TABLES

FIGURES

1.0 PROJECT DESCRIPTION AND OBJECTIVES

1.1 PURPOSE

In December 2000, EPA determined that regulations are needed to control the risks of mercury (Hg) emissions from coal-fired power plants. A number of Hg control options are currently being evaluated through bench-scale and full-scale demonstrations. For each of the technologies that appear to have commercial application, the resulting residues are to be evaluated to determine any potential cross-media impacts through either waste management of these residues or use in commercial applications. Coal combustion residues (CCRs) include bottom ashes, fly ashes, and scrubber sludges from flue gas desulfurization (FGD) systems. The questions to be addressed through this research include:

- What are the changes to CCRs resulting from application of control technology at coal-fired power plants including changes in pH, metals content, and other parameters that may influence environmental release?
- For CCRs that are land disposed, the questions to be addressed include:
    - Will any of these changes result in an increase in the potential for leaching of Hg and other metals such as As, Se, Pb, and Cd leach from disposal of CCRs in impoundments, monofills, and minefills?
    - What is the fate of Hg and other metals from CCRs that are land disposed?
    - Is there a potential for organo-mercury being formed when anaerobic decomposition conditions exists?
- For CCRs that are used in commercial applications, the questions to be addressed include:
    - Will any of the changes to CCRs, from application of control technologies at coal-fired power plants, impact their use in commercial applications?
    - What is the fate of Hg and other metals in CCRs when used in commercial applications?

- What is the extent of Hg, As, Pb, Se and Cd release during high temperature manufacturing processes used to produce cement clinkers, asphalt, and wallboard?

- Are Hg and other pollutants such as As, Se, Pb and Cd present in CCRs that are used in commercial applications such as highway construction subject to conditions that would result in their release to the environment?

EPA's Air Pollution Prevention and Control Division (APPCD) through an on-site laboratory support contract with ARCADIS is to conduct a comprehensive study on the fate of mercury (Hg), arsenic (As), selenium (Se), lead (Pb) and cadmium (Cd) in CCRs. This research will be conducted in four tasks. Task I will focus on the characterization of different CCRs and the impact of Hg control technologies on these characteristics. Task II will focus on evaluating the potential for leaching of these toxic metals from CCRs that are generated with and without implementation of Hg control technologies under a range of management scenarios. Task III will focus on the release of these toxic metals during high and low temperature utilization of CCRs in commercial processes. Task IV will study the potential formation and volatilization of organo-mercury and inorganic mercury during simulated anaerobic decomposition processes. The scope of this QAPP covers Task I through Task III. Task IV will be addressed in a separate document.

1.2 PROJECT OBJECTIVES

EPA's Office of Solid Waste (OSW) has been asked to provide general guidance on appropriate testing to evaluate the release potential of Hg and four other metallic contaminants (As, Se, Pb, and Cd) from CCRs via leaching, run-off, and volatilization when disposed in landfills and incorporated into commercial products using high/low temperature commercial processes. This evaluation in projected disposal and reuse situations (different waste management scenarios; see Section 1.1) will both help assess the likely suitability of new or modified wastes for reuse, and ensure that Hg, As, Se, Pb, and Cd removed from stack emissions are not subsequently released to the environment in significant amounts as a result of CCR reuse or disposal practices.

The primary objective of this project is to generate a comprehensive database that will enable EPA/OSW to (1) evaluate changes in CCRs resulting from the implementation of different Hg control technologies (see Section 3.1), and (2) assess environmental releases of these toxic metals during CCR management practices including land disposal and commercial applications. OSW will be using the results to determine needs in regard to future policies for managing CCRs whose characteristics are changing as a result of the MACT under development for coal fired power plants. OAR will be using the data to determine the potential for cross-media impacts and potential changes to disposal and reuse practices which impact the economics of potential regulations for coal-fired power plants. The data will also be used to address questions raised by Congress and others regarding establishing the net benefit of potential requirements for reducing emissions from coal-fired power plants.

