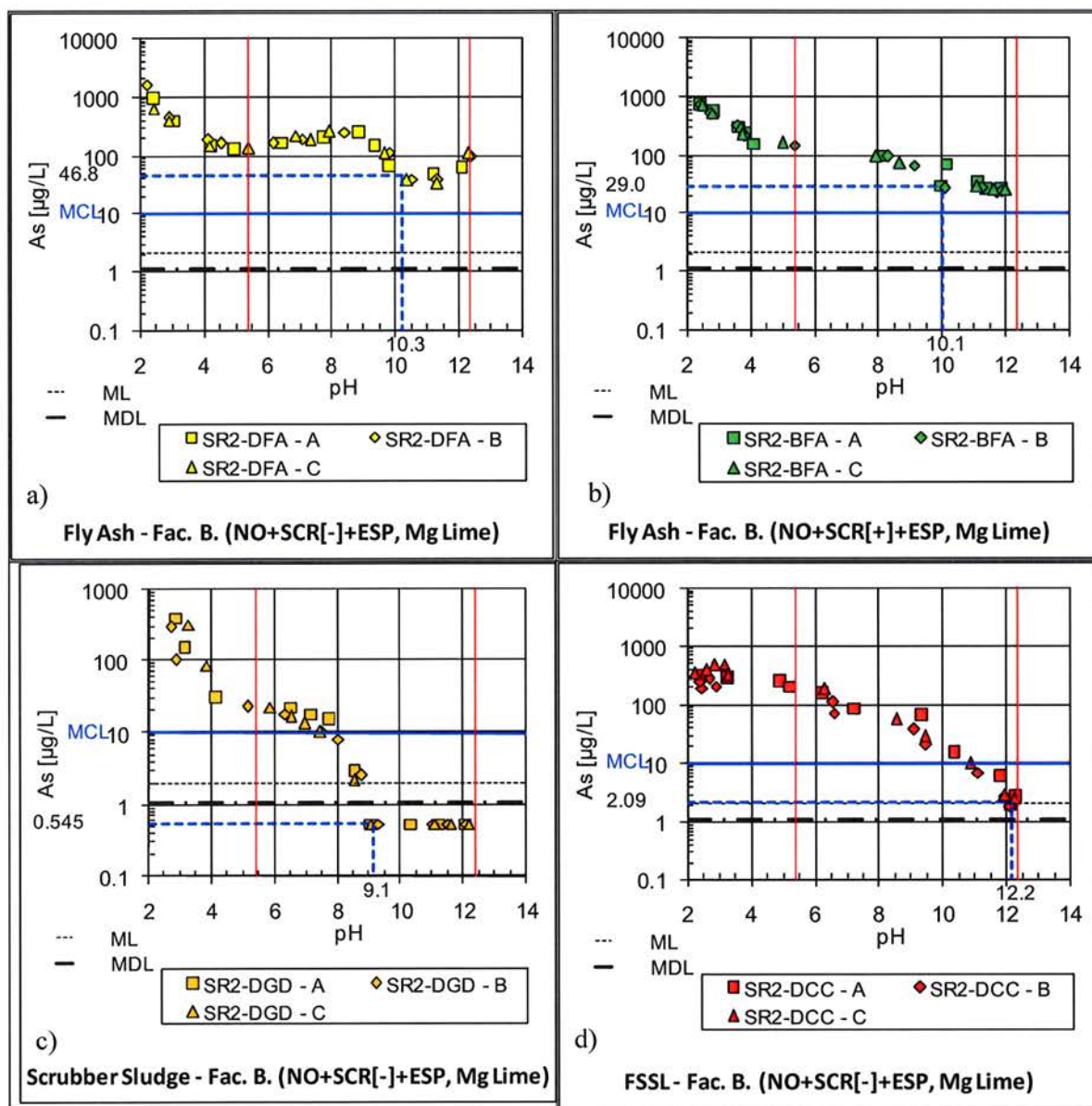


Figure 33. Arsenic. Examples of characteristic leaching behavior as a function of pH.

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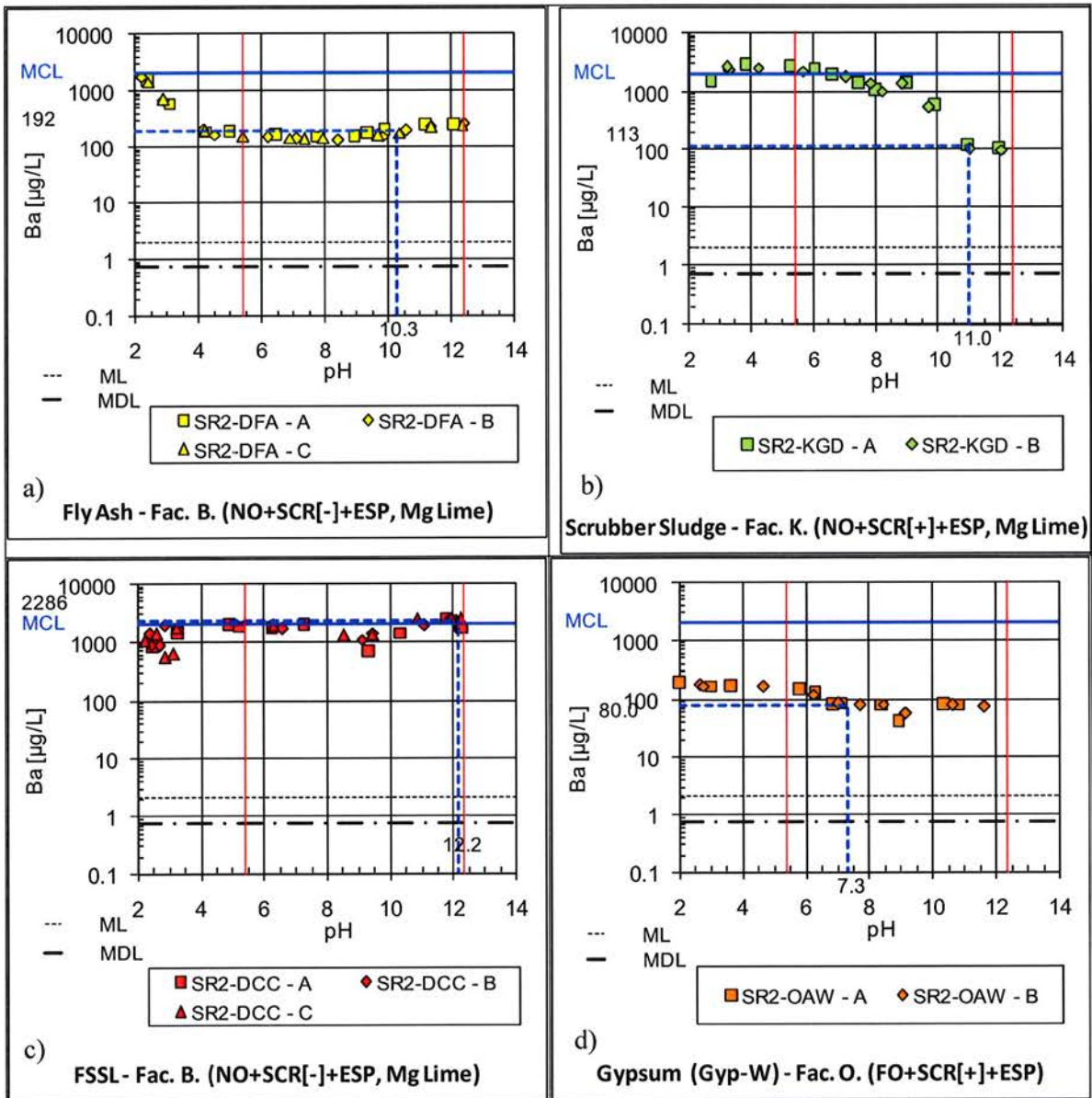


Figure 34. Barium. Examples of characteristic leaching behavior as a function of pH.

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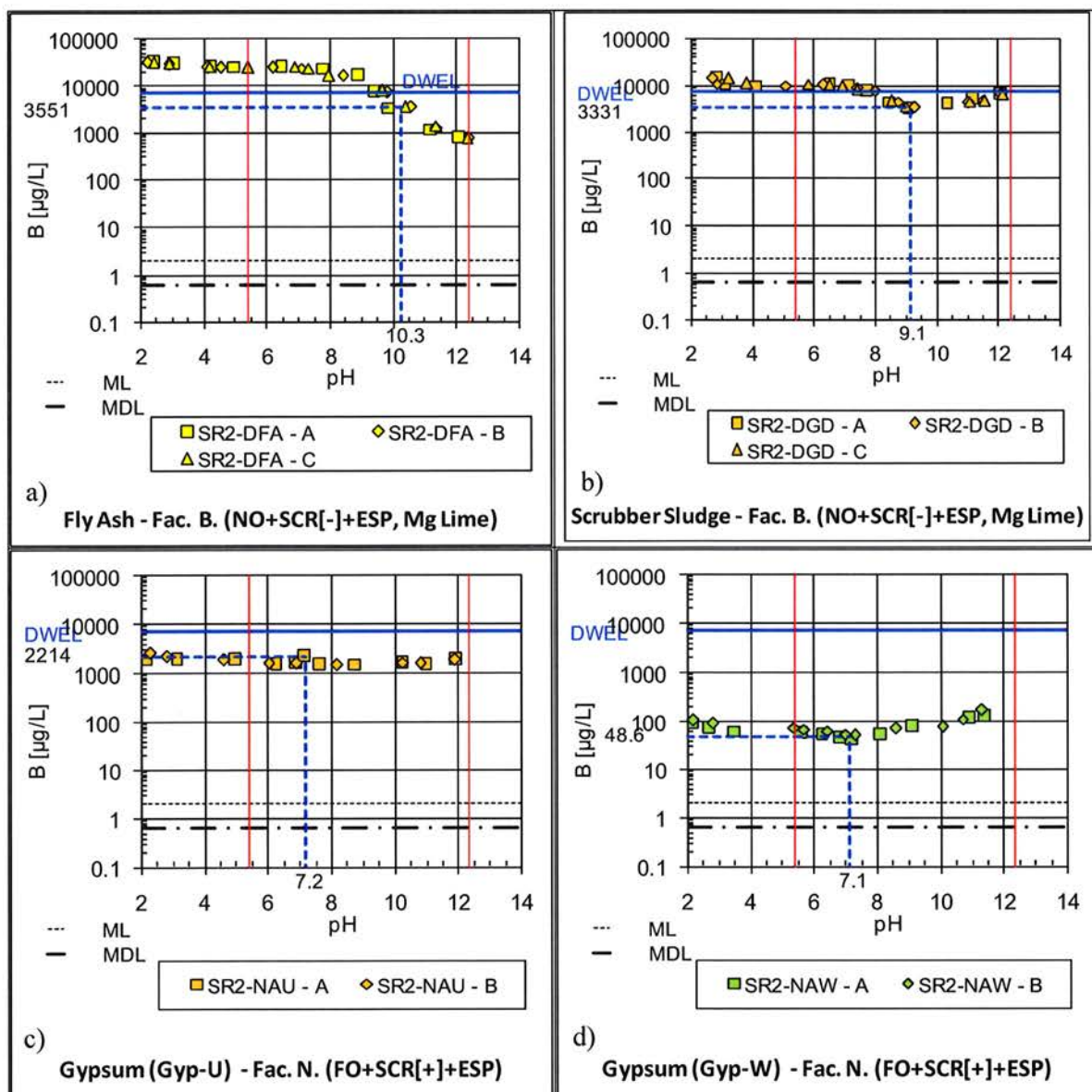


Figure 35. Boron. Examples of characteristic leaching behavior as a function of pH.