Data on the chemical stability of these metals (leaching tests) will be generated using the EPA/OSW recommended methods (EPA, 2002b) developed by Dr. David Kosson and Dr. Florence Sanchez of Vanderbilt University titled *An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials* (Kosson et al., 2002a). The ability of these EPA/OSW methods to assess leaching of the metals of interest will be further demonstrated with the use of a NIST standard reference material (SRM) with certified amounts of trace metals. Data on the thermal stability of these toxic metals during CCRs commercial applications will also be determined by implementing temperature program desorption techniques (see Section 4.4). The time/temperature profiles experienced by CCRs in their commercial applications (highway construction, cement, asphalt, and wallboard manufacturing) as determined based on the study conducted by RTI International and presented in the publication titled *Characterization and management of Residues from Coal-Fired Power Plants/Interim Report*, prepared for APPCD/NRMRL/EPA (EPA, 2002a). Using this comprehensive database, EPA/OSW will determine the feasibility of the application of the above methods to CCRs and they will assess the environmental impacts of different types of CCRs' waste management practices.

A secondary objective of this project is to modify and develop a QA/QC framework for the proposed leaching assessment approach developed by Kosson et al. The reference fly ash may be an appropriate candidate for a method QC sample. These activities will be carried out in cooperation with Drs. Kosson and Sanchez during implementation of the proposed methods (see Task II, Section 3.2).

2.0 PROJECT ORGANIZATION

The organizational chart for this project is shown in Figure 2-1. The roles and responsibilities of the project personnel are discussed in the following paragraphs. In addition, contact information is also provided.

EPA Work Assignment Manager, Susan Thorneloe: The EPA WA Manager is responsible for communicating the scope of work, data quality objectives and deliverables required for this work assignment. The EPA WA Manager is also responsible for providing ARCADIS with the various types of CCRs to be characterized.

Phone: (919) 541-2709

E-mail: thorneloe.susan@epamail.epa.gov

EPA QA Representative, Shirley Wasson: The EPA QA Representative will be responsible for reviewing and approving this QAPP. This project has been assigned a QA category III and may be audited by EPA QA. Ms. Wasson is responsible for coordinating any EPA audits.

Phone (919) 541-5510

E-mail: wasson.shirley@epamail.epa.gov

ARCADIS Work Assignment Leader, Robert Keeney: The ARCADIS WA Leader is responsible for preparing project deliverables and managing the work assignment. He will ensure the project meets scheduled milestones and stays within budgetary constraints agreed upon by EPA. The WA Leader is also responsible for communicating any delays in scheduling or changes in cost to the EPA WA Manager as soon as possible.

Phone (919) 541-3284

E-mail: rkeeney@arcadis-us.com

ARCADIS Inorganic Laboratory Manager, Robert Keeney. In addition to being the work assignment leader, Robert Keeney is also responsible for the operation of EPA's in-house Inorganic Laboratory. Mr. Keeney will review and validate all analytical data reports and ensure that the leaching studies are performed properly. He will also operate the TGA and surface area analyzers. For the leaching studies and mercury and metals analyses, Mr. Keeney will be supported by one chemist: Gene Gallagher and one technician: John Foley.

Mr. Gallagher will perform HF extractions of solid CCR and SRM samples and also be responsible for mercury analysis of samples by CVAA. John Foley will perform the leaching test. Mr. Keeney and Mr. Gallagher will submit the remaining HF digestates to the subcontract analytical laboratory, STL-Savannah for ICP/MS analysis of the other target metals. Mr. Keeney will also be responsible for assisting Drs. Kosson and Sanchez in the development of appropriate QA/QC procedures for the leaching assessment methods.

Phone (919) 541-3284

E-mail: rkeeney@arcadis-us.com

STL-Savannah Analytical Manager, Angie Weimerskirk: Ms. Weimerskirk will review and validate the ICP/MS results and report them to Mr. Keeney.

Phone (912) 354-7858

E-mail: aweimerskirk@stl-inc.com

ARCADIS Thermal Desorption Task Manager (Task III), Behrooz Ghorishi: The ARCADIS Thermal Desorption Task Manager is responsible for preparing task III deliverables and managing task III. He will ensure the task meets scheduled milestones. The Thermal Desoption Task Manager is also responsible for communicating any delays in scheduling to the ARCADIS Work Assignment Leader. EPA WA Manager as soon as possible. Dr. Ghorishi will be assisted by Jarek Karwowski. Mr. Karwowski will perform the thermal desorption test and submit the samples to the laboratory.