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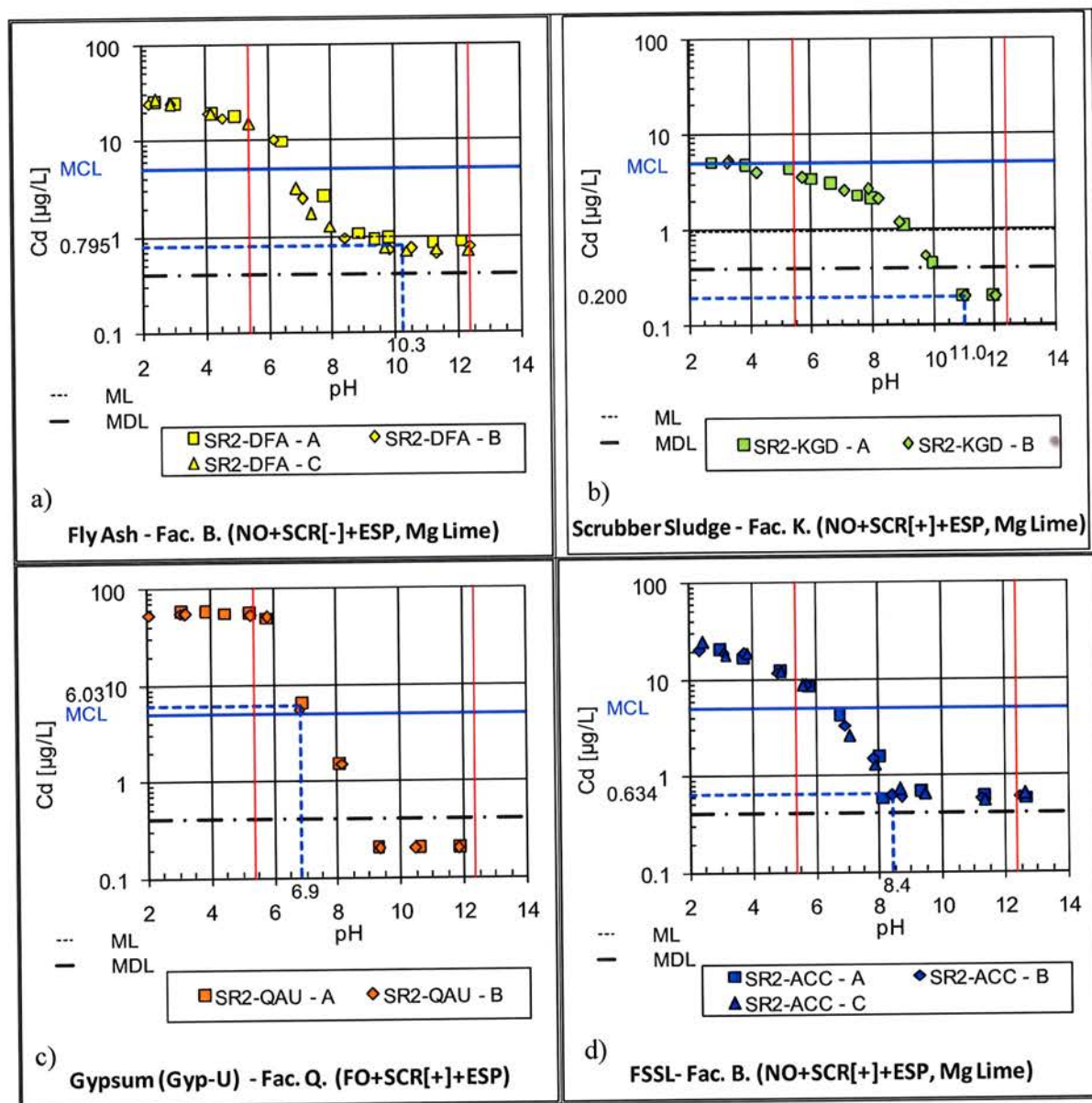


Figure 36. Cadmium. Examples of characteristic leaching behavior as a function of pH.

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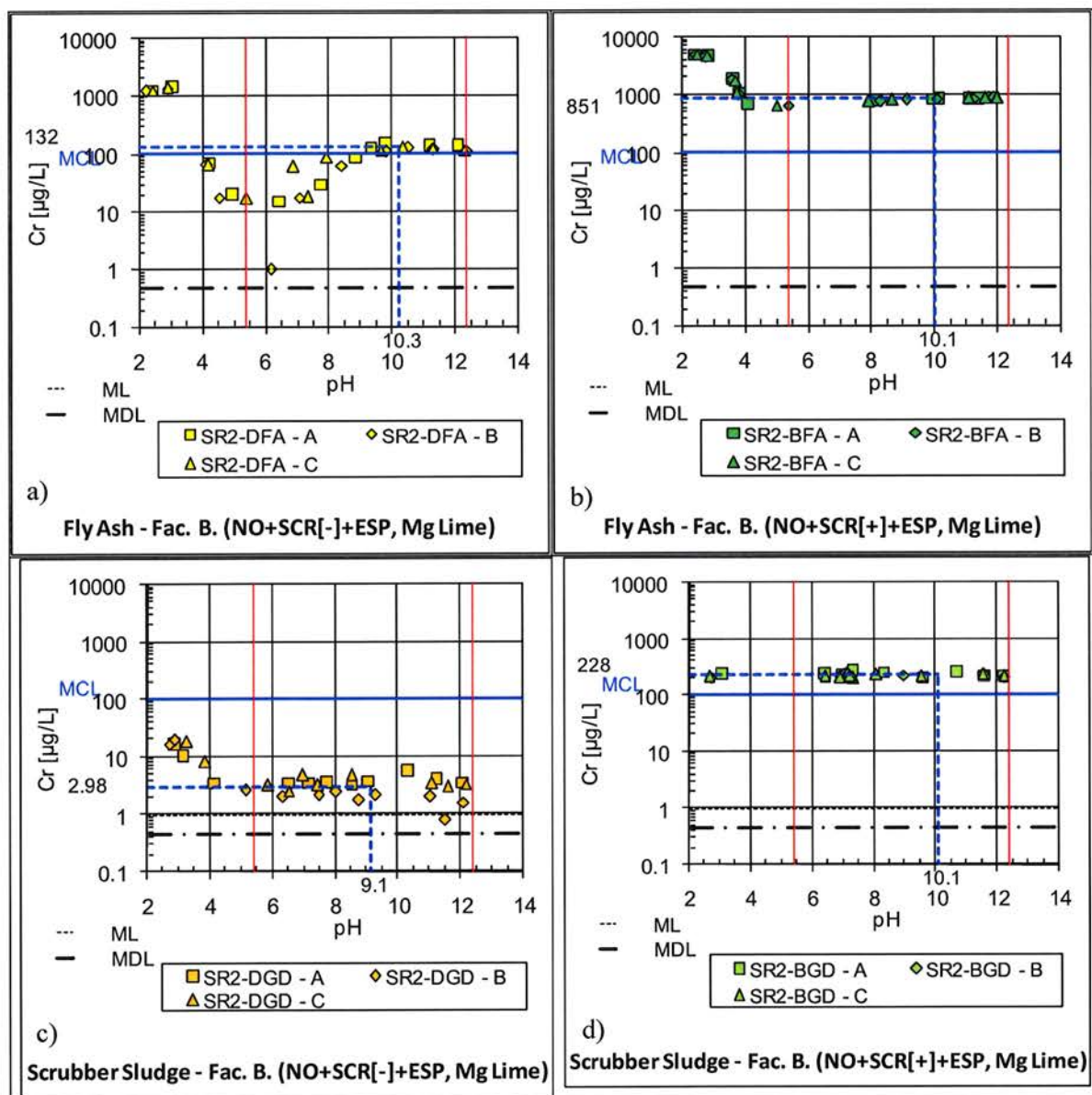


Figure 37. Chromium. Examples of characteristic leaching behavior as a function of pH.

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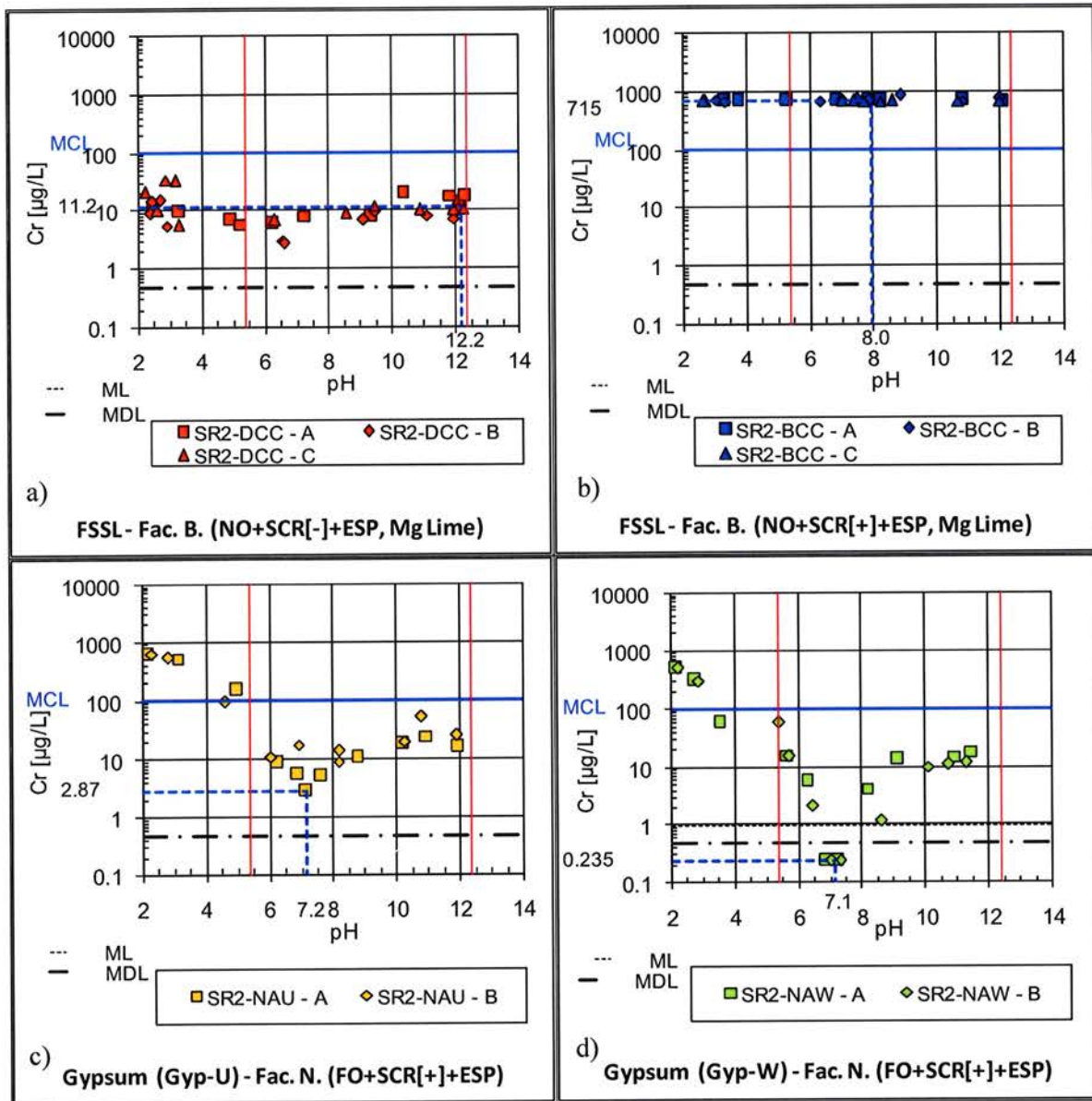


Figure 38. Chromium. Examples of characteristic leaching behavior as a function of pH.