ARCADIS Designated QA Officer, Laura Nessley: The ARCADIS QA Manager, Laura Nessley, has been assigned QA responsibilities for this work assignment. Ms. Nessley will be responsible for reviewing this QAPP prior to submission to EPA QA for review. Ms. Nessley will also ensure the QAPP is implemented by project personnel by performing internal assessments. All QA/QC related problems will be reported directly to the ARCADIS WAL, Robert Keeney.

Phone: (919) 544-2260 ext. 258

E-mail: lnessley@arcadis-us.com

Vanderbilt University, Methods Development, Professors David Kosson and Florence Sanchez: Dr. Kosson in cooperation with Dr. Florence Sanchez developed the leachability methods being evaluated on this project. He will be available to consult regarding method optimization and development of QA/QC procedures. Dr. Kosson and Dr. Sanchez will be on-site in the early stages of the project to assist in setting up the procedures. Phones: (615) 322-1064; (615) 322-5135
E-mail: David.Kosson@vanderbilt.edu
Florence.Sanchez@vanderbilt.edu

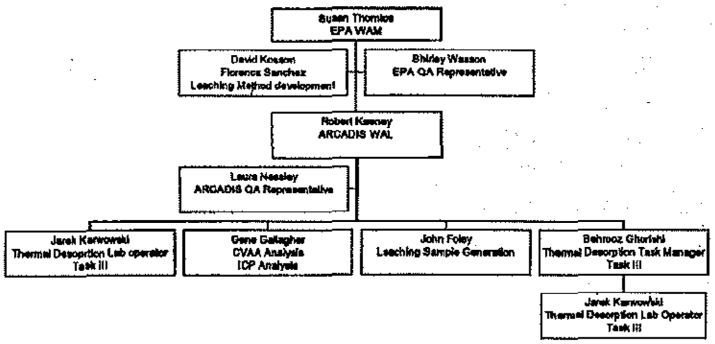

Figure 2-1- Project Organizational Chart

3.0 EXPERIMENTAL APPROACH

3.1 TASK I: CHARACTERIZATION OF CCRS

This task will focus on physical and chemical characterization of as-received CCRs. CCRs from different power plants and various types of control technologies will be selected and provided to ARCADIS by the EPA WA Manager. These CCRs will include fly ashes and scrubber sludges from DOE test facilities. These full-scale facilities are being used to test two different Hg control technologies: activated carbon injection as an adsorbent and addition of agents to wet scrubbers that maintain Hg in an oxidized state to facilitate removal by aqueous scrubbing. Physical characteristics of CCRs to be determined include specific surface area, moisture content and density. Chemical characterization will include total carbon analysis, pH of extract, total concentration of target metals (Hg, As, Se, Pb, and Cd) and principal constituents (i.e., Fe, Cl^-, SO_4^{2-}, CO_3^{2-})[1]. The types of analyses and instrumentations used to perform this characterization are further described in Section 5.0. Identical characterizations will be performed on the reference fly ash. Task I results will reveal the effect of implementing the two Hg control technologies on the final characteristics of CCRs. This information will help in decision-making regarding different waste management scenarios.

3.2 TASK II: CHEMICAL STABILITY OF TARGET METALS

This task will investigate the fate of Hg, As, Se, Cd, and Pb during CCR management practice of land disposal. Using the recently proposed test methods developed by Kosson et al in coordination with EPA's Office of Solid Waste, leaching studies will first be conducted on a reference fly ash. The reference fly ash is a high quantity fly ash that has been characterized by ICP/MS and CVAA analyses. The ICP/MS and CVAA analyses will be checked using the NIST SRM 1633b. NIST SRM 1633B is a bituminous coal fly ash that is fully described in Section 4.2.2. The results obtained from the reference fly ash leaching studies will be critical in evaluating the performance of the method. Using a known standard in place of the CCR material, will also allow optimization of the proposed test methods. The quality control procedures regarding the reference fly ash tests are described in section 6.

A summary of testing that will be carried out on the reference fly ash is presented in Table 3-1 along with the number of replicates, the material mass required and the number of extracts that will be generated. Detailed descriptions of the methods listed in Table 3-1 can be found in the document titled An Integrated Framework for Evaluating Leaching in Waste management and Utilization of Secondary materials (Kosson et al., 2002a).

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[1] This will provide valuable insights concerning the characteristic behavior of the CCRs.

TABLE 3-1. SUMMARY OF TESTING UNDER TASK II TO BE PERFORMED ON THE REFERENCE FLY ASH

Sample type	Level of testing	Tests	Material particle size	Number of replicates	Mass material/ aliquot* (g)	Mass material/ test replicate (g)	Total mass of material required (g)	Number of analytical samples
Baseline	Detailed	pH001.1 (pH Titration Pretest)	< 2 mm	2	8	8	16	NA
Fly Ash**	characterization							
		Moisture Content	< 2 mm	3	8	8	24	NA
		AV002.1	< 2 mm	3	8	24	72	3
		Availability at pH 7.5 with EDTA (3 target points)						
		SR002.1	< 2 mm	3	40	440	1320	33
		Alkalinity, Solubility and Release as a Function of pH (11 pHs tested from 2 to 12)						
		SR003.1	< 2 mm	3		430	1290	15
		Solubility and Release as a Function of LS ratio (LS=10, 5, 2, 1, 0.5 mL/g)						
		LS 10 mL/g			40			
		LS 5 mL/g			40			
		LS 2 mL/g			50			
		LS 1 mL/g			100			
		LS 0.5 mL/g			200			
		MT002.1					2500	30
		Mass Transfer Rate in Granular Materials (10 extracts in 30 days)						
		- Optimum moisture content	< 2 mm	2	500	500		
		- Leach test	< 2 mm	3	500	500		
				Total mass material required (g)			5222	

* Sample size required for each condition within the test method. For example, one replicate of SR002.1 requires eleven sample aliquots.

** Baseline fly ash is a fly ash that will be used as a reference material. Total elemental content will be determined by NAA/XRF analysis.

After the proposed test methods have been successfully demonstrated on the reference fly ash, leaching studies will be conducted on high priority CCRs that will allow estimating constituent release by leaching for a range of conditions that are likely to occur during management practices. A separate test plan for the leaching experiments under this task is provided by its developers (Drs. Kosson and Sanchez). This test plan, titled "Draft (Revision #2), Sampling and Characterization Plan for Coal Combustion Residues from Facilities with Enhanced Mercury Emissions Reduction Technology" (Kosson et al., 2002b) together with this QAPP will cover all the issues regarding Task II. Two levels of testing will be performed. The first level will provide detailed characterization of representative samples of CCRs that reflect each dominant CCR chemistry with respect to mercury release. This will define the behavior of the general class of CCR chemistry. This detailed characterization would establish a baseline for comparison of subsequent test results. A summary of testing that will be carried out on each dominant CCR chemistry is presented in Table 3-2 along with the number of replicates, the material mass required and the number of extracts that will be generated.

The second level will provide screening evaluation of additional samples anticipated to be representative of each dominant CCR chemistry. The second level screening will be used to determine if the CCR being tested exhibits the same leaching behavior as the general class of CCRs, which is assumed to have the same dominant chemistry. If the leaching behavior is found to be significantly different than anticipated, then more complete characterization can be completed. A summary of testing that will be carried out for the screening level is presented in Table 3-3 along with the number of replicates, the material mass required and the number of extracts that will be generated.

Residues collected before and after application of enhanced Hg control technologies will be examined to evaluate the effect of the enhanced systems on the leaching behavior of CCRs.

Estimates of the extent of release of the metals of concern during management scenarios that include percolation through the CCRs or infiltration flow around the CCRs (e.g., when compacted to low permeability or otherwise expected to behave as a monolithic material) will be determined. These data will be used to determine the risk of land disposal of the different CCRs. Mass balances for each metal will be determined using the chemical characterization data obtained in Task I. Utilization of mass balance as a QA/QC tool is described in section 6. Details of this QA/QC procedure are outlined in section 6. In addition to testing of the CCRs as generated, CCRs as used in commercial products will be examined. Only commercial uses for which there is a potential for release of Hg during leaching will be considered. One commercial use of CCRs that may be of concern for Hg leaching is cement-based materials (i.e., concrete/grout, waste stabilization, road base/subbase). A generic cement-based product made from samples representative of the major coal fly ash categories will be examined. A second commercial use of CCRs that may be of concern is incorporation in gypsum board. In this case leaching of Hg after disposal is of concern. This task will consider the potential for Hg leaching after disposal from a representative gypsum board product.