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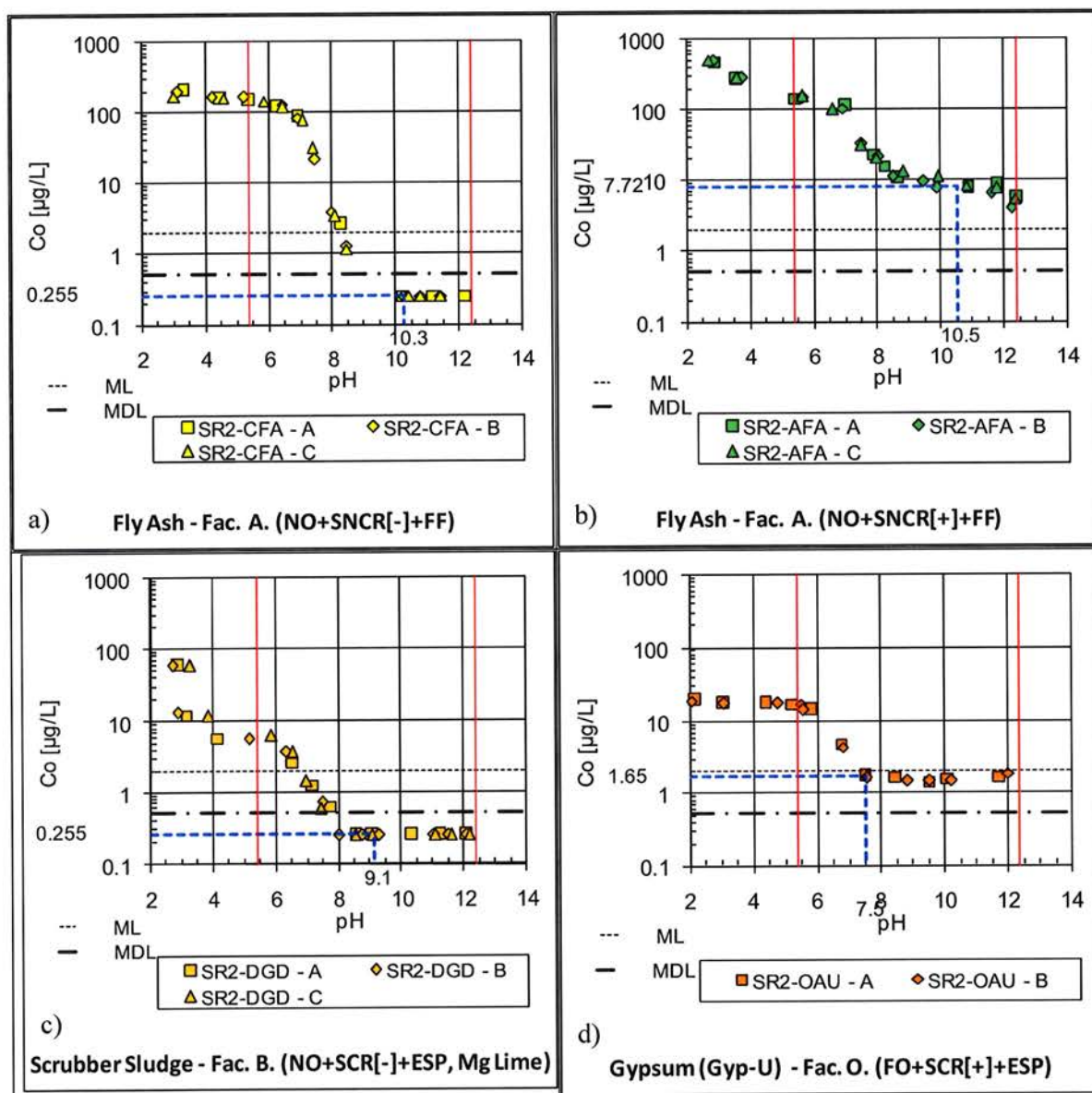


Figure 39. Cobalt. Examples of characteristic leaching behavior as a function of pH.

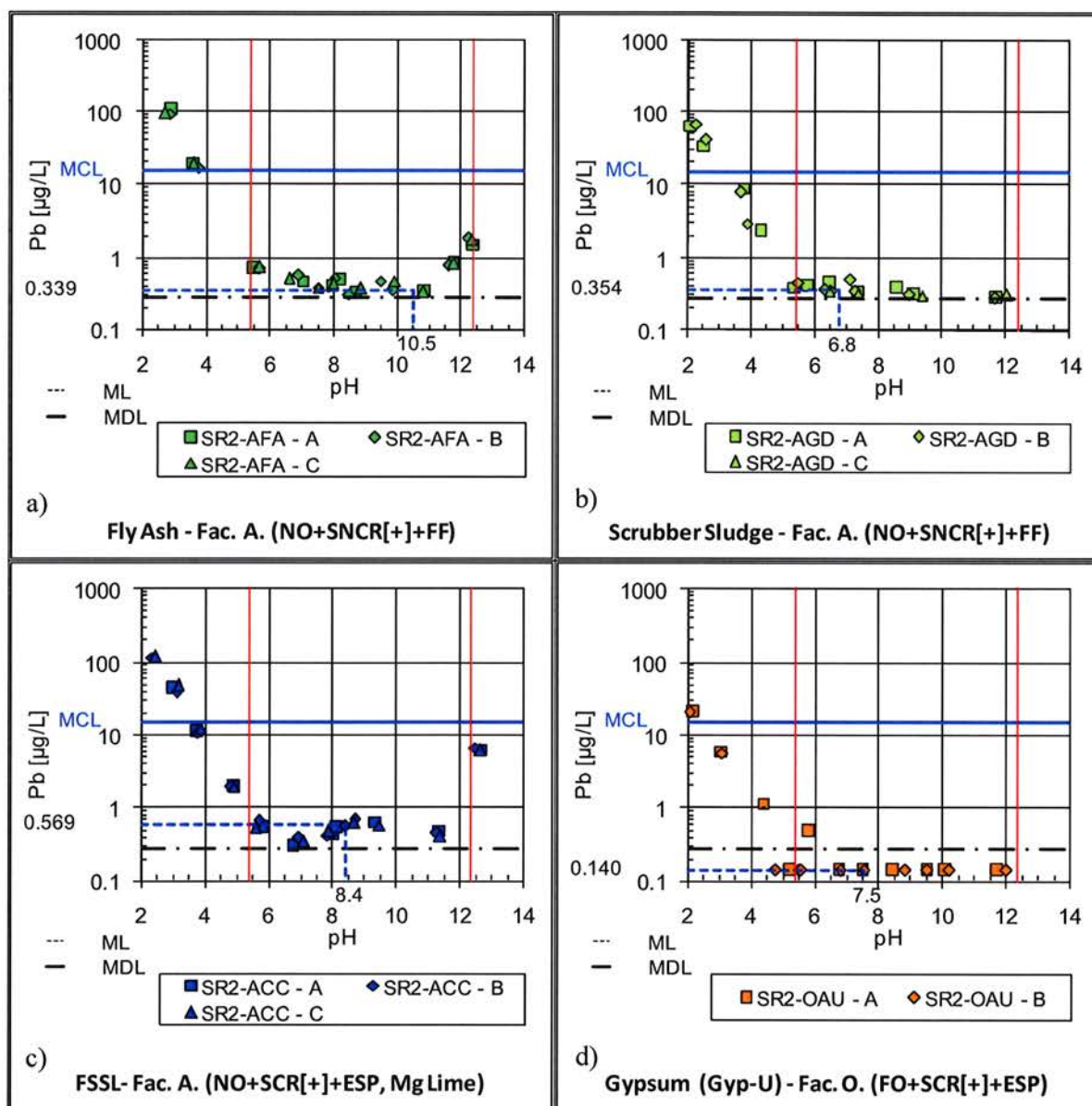


Figure 40. Lead. Examples of characteristic leaching behavior as a function of pH.

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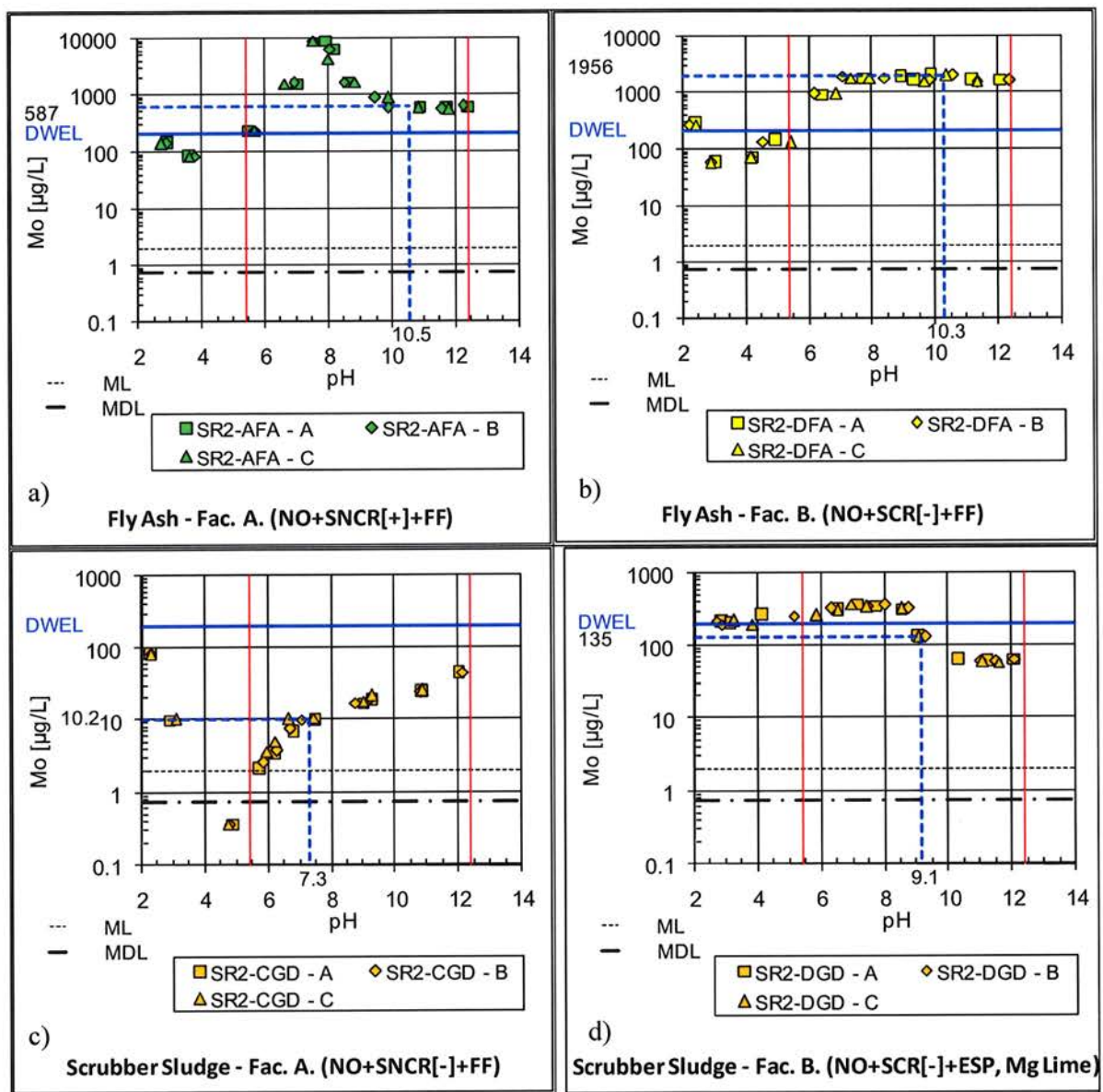


Figure 41. Molybdenum. Examples of characteristic leaching behavior as a function of pH.