Category III

TABLE 3-2. SUMMARY OF TESTING UNDER TASK II TO BE PERFORMED FOR DETAILED CHARACTERIZATION OF CCRS

Sample type	Level of testing	Tests	Material particle size	Number of replicates	Mass material/ aliquot* (g)	Mass material/ test replicate (g)	Total mass of material required (g)	Number of analytical samples
Sample reflecting dominant CCR chemistry	Detailed characterization	pH001.1 (pH Titration Pretest)	< 2 mm	2	8	8	16	NA
		Moisture Content	< 2 mm	3	8	8	24	NA
		AV002.1**	< 2 mm	2	8	24	48	2
		Availability at pH 7.5 with EDTA (3 target points)						
		SR002.1	< 2 mm	2	40	440	880	22
		Alkalinity, Solubility and Release as a Function of pH (11 pHs tested from 2 to 12)						
		SR003.1	< 2 mm	2		430	860	10
		Solubility and Release as a Function of LS ratio (LS=10, 5, 2, 1, 0.5 mL/g)						
		LS 10 mL/g			40			
		LS 5 mL/g			40			
		LS 2 mL/g			50			
		LS 1 mL/g			100			
		LS 0.5 mL/g			200			
		MT002.1	< 2 mm	2			2000	20
		Mass Transfer Rate in Granular Materials (10 extracts in 30 days)						
		- Optimum moisture content			500			
		- Leach test			500			
				Total mass material required (g)			3828	

* Sample size required for each condition within the test method. For example, one replicate of SR002.1 requires eleven sample aliquots.

** Optional

Category III

TABLE 3-3. SUMMARY OF TESTING UNDER TASK II TO BE PERFORMED FOR SCREENING EVALUATION OF CCRs

Sample type	Level of testing	Tests	Material particle size	Number of replicates	Mass material/ aliquot* (g)	Mass material/ test replicate (g)	Total mass of material required (g)	Number of analytical samples
Additional samples anticipated to be representative of each dominant CCR chemistry	Screening							
		Moisture Content	< 2 mm	3	8	8	24	NA
		SR002.1 - A	< 2 mm	3	40	120	360	3
		(3 pHs @ LS 10mL/g: acidic, neutral, alkali)						
		SR003.1 - A	< 2 mm	3		240	720	6
		(LS = 10, 0.5 mL/g)						
		LS 10 mL/g			40			
		LS 0.5 mL/g			200			
		MT002.1 - A	< 2 mm				2500	12
		(4 extractions in 5 days)						
		- Optimum moisture content		2	500	500		
		- Leach test		3	500	500		
				Total mass material required (g)			3604	

* Sample size required for each condition within the test method. For example, one replicate of SR002.1-A requires three sample aliquots.

3.3 TASK III: THERMAL STABILITY OF TARGET METALS

This task will investigate the potential release of the target metals during their commercial applications such as cement, wallboard and asphalt manufacturing. The potential long-term evaporation of these metals during low temperature applications such as structural fills, highway construction, snow/ice control, and soil amendment will also be determined. Representative samples of CCRs will be tested in an in-house, bench-scale, fixed-bed reactor system called the Thermal Program Desorption (TPD) system. CCRs will be exposed to conditions that are experienced in actual situations. The effluent of the fixed-bed reactor will be sampled and analyzed for inorganic Hg (speciated, elemental and ionic), As, Se, Pb, and Cd using established methods such as EPA Method 29 for metals and Ontario Hydro Method for mercury. Mass balances for the metals will be determined using the chemical characterization data obtained in Task I. The reference fly ash will also be tested in the reactor and the results will be used as a quality control check (see section 6).

3.4 TASK IV: BIOLOGICAL TRANSFORMATION AND VOLATILIZATION OF ORGANO-MERCURY

This task will investigate the potential formation and release of organo-mercury during anaerobic decompositions. This will be simulated in a bioreactor and the effluent will be sampled for speciated inorganic and organic mercury. The details of these tests will be described in a separate QAPP. Due to the health and safety related concerns regarding organo-mercury compounds, prior to preparation of the QAPP, an extensive literature survey will be performed to select the most appropriate methods for sampling and analysis of these types of compounds.

4.0 SAMPLING PROCEDURES

The following subsections describe the sampling procedures to be used for each task. Whenever possible, standard methods will be followed. In some cases, draft methods may be evaluated and implemented. Each method to be used will be cited and any deviations from the methods will be documented.

4.1 SAMPLE CUSTODY PROCEDURES

The following types of samples will be generated during these tests:

1- "As-received" CCR samples before and after application of Hg control technologies, SRM and reference fly ash samples (solid samples) and treated CCR samples as used in commercial applications
2- Post –leaching and post-thermal desorption CCR, reference fly ash samples and treated CCR samples (solid samples)
3- Leachate samples (liquid samples)
4- Method 29 and Ontario Hydro Train samples (liquid samples)

Each sample generated will be analyzed in-house but chain-of-custody procedures will be required. CCRs will be logged as they are received by the ARCADIS WAL, Mr. Robert Keeney. Information regarding where each CCR originated and any other descriptive information available will be recorded in a dedicated laboratory notebook by Mr. Keeney. A 200 g grab sample will be taken from each "as-received" CCR and processed for physical and chemical characterization. All samples will be properly contained and identified with a unique sample ID and sample label. Sample labels at a minimum will contain the sample ID, date sampled, and initials of the analyst responsible for preparing the sample. Chain-of-custody forms will be generated for all samples prior to transfer for analysis.

Handling of CCR samples for the leaching tests (Task II) is described in detail by the leaching procedure provided by its developers (Kosson et al., 2002a). For Task III, a 10g grab sample will be taken from each "as received" CCR and will be subjected to the TPD procedures (see section 4.2.3)

4.2 CCR, AND REFERENCE FLY ASH SAMPLES

As mentioned, the focus of this program is to obtain information on the effect of Hg control technologies on the stability of Hg, As, Se, Cd, and Pb in CCRs. Currently, two different Hg control technologies are being tested in full-scale facilities. The focus of the first technology is on powdered activated carbon (PAC) injection upstream of particulate matter control devices. The PAC injection technology affects the properties of fly ashes collected in electrostatic precipitators and baghouses. These facilities are listed in the Vanderbilt test plan "Draft (Revision #2), Sampling and Characterization Plan for Coal Combustion Residues from Facilities with Enhanced Mercury Emissions Reduction Technology" (Kosson et al., 2002b). The second technology focuses on Hg capture by wet scrubbers. Chemical modifications are being implemented in wet scrubbers to enhance the Hg capture. The scrubber sludge from these facilities will be impacted by this control technology. The scrubber sludge samples from these facilities will be included in this test program.

The Hg control testing facilities will be identified and their test reports will be obtained and amended to this QAPP. The test reports will include information on the history/origin of each CCR sample, facility process description, CCR type, sampling location, sampling time and method, coal type, operating condition, and sample storage condition. Section 4.1 describes the sampling custody procedure.

4.2.1 Physical and Chemical Characterization Samples

"As received" CCR will be well mixed prior to taking samples for physical characterization. Mixing of the sub-samples collected at the site will be done using a riffle splitter. To ensure a good homogeneity of the final composite sample that will be used for the study, the first two composite samples exiting the splitter will be reintroduced at the top of the splitter. This procedure should be repeated at least 6 times. At the end, the two resulting homogeneous composite samples will be combined in the same bucket and stored until laboratory testing. A 200 g representative sample will be taken from the "as received" CCR and subjected to physical characterization measurements. Samples will also be taken of any CCRs that undergo size-reduction techniques (if size reduction is needed for testing purposes). The reference fly ash samples will be processed in the same manner as the CCRs. They will be tracked by lot number and will not require size-reduction.

4.2.2 Leaching Study Samples

CCRs used for leaching studies may undergo size reduction to acquire an adequate sample for testing. The size reduction method is outlined in the leaching test methods (Kosson et al., 2002a). If "as-received" CCRs are altered in any way prior to leaching studies, a representative sample will be submitted for physical and chemical characterization. SRM samples will not require size reduction. The NIST 1633B SRM is a bituminous coal fly ash that has been sieved through a nominal sieve opening of 90 μm and blended to assure homogeneity. The certified values for the constituent elements are given in Table 4-1. The reference fly ash will also be certified using ICP/MS and CVAA.