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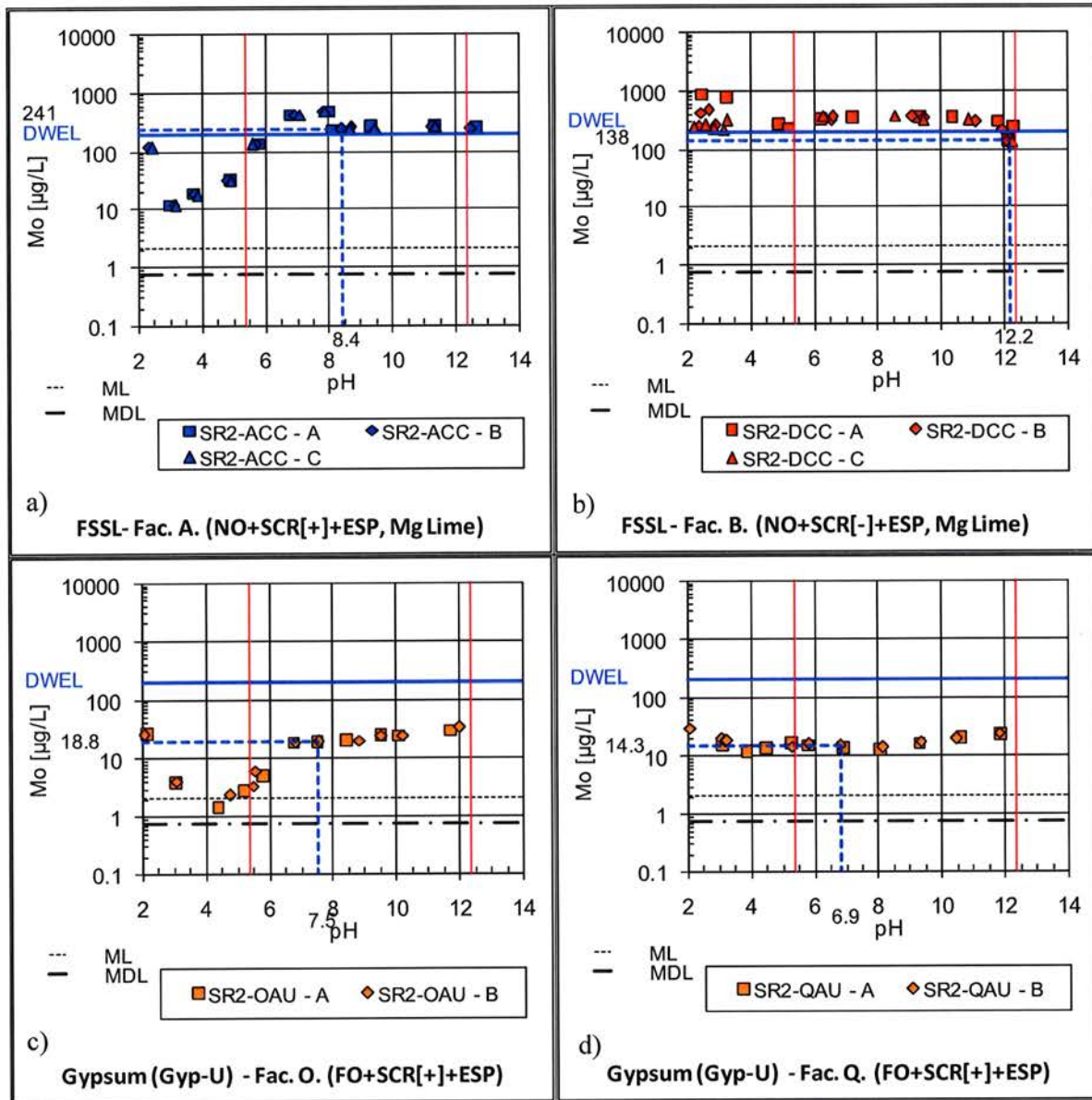


Figure 42. Molybdenum. Examples of characteristic leaching behavior as a function of pH.

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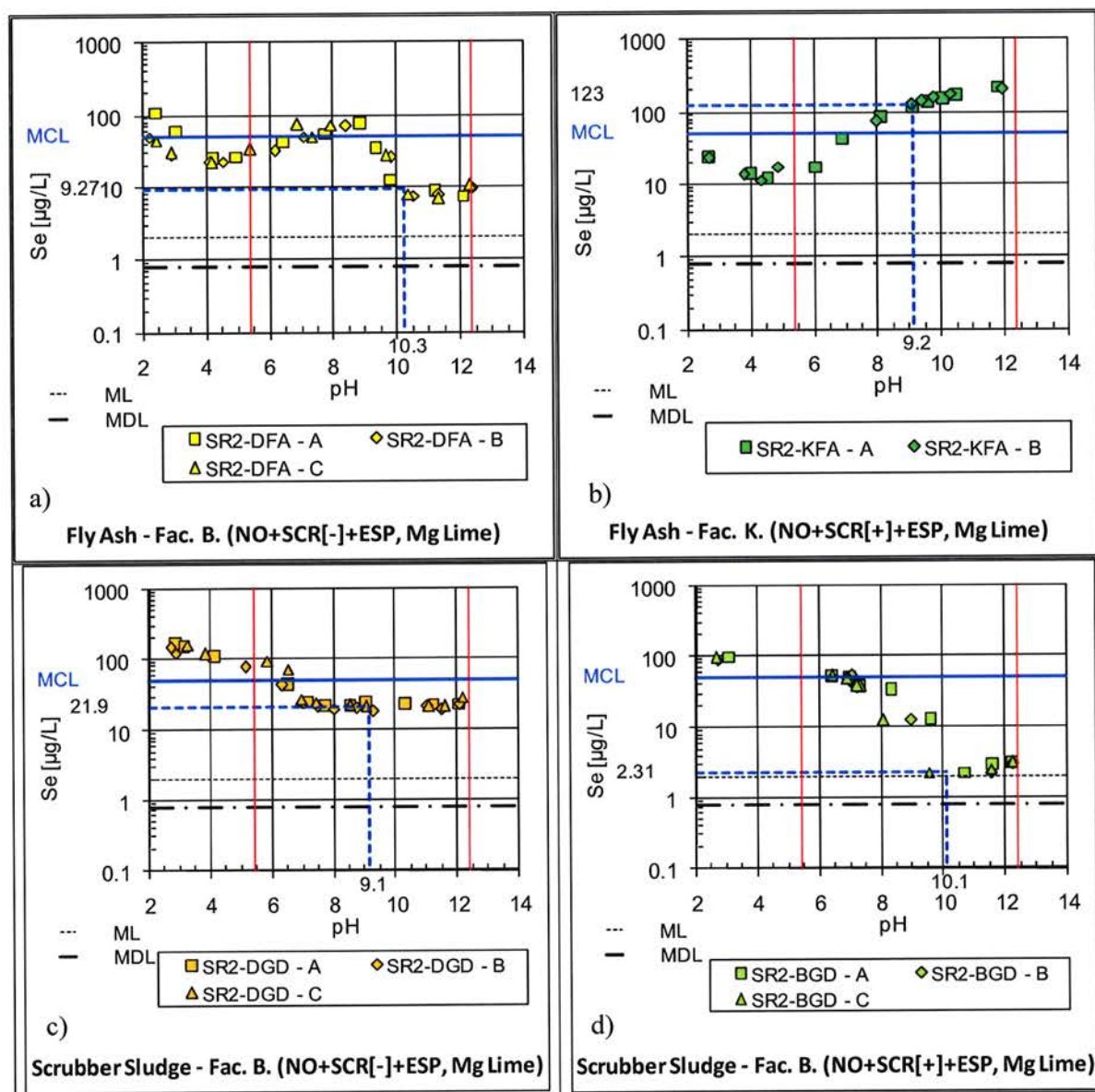


Figure 43. Selenium. Examples of characteristic leaching behavior as a function of pH.

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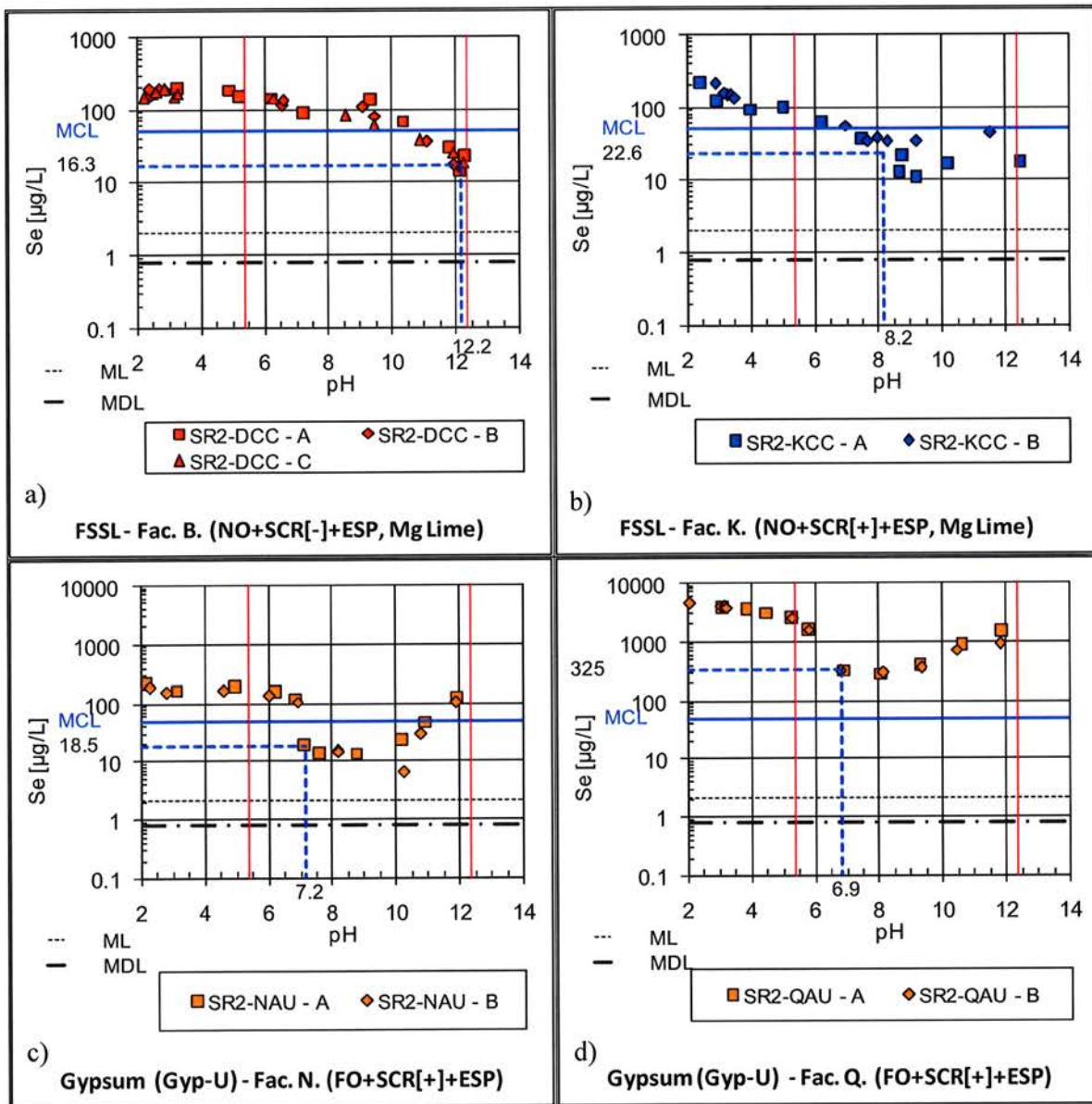


Figure 44. Selenium. Examples of characteristic leaching behavior as a function of pH.

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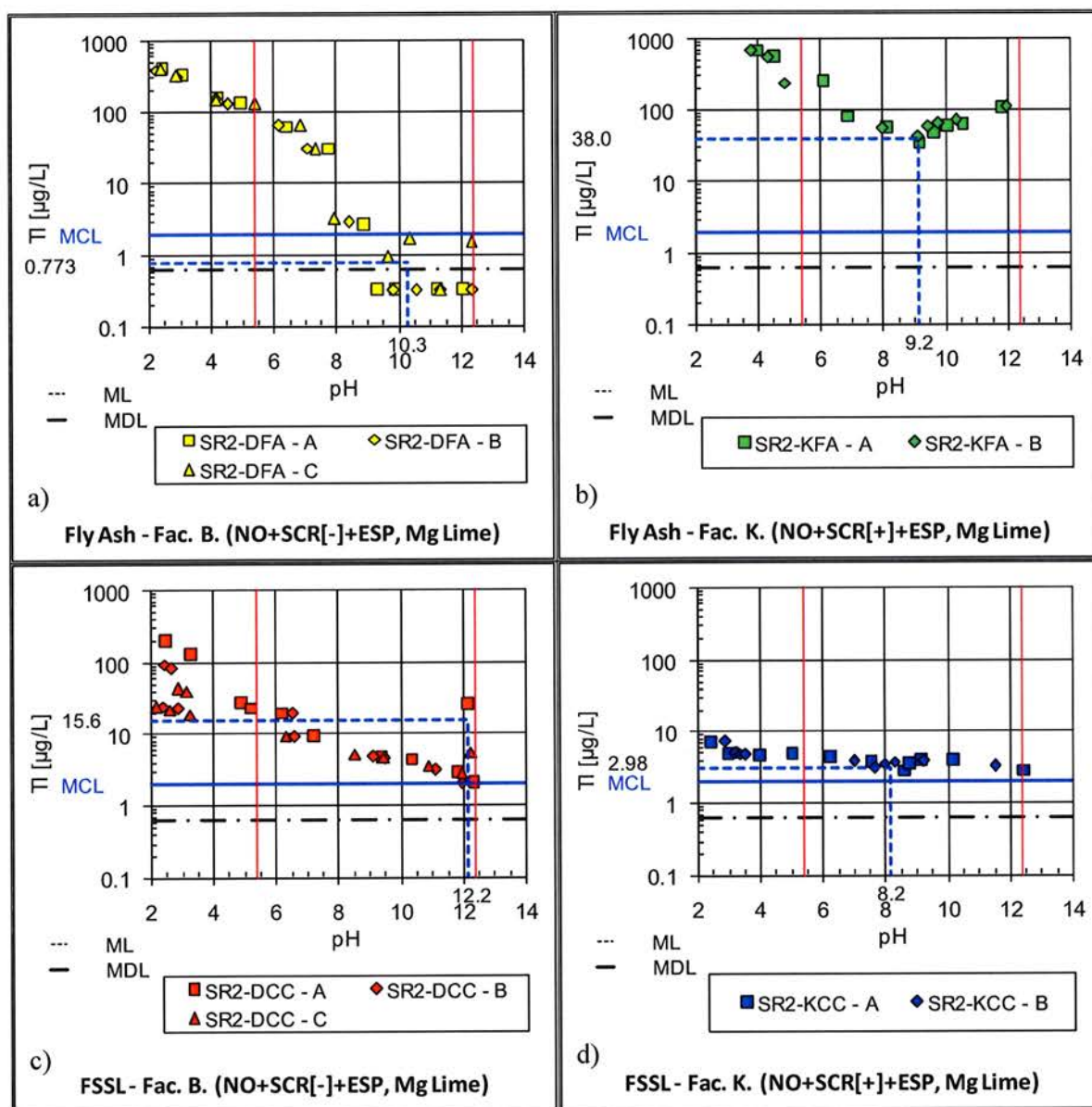