4.2.3 Fixed-Bed Reactor Samples

Reactor samples will be essentially the same as the CCR samples used in the leaching studies. Amount of material may be reduced, but physical and chemical characteristics will not be affected.

TABLE 4-1. SRM CERTIFIED VALUES

Element	Concentration (mg/kg)
Arsenic	136.2 ± 2.6
Barium	709 ± 27
Cadmium	0.784 ± 0.006
Chromium	198.2 ± 4.7
Copper	112.8 ± 2.6
Lead	68.2 ± 1.1
Manganese	131.8 ± 1.7
Mercury	0.141 ± 0.019
Nickel	120.6 ± 1.8
Selenium	10.26 ± 0.17

Strontium	1041 ± 14
Thorium	25.7 ± 1.3
Uranium	8.79 ± 0.36
Vanadium	295.7 ± 3.6

4.3 LEACHATE COLLECTION

The proposed test method described in the publication titled *An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials* (Kosson, et. al., 2002a) will be used to conduct leaching studies. There are three tiers to this test method:

Tier 1) Screening based assessment (availability)
Tier 2) Equilibrium-based assessment over a range of pH and Liquid/solid (LS) ratios
Tier 3) Mass transfer based assessment

The Tier 1 screening test provides an indication of the maximum potential for release under the limits of anticipated environmental conditions expressed on a mg contaminant leached per kg waste basis. Tier 2 defines the release potential as a function of liquid-to-solid (LS) ratio and pH. Tier 3 uses information on LS equilibrium in conjunction with mass transfer rate information. As mentioned previously, prior to testing CCR, a reference fly ash will be used to demonstrate the effectiveness of the proposed test methods. Procedures for each tier are discussed in the following subsections.

If needed, prior to tier testing, the "as-received" CCR will be size reduced using the procedure **PS001.1 Particle Size Reduction** (Kosson et al., 2002a) to minimize mass transfer rate limitation through larger particles. The pH will be then tested using the method **pH001.0 pH Titration Pretest** (Kosson et al., 2002a).

4.3.1 Tier 1 Screening Tests

Test Method **AV002.1 Availability at pH 7.5 with EDTA** (Kosson et al., 2002a) will be used to perform the screening test. This method measures availability in relation to the release of anions at an endpoint pH of 7.5±0.5 and cations under enhanced liquid-phase solubility due to complexation with the chelating agent. Constituent availability is determined by a single challenge of an aliquot of the reference fly ash or size reduced CCR material to dilute acid or base in DI water with the chelating agent, ethylenediamine-tetraacetic acid (EDTA). Extracts are tumbled end-over-end at 28±2 rpm at room temperature for a contact time of 24 hours. At the end of the 24-hour period, the leachate pH value of the extraction is measured. The retained extract is filtered through a 0.45 µm polypropylene filtration membrane and the sample is stored at 4°C until analysis.

The results from this test are used to determine the maximum quantity, or the fraction of the total constituent content, of inorganic constituents (Hg, As, Se, Pb, and Cd) in a solid matrix that potentially can be released from the solid material in the presence of a strong chelating agent. The chelated availability, or mobile fraction, can be considered (1) the thermodynamic driving force for mass transport through the solid material, or (2) the potential long-term constituent release. Also, a mass balance based on the total constituent concentration provides the fraction of a constituent that may be chemically bound, or immobile in geologically stable mineral phases.

4.3.2 Tier 2 Solubility and Release as a Function of pH and LS Ratio

Test Method **SR002.1 Alkalinity, Solubility and Release as a Function of pH** (Kosson et al., 2002a) is the method to be used for Tier 2 pH Screening. The protocol consists of 11 parallel extractions of particle size reduced material at a liquid-to-solid ratio of 10 mL extractant per gram of dry sample. An acid or base addition schedule is formulated for 11 extracts with final solution pH values between 3 and 12, through addition of aliquots of HNO_3 or KOH as needed. The exact pH schedule is adjusted based on the nature of the CCR; however, the range of pH values must include the natural pH of the matrix, which may extend the pH domain. The extraction schedule and the range of tested pHs are outlined in the developers' leaching test plan, "Draft (Revision #2), Sampling and Characterization Plan for Coal Combustion Residues from Facilities with Enhanced Mercury Emissions Reduction Technology" (Kosson et al., 2002b).