Figure 45. Thallium. Examples of characteristic leaching behavior as a function of pH.

3.3.2. Comparisons of the Ranges of Constituent Concentrations from Laboratory Testing with Measurements of Field Samples and the EPA Risk Report Database

Figure 46 through Figure 59 present comparisons of the range of constituent concentrations observed in laboratory extracts from testing as a function of pH and LS (SR002.1 and SR003.1) over the pH range from 5.4 to 12.4 and LS ratios from 0.5 to 10. This pH range represents the 5th and 95th percentiles of pH observed in field samples from CCR landfills and surface impoundments, as discussed in Section 2.6. For laboratory leaching test extracts, the presented data represent the observed minimum, natural pH, and maximum concentration, considering all results from both test methods. Including results from testing as a function of LS allows consideration of potentially higher concentrations observed for initial releases that may occur at low LS ratios in the field. The MCL or DWEL is included in each figure as a dashed horizontal line to provide a reference value. However, the concentration ranges indicated in the figures as results of this study are direct measurements of laboratory extracts and do not consider attenuation that may occur in the field. Ranges of field observations are included for comparison as derived from the EPRI database, considering only observations from disposal sites associated with facilities that have wet FGD scrubbers. The 5th, median, and 95th percentile of field data is presented for surface impoundments ["Surface Imp. (EPRI)"] and landfills ["Landfill (EPRI)"]. Surface impoundment data are compared with scrubber sludge results because scrubber sludges are most likely to be disposed in this manner (see Section 1). Landfill data are compared with FSS and FSSL because these blended materials are the likely to be disposed in landfills. Also included for comparison is the 5th, median, and 95th percentile of the database used to carry out human and ecological health risk evaluations in the EPA Risk Report (EPA, 2007) ("CCW Ash," "CCW FGD," and "CCW Ash and Coal Waste" referring to monofilled fly ash, disposed FGD scrubber sludge, and combined CCR disposal, respectively).

pH. The natural pH of the fly ash samples evaluated in this report was alkaline²⁴, scrubber sludge samples were neutral to alkaline, gypsum samples were neutral and FSS samples were mildly alkaline (pH ~8) to very alkaline (pH>11), most likely depending on the amount of lime added.

Mercury. Laboratory extract concentration ranges for two of the scrubber sludge samples (Facility B) and four of the FSS samples (facilities B, K, M) exceeded the MCL for mercury. The mercury concentration ranges indicate that the greatest leaching concentrations are expected from scrubber sludge and blending with fly ash and lime to produce FSS does not substantially decrease, and may increase, mercury leaching. All natural pH samples were less than the MCL, most by more than an order of magnitude. All fly ash and gypsum data were less than the MCL, regardless of pH. Mercury field data were very sparse.

Aluminum. There was no reference limit available for aluminum. The range of laboratory extract concentrations from scrubber sludge samples agreed well with field observations. The range of field observations for landfills tended to be similar to somewhat lower than the values observed for laboratory extracts. However, the range used in the EPA Risk Report (EPA, 2007) had an upper bound approximately one order of magnitude greater than the field data and the laboratory extracts.

²⁴ Some fly ash samples reported on in Sanchez et al. (2006) were acidic.

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Antimony. Fly ash and FSS had the highest concentrations of antimony in laboratory extracts. The range of field observations for surface impoundments (EPRI) was much greater than for laboratory extracts of scrubber sludge, but also likely reflects co-disposal of fly ash with scrubber sludge in surface impoundments. If the field data includes co-disposal data, then the concentration range reported for field observations is entirely consistent with the laboratory testing. The range of field observation for landfills (EPRI) was lower than observed in laboratory extracts. This comparison suggests the potential for attenuation or immobilization under field conditions, many of which may be reducing in contrast to the oxidizing conditions used in the laboratory testing. For gypsum, all natural pH results were less than the MCL.

Arsenic. Leachable arsenic appears to be distributed between fly ash and scrubber sludge. Results for Facility A (fly ash, scrubber sludge, and FSS), Facility B (scrubber sludge and FSS) and Facility M (FSS) suggest that NO_x controls increase the leachability of arsenic at the material's natural pH. Results from field observations indicate narrower ranges than laboratory testing. Ranges used in the EPA Risk report (EPA, 2007) appear to be much higher than the laboratory testing results, except for Facility M. All results for gypsum were less than the MCL.

Barium. Laboratory testing results indicate a much broader range of concentrations than field observations. Two samples of FSS, both with NO_x controls off (Facility B and Facility M), had much greater laboratory extract concentrations than the other samples. All natural pH results were less than the MCL for fly ash, scrubber sludge and gypsum.

Boron. Most notable for boron is a reduction of approximately an order of magnitude in leachable boron from gypsum as a consequence of washing (facilities N, O). There is no clear trend amongst the material types for boron. Laboratory results are consistent with field observations. All gypsum natural pH results were less than the DWEL.

Cadmium. Cadmium concentrations in laboratory extracts were generally lower for the scrubber sludge than for the other materials. For scrubber sludge, cadmium concentrations observed in laboratory extracts were less than the concentrations reported for field observations for surface impoundments. For all cases, cadmium concentrations in laboratory extracts were consistent with field observations for landfills. In addition, the measured concentrations in laboratory extracts from this study and reported for field results are approximately an order of magnitude less than the upper bound reported for CCW and coal waste in the Risk Report (EPA 2007).

Chromium. The range of field observations appears low in comparison to the laboratory testing results. The increase in chromium leaching, apparently as a consequence of NO_x controls, is evident for facilities A, B and M. Six cases exceed the MCL by greater than one order of magnitude. Test results for all of the gypsum samples are well below the MCL. The field observations for both surface impoundments and landfills are up to two orders of magnitude less than the laboratory testing results.

Cobalt. The use of NO_x controls appears to increase cobalt leaching from fly ash based results for facilities A and B. The data range used by the EPA risk report (EPA, 2007) for combined management of ash and coal waste is one to two orders of magnitude greater than the observations for laboratory extracts and field observations.

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Lead. Laboratory test results indicate concentration ranges generally lower than or consistent with field observations for surface impoundments and landfills and much lower than the values used in the EPA risk report (EPA, 2007). All fly ash and gypsum samples were less than the MCL.

Molybdenum. Leachate molybdenum concentrations exceeding the DWEL by up to two orders of magnitude were observed for fly ash and FSS. Leachate molybdenum concentrations generally less than the DWEL were observed for gypsum.

Selenium. Similar ranges of selenium concentrations are expected for all materials.

Thallium. Laboratory test results indicate a concentration range in excess of two orders of magnitude for all materials and the observed concentration can exceed the MCL for thallium by more than one order of magnitude. Washed gypsum had significantly lower extract concentrations of thallium than unwashed gypsum.

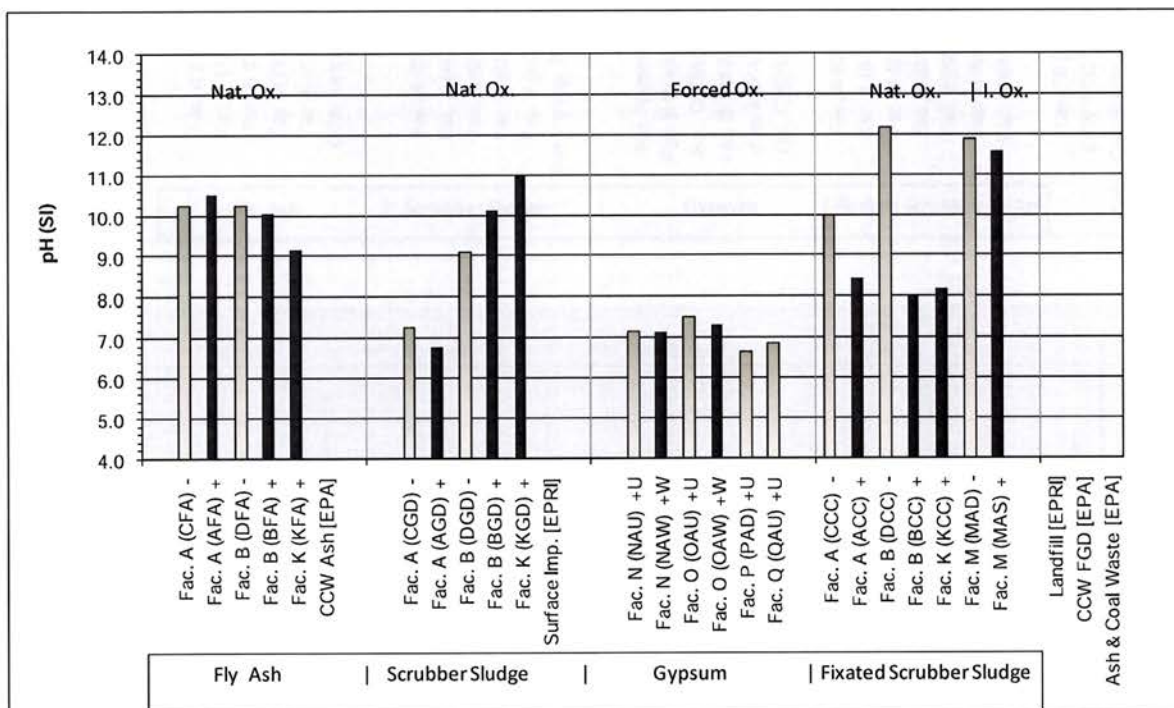


Figure 46. Natural pH (pH in distilled water at LS=10) observed in SR02 extracts.

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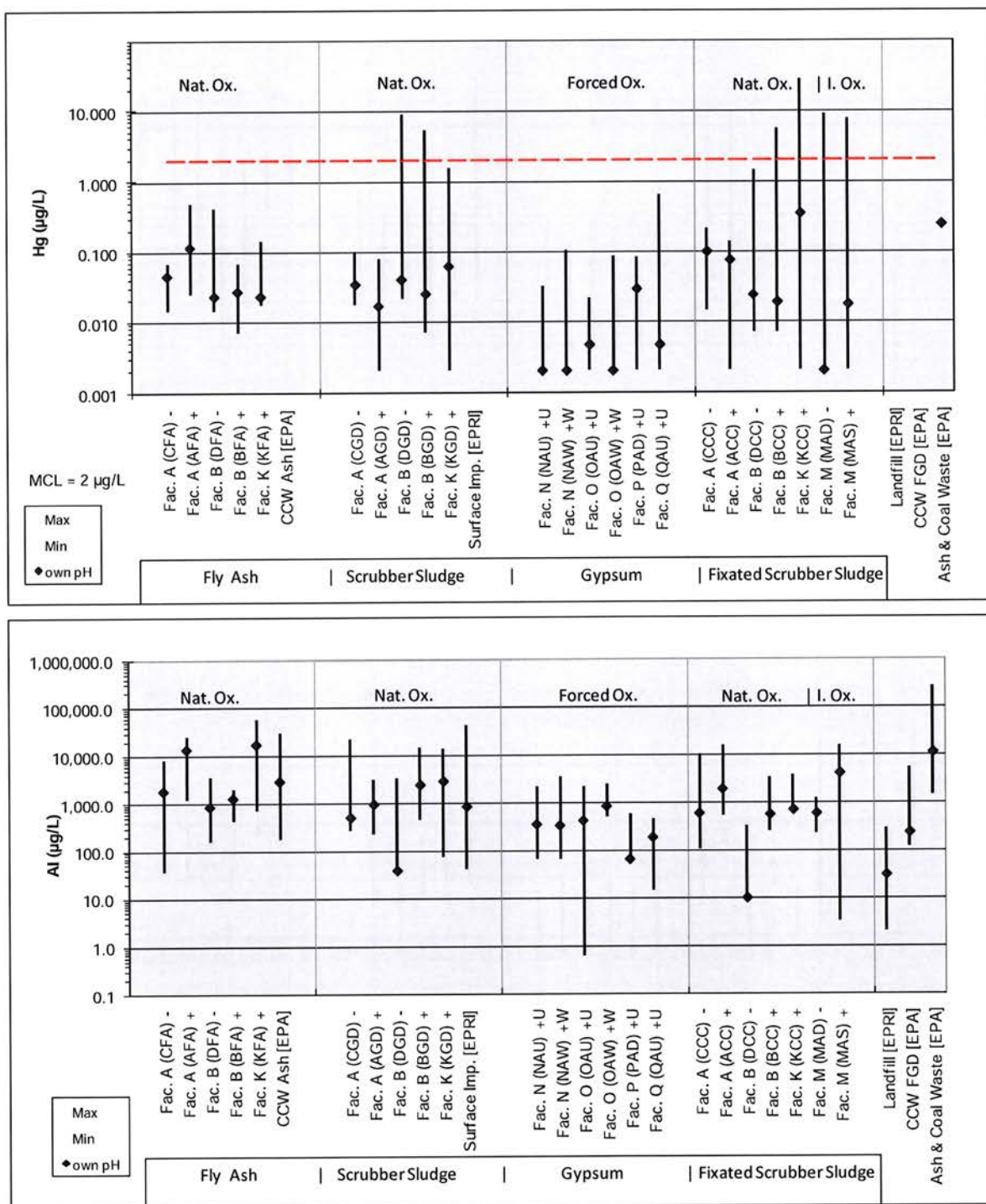


Figure 47 and Figure 48. Mercury and Aluminum. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NO_x control off; + = NO_x control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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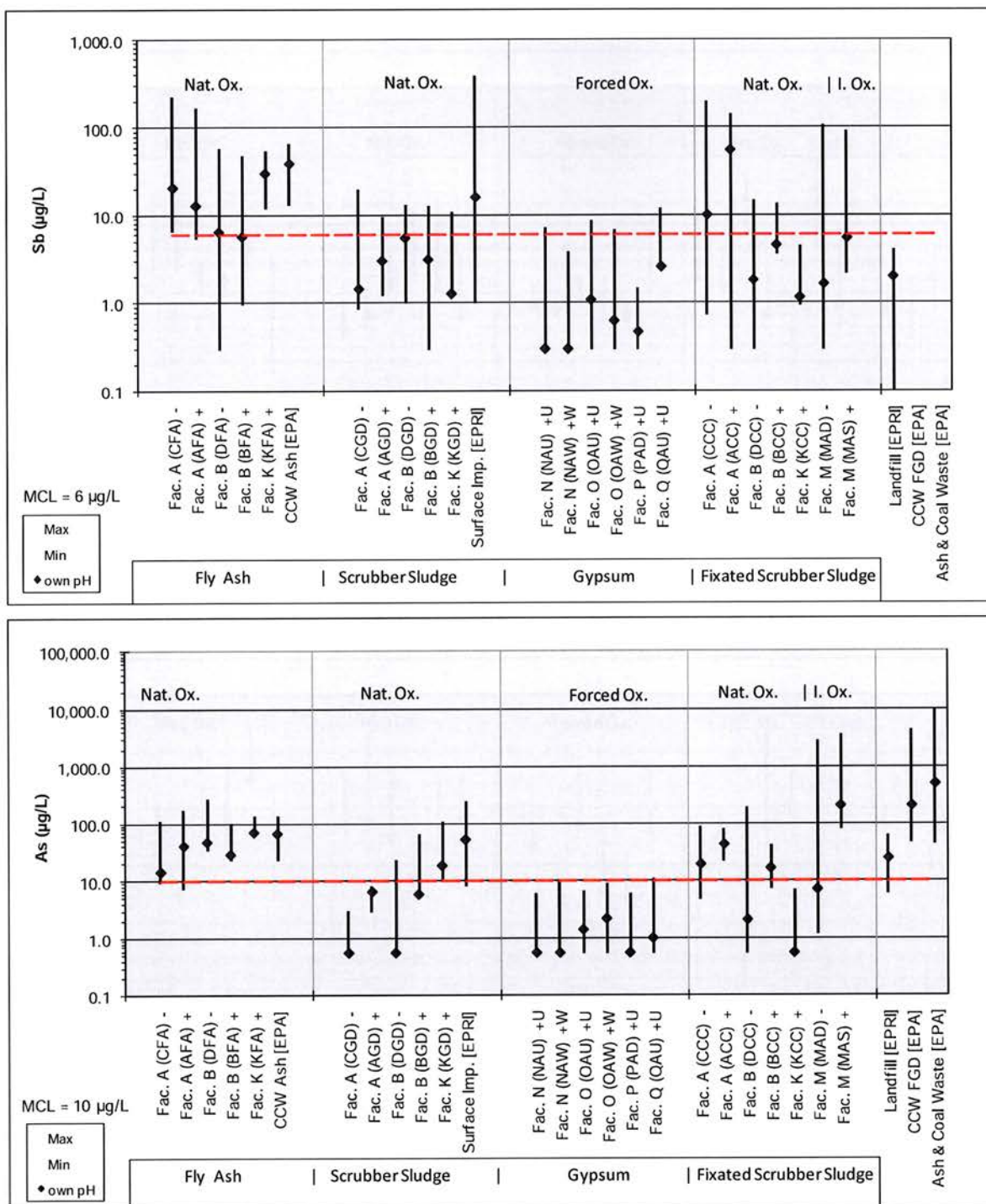


Figure 49 and Figure 50. Antimony and Arsenic. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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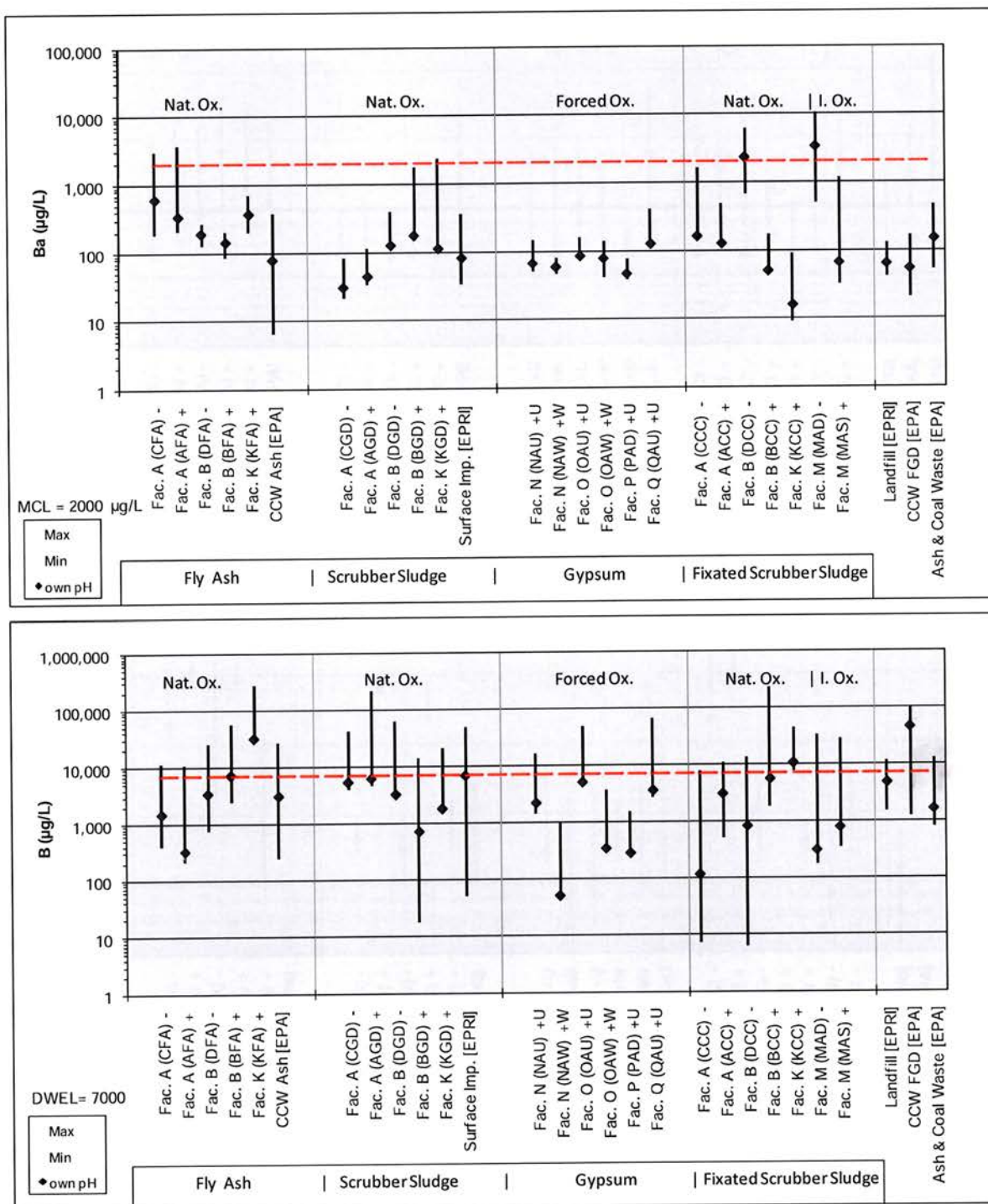


Figure 51 and Figure 52. Barium and Boron. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NO_x control off; + = NO_x control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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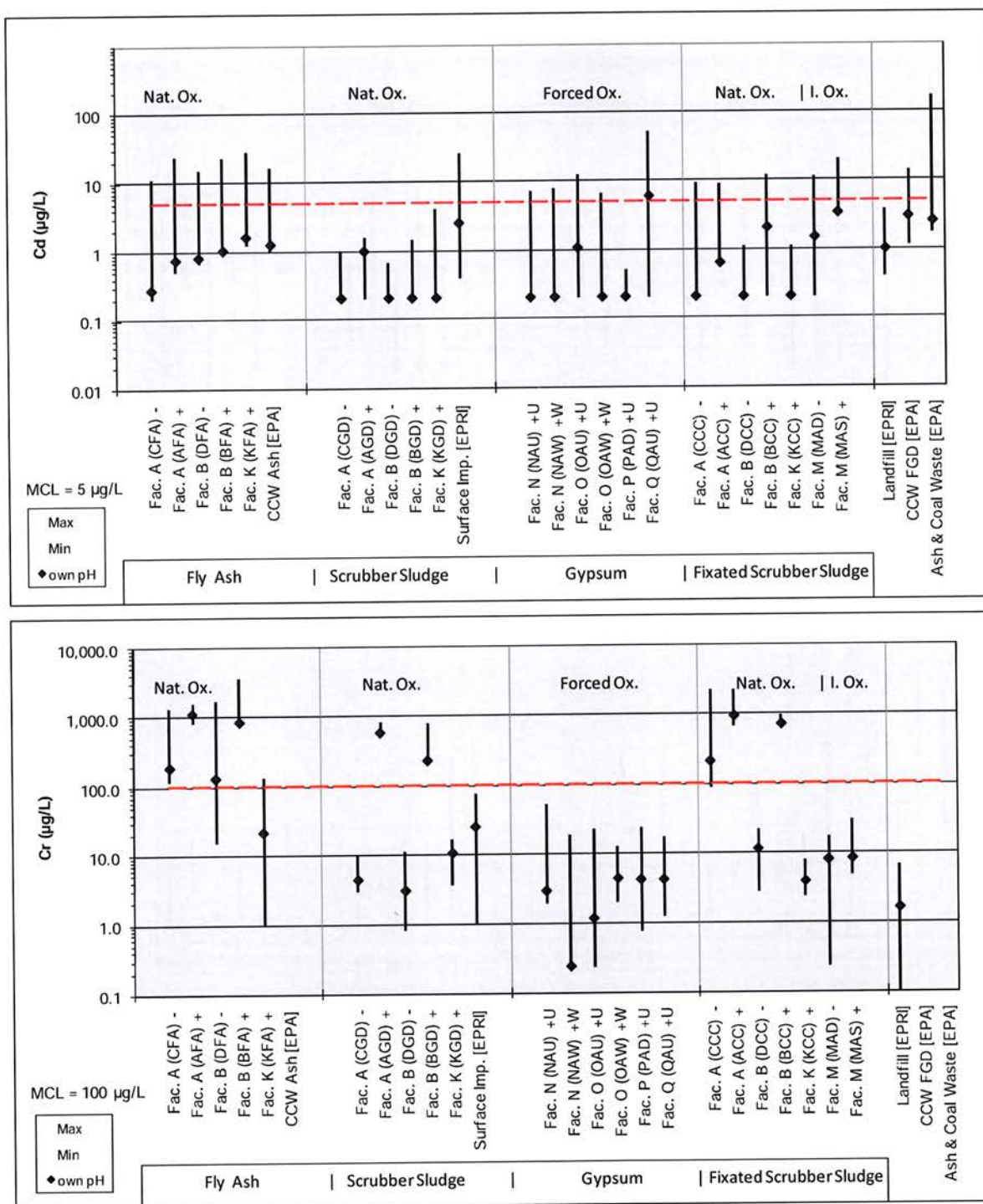


Figure 53 and Figure 54. Cadmium and Chromium. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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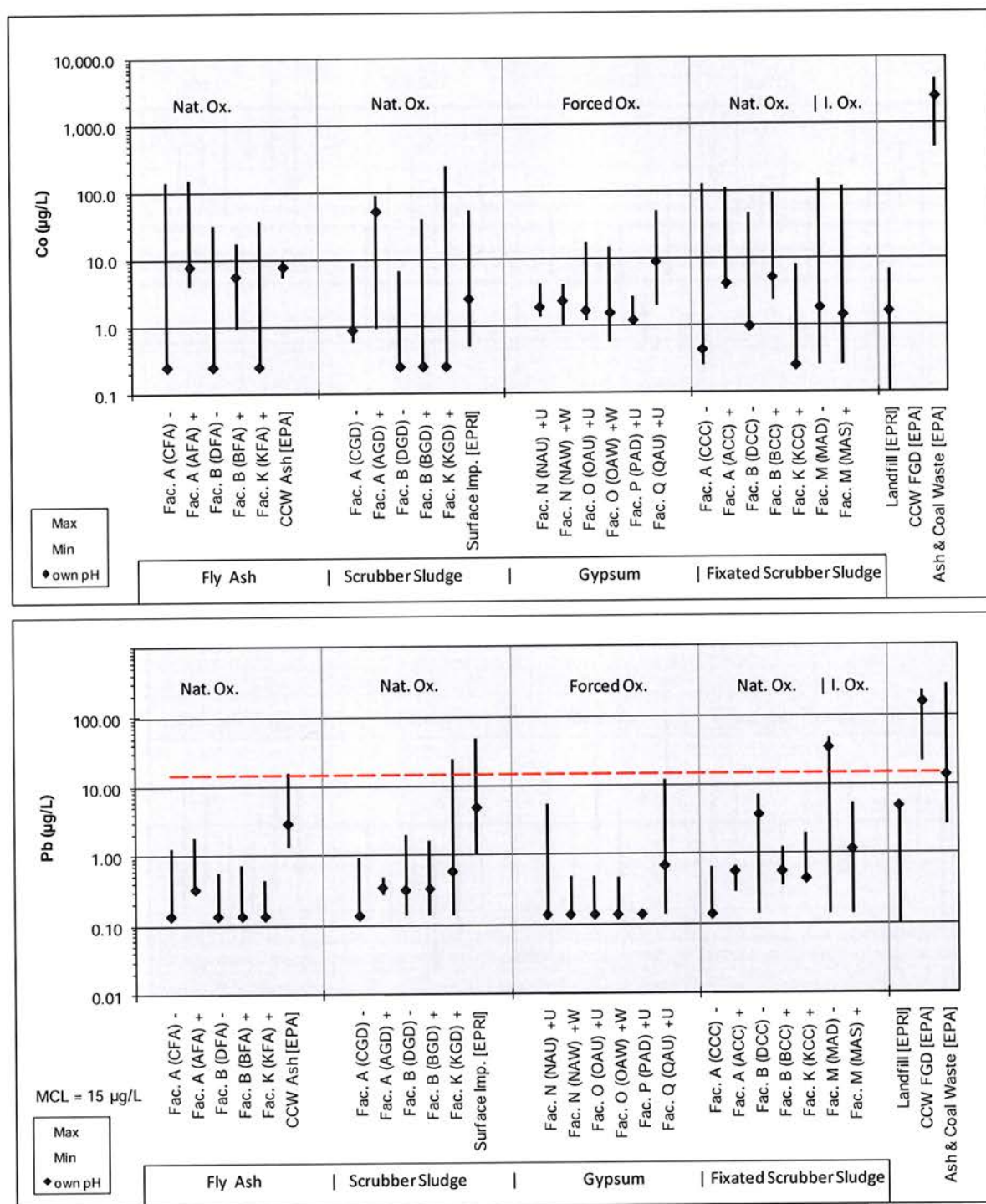


Figure 55 and Figure 56. Cobalt and Lead. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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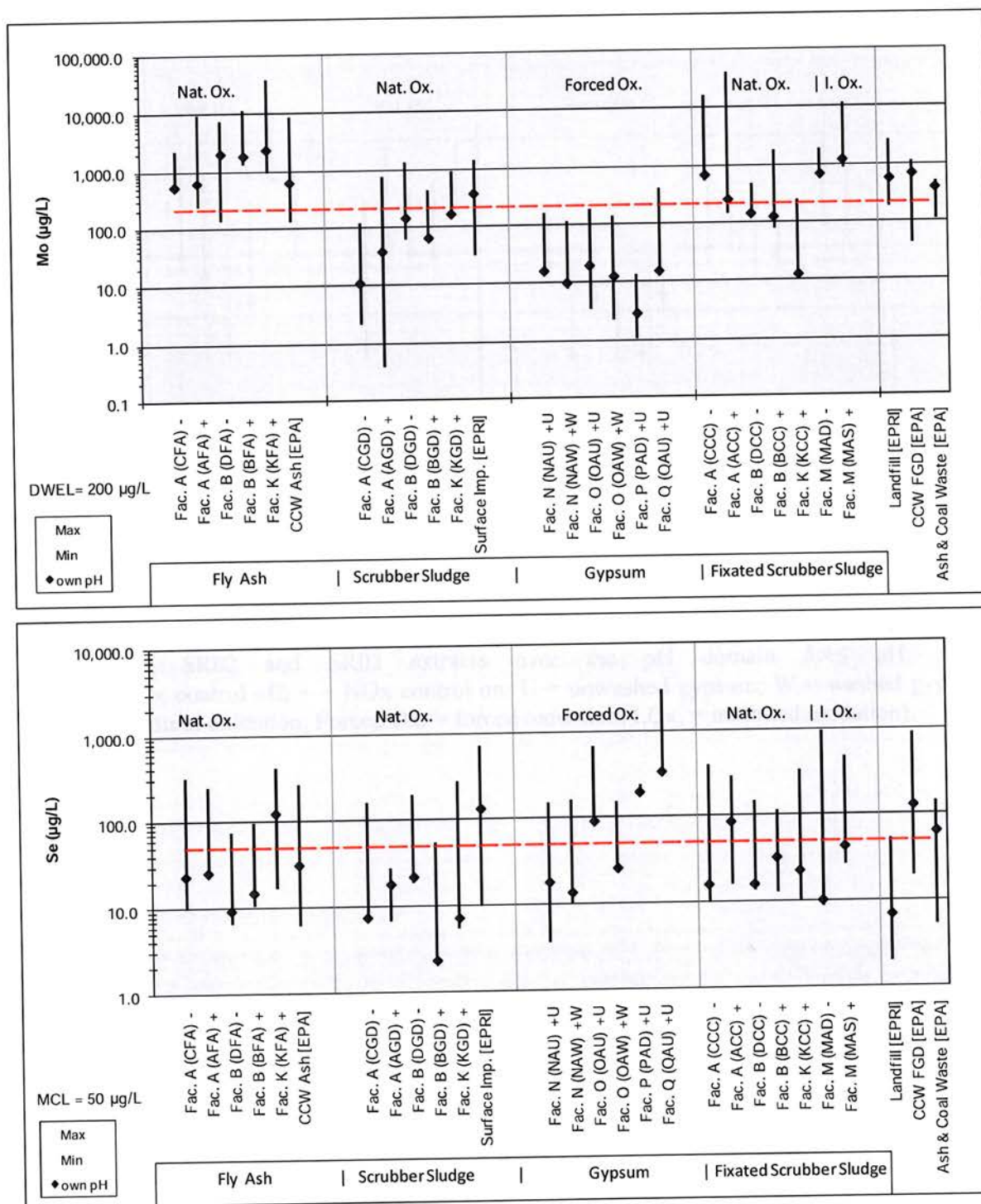


Figure 57 and Figure 58. Molybdenum and Selenium. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

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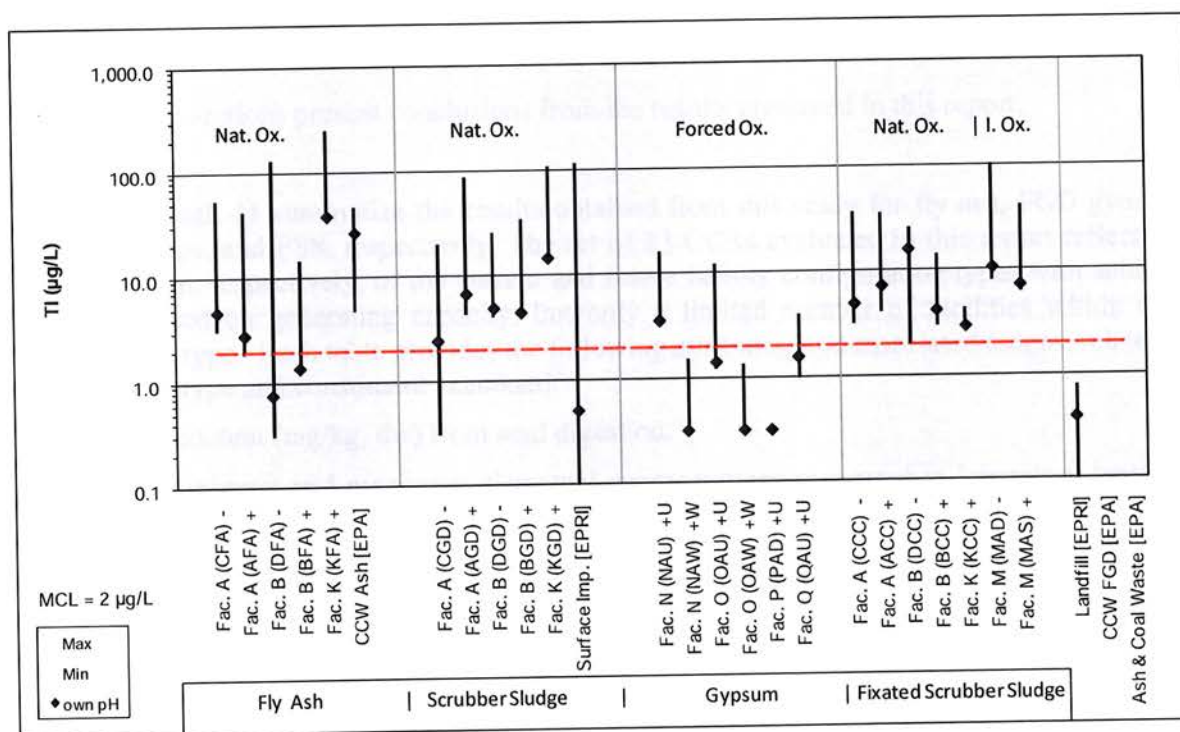


Figure 59. Thallium. Comparison of maximum, minimum and natural pH concentrations observed in SR02 and SR03 extracts over the pH domain $5.4 \leq \text{pH} \leq 12.4$. (key: - = NOx control off; + = NOx control on; U = unwashed gypsum; W = washed gypsum; Nat. Ox. = natural oxidation; Forced Ox. = forced oxidation; I.Ox. = inhibited oxidation).

4. SUMMARY OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS

The following sections present conclusions from the results presented in this report.

Tables 8 through 11 summarize the results obtained from this study for fly ash, FGD gypsum, scrubber sludge, and FSS, respectively. The set of 23 CCRs evaluated in this report reflects 84 and 74 percent, respectively, of the current and future facility configuration types with acid gas scrubbers based on generating capacity, but only a limited number of facilities within each configuration type. Each table provides the following attributes, and associated ranges, related to each material type and constituent examined:

1. Total content (mg/kg, dw) from acid digestion.
2. The minimum and maximum elemental concentrations measured in laboratory leaching test extracts over the domain of $5.4 \leq \text{pH} \leq 12.4$ from leaching evaluation as a function of pH at $\text{LS} = 10 \text{ mL/g}$ (SR002.1) and as a function of $0.5 \leq \text{LS} \leq 10 \text{ mL/g dw}$ (SR003.1). This range is intended to represent the potential range of leachate concentrations expected to be observed in the field from management of each of the material types in monofilled management conditions. Concentration ranges for individual samples of each material type are compared in Section 3.3.2.
3. The minimum and maximum elemental concentrations measured in laboratory leaching test extracts when extracted with deionized water only ("natural pH") and $0.5 \leq \text{LS} \leq 10 \text{ mL/g dw}$ (SR003.1). The resulting pH range is also indicated.
4. The MCL or DWEL and TC (as available) for each constituent to provide reference concentrations for evaluation of the concentration results summarized as described above. However, the expected leachate concentration ranges derived directly from laboratory testing and probabilistic assessments do not include any dilution and attenuation that may occur prior to impacting water resources. Previous studies have indicated dilution and attenuation factors of as low as 2 to 10 on a national basis or as high as 8,000 at a particular site²⁵. Thus, comparisons with the MCL, DWEL or TC for any constituent must be done with caution.
5. Variability in extract concentration as a function of pH based on results from laboratory leaching testing (SR002.1). Classification of variability is as follows: (a) Low = concentration range ≤ 1 order of magnitude, (b) Med. = concentration range of 1 to 2 orders of magnitude, (c) High = concentration range of >2 orders of magnitude.

In addition, results are emphasized through coding as follows:

1. Expected concentration values that exceed either the MCL or DWEL for the given constituent are in **red bold typeface**.
2. Constituents are underlined in the column heading (e.g., Cd in Table 9) when one of the expected concentration ranges exceeds either the MCL or DWEL.

²⁵ See Section 3.3.

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Based on the results of testing and evaluations in this study, the following conclusions are drawn:

1. For each CCR type the following constituents exceeded either the maximum contaminant level (MCL) or drinking water equivalent level (DWEL) in at least one laboratory leaching test condition over the range of pH and LS ratios considered, and therefore potentially may present unacceptable environmental risks under some management scenarios. These cases warrant more detailed evaluation, including consideration of site-specific conditions.
 - a. Fly ash – antimony, arsenic, boron, cadmium, chromium, molybdenum, selenium and thallium.
 - b. FGD gypsum – boron, cadmium, molybdenum, selenium and thallium.
 - c. Scrubber sludge – mercury, antimony, arsenic, boron, chromium, lead, molybdenum, selenium and thallium.
 - d. Fixated scrubber sludge – mercury, antimony, arsenic barium, boron, cadmium, chromium, lead, molybdenum, selenium and thallium.

However, (i) typically, evaluation results from only a subset of samples of a given material type exceeded the indicated criteria, (ii) never did the full range reported exceed the indicated threshold, and (iii) this analysis does not account for additional dilution and attenuation processes that may occur under field management scenarios. These results suggest that (i) consideration of dilution and attenuation factors for specific management scenarios may indicate that release concentrations may be higher than exposure concentrations, and that release concentrations above the MCL or DWEL may not result in exposure concentrations above those levels; (ii) linear partition coefficients (K_{ds}) are not appropriate for representing source term release from CCRs for a range of constituents and materials; and, (iii) evaluation of individual CCR sources may indicate that the environmental compatibility of specific types of CCRs with general management scenarios will depend on the source (reflected through leaching characteristics) of the material.

2. Leaching of individual constituents may vary over several orders of magnitude, depending on the conditions of the management scenario. Thus, these results can be used to suggest design conditions that would reduce or minimize constituent release (e.g., pH, and other conditions).
3. Leaching concentrations do not correlate with total content except for specific constituents in selected materials where the constituent (a) is weakly retained, and (b) leaching concentrations have a low variability relative to pH. Thus, total content is not a good indicator of leaching.
4. Results of this study suggest that it appears that Cr leachability is associated with the use of post-combustion NO_x controls. This is based on a limited set of paired samples from the same facility operating with and with SCR or SNCR in use. This finding will be further evaluated as additional data are collected.
5. The systematic leaching behavior of COPCs observed in the range of samples evaluated suggests that the geochemical mechanisms controlling leaching can be discerned and

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quantified using geochemical speciation modeling, which in turn, can serve as the basis for evaluating and improving design of CCR management scenarios. Development of generalized geochemical speciation models for the materials evaluated in this study is recommended.

6. Ranges of concentrations of some constituents in laboratory leaching test extracts and field data included in this study suggest applicable concentration ranges for risk evaluation are different from the concentration ranges used in a recent report by USEPA (EPA, 2007). The new information reported here will help provide a more up-to-date and comprehensive dataset for future risk assessments.

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Table 8. Fly Ash. Summary of results.

	<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>Tl</u>
Total in Material (mg/kg)	0.04 - 0.6	3 - 15	70 - 90	600 - 1,500	NA	0.7 - 1.5	100 - 200	20 - 50	40 - 90	10 - 20	2 - 30	3 - 13
Leaching test and assessment results												
Conc. Range for 5.4≤pH≤12.4 (µg/L)	<0.01 - 0.5	<0.3 - 200	7 - 300	90 - 4,000	200 - 300,000	<0.2 - 30	1 - 4,000	<0.3 - 200	<0.2 - 2	100 - 40,000	7 - 400	<0.3 - 300
Conc. range at natural pH (7.7≤pH≤11.1)	<0.01 - 0.4	<0.3 - 50	7 - 75	90 - 4,000	300 - 300,000	<0.2 - 30	20 - 4,000	<0.3 - 20	<0.2 - 0.7	400 - 40,000	7 - 400	<0.3 - 300
MCL (or DWEL) (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2
TC (µg/L)	200	-	5,000	100,000	6,500	1,000	5,000	5,000	5,000	-	1,000	-
Variability relative to pH	Low to High	Med. To High	Low to Med.	Low	Med. to High	High	Low to Med.	High	Med.	Low to Med.	Low to Med.	Med.

NA – not analyzed (total content for boron estimated based on leaching test results); ND – not determined.

Table 9. FGD Gypsum. Summary of results.

	<u>Hg</u>	<u>Sb</u>	As	Ba	<u>B</u>	<u>Cd</u>	Cr	Co	Pb	<u>Mo</u>	<u>Se</u>	<u>Tl</u>
Total Material (mg/kg)	0.01 - 0.5	2 - 6	2 - 4	3 - 60	NA	0.3 - 0.5	6 - 20	1 - 4	1 - 12	2 - 12	2 - 30	0.6 - 2
Leaching test and assessment results												
Conc. Range for 5.4 ≤ pH ≤ 12.4 (µg/L)	<0.01 - 0.1	<0.3 - 9	<0.5 - 10	40 - 400	40 - 70,000	<0.2 - 50	<0.3 - 50	<0.6 - 50	<0.2 - 10	1 - 400	4 - 3,000	<0.3 - 20
Conc. range at natural pH (3.8 ≤ pH ≤ 8.1)	<0.01 - 0.1	<0.3 - 15	<0.5 - 9	40 - 150	40 - 70,000	<0.2 - 15	<0.3 - 20	1 - 50	<0.2 - 12	3 - 400	4 - 3,000	<0.3 - 20
MCL (or DWEL where indicated) (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2
TC (µg/L)	200	-	5,000	100,000	6,500	1,000	5,000	5,000	5,000	-	1,000	-
Variability relative to pH	Low - Med.	Low	Low - Med.	Low	Low - Med.	High	Med. - High	Low	Low	Low	Low - Med.	Low

NA – not analyzed (total content for boron estimated based on leaching test results); ND – not determined.

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Table 10. Scrubber Sludge. Summary of results.

	<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>Tl</u>
Total in Material (mg/kg)	0.04 – 0.6	4 - 15	4 - 40	80 – 2,500	NA	0.3 – 1.5	9 - 350	1 - 40	2 - 30	9 - 30	2 - 4	2 - 12
Leaching test and assessment results												
Conc. Range for 5.4 ≤ pH ≤ 12.4 (µg/L)	<0.01 - 9	<0.3 - 20	0.6 - 100	20 - 2,000	20 - 200,000	<0.2 - 4	<0.8 - 800	<0.3 - 250	<0.2 - 25	0.4 - 1,500	2 - 300	<0.3 - 100
Conc. range at natural pH (6.5 ≤ pH ≤ 11.0)	<0.01 - 0.07	<0.3 - 10	0.6 - 20	30 - 950	20 - 200,000	<0.2 - 4	2 - 800	<0.3 - 60	<0.2 - 25	10 - 1,500	2 - 200	2 - 90
MCL (or DWEL where indicated) (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2
TC (µg/L)	200	-	5,000	100,000	6,500	1,000	5,000	5,000	5,000	-	1,000	-
Variability relative to pH	Low - High	Low - Med.	Med. - High	Low - Med.	Low - High	High	Low	High	Low	Low - High	Med.	High

NA – not analyzed (total content for boron estimated based on leaching test results); ND – not determined.

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Table 11. Fixedated Scrubber Sludge. Summary of results.

	<u>Hg</u>	<u>Sb</u>	<u>As</u>	<u>Ba</u>	—	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Pb</u>	<u>Mo</u>	<u>Se</u>	<u>Tl</u>
Total in Material (mg/kg)	0.02 - 1.0	5 - 20	3 - 70	80 - 1,000	NA	0.7 - 2	40 - 150	2 - 50	4 - 100	9 - 30	2 - 30	0.8 - 8
Leaching test and assessment results												
Conc. Range for 5.4≤pH≤12.4 (μg/L)	<0.01 - 30	<0.3 - 200	0.5 - 4,000	9 - 10,000	6 - 200,000	<0.2 - 20	<0.3 - 2,000	<0.3 - 150	<0.2 - 50	10 - 40,000	9 - 1,000	2 - 100
Conc. range at natural pH (5.8≤pH≤12.3)	<0.01 - 0.7	<0.3 - 60	0.5 - 4,000	15 - 10,000	100 - 200,000	<0.2 - 20	<0.3 - 2,000	<0.3 - 50	<0.2 - 50	10 - 40,000	9 - 500	3 - 50
MCL (or DWEL where indicated) (μg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2
TC (μg/L)	200	-	5,000	100,000	6,500	1,000	5,000	5,000	5,000	-	1,000	-
Variability relative to pH	Low - High	Low - High	Med - High	Low - Med.	High	Low - High	Low	High	Low	Low	Low - Med.	Low - Med.

NA – not analyzed (total content for boron estimated based on leaching test results); ND – not determined.

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