If necessary, the material being evaluated is particle size reduced to <0.3 mm by sieving to remove any large pebbles present. A mortar and pestle may be used to break up clumps of material. A 40 g dry sample of the reference fly ash or size reduced CCR is used for these tests. Using the schedule, equivalents of acid or base are added to a combination of deionized water and the reference fly ash or particle size reduced CCR. The final liquid-to-solid (LS) ratio is 10 mL extractant per gram of sample, which includes DI water, the added acid or base, and the amount of moisture that is inherent to the waste matrix as determined by moisture content analysis. The 11 extractions are tumbled in an end-over-end fashion at 28 rpm for a contact time of 24 hrs. Following gross separation of the solid and liquid phases by settling, leachate pH measurements are recorded and the phases are separated by pressure filtration through 0.45 μm polypropylene filtration membranes. Analytical samples of the leachates are collected and preserved as appropriate for chemical analysis. For metal analysis, leachates are preserved by acidification with HNO_3 to a pH <2 and stored at 4 °C until analysis. For anion analysis, leachates are stored at 4°C until analysis.

Test method **SR003.1 Solubility and Release as a Function of LS Ratio** (Kosson et al., 2002a) is the method to be used for Tier 2 LS ratio screening. The protocol consist of five parallel batch extractions over a range of LS ratios (0.5, 1, 2, 5, and 10 mL/g dry material) using the particle size reduced CCR and DI water as the extractant. Extractions are conducted at room temperature in leak-proof vessels that are tumbled at 28±2 rpm for 24 hours. Solid and liquid phases are separated by settling and pH and conductivity measurements are taken. The liquid is further separated by pressure filtration using a 0.45 μm polypropylene filter membrane. Leachates are collected for each of the 5 LS ratios and preserved as appropriate for chemical analysis. For metal analysis, leachates are preserved by acidification with HNO_3 to a pH <2 and stored at 4 °C until analysis. For anion analysis, leachates are stored at 4°C until analysis. The range of tested LS ratios is outlined in the leaching test plan, "Draft (Revision #2), Sampling and Characterization Plan for Coal Combustion Residues from Facilities with Enhanced Mercury Emissions Reduction Technology" (Kosson et al., 2002b).

4.3.3 Tier 3 Mass Transfer Rate

Test method **MT002.1 Mass Transfer Rates in Granular Materials** (Kosson et al., 2002a) is the method to be used for Tier 3 testing. This protocol involves continuous water-saturation of the reference fly ash or CCR material. Compacted granular material is contacted with DI water using a liquid to surface area ratio of 10 mL DI water for every cm^2 of exposed solid surface. Fresh DI water is exchanged with leached material at specific intervals (2, 5 and 8 hours, 1, 2, 4, and 8 days). The pH, and conductivity for each time interval is also recorded. Each leachate sample is prepared for chemical analysis by pressure filtration through a 0.45 μm polypropylene filtration membrane and preserved as appropriate for chemical analysis. For metal analysis, leachates are preserved by acidification with HNO_3 to a pH <2 and stored at 4 °C until analysis. For anion analysis, leachates are stored at 4°C until analysis. In some cases, this test will be extended up to a cumulative leaching time of *ca.* 30 days to provide more information about long-term material behavior.

Test method MT001.1 Mass Transfer in Monolithic Materials will be used on the treated CCR samples when applicable instead of the MT002.1 protocol (Kosson et al., 2002a).

4.4 FIXED-BED, TPD REACTOR SAMPLING

Data on the thermal stability of toxic metals on CCRs during their commercial applications will be obtained using simulated conditions in a fixed-bed reactor called the Thermal Program Desorption (TPD) system. The time/temperature profiles experienced by CCRs in their commercial applications, type of other materials that CCRs are mixed with, and the composition of the flue gas that is in contact with CCRs have been determined by a separate study conducted by RTI International (EPA, 2002a). The information from this report has been used to create simulated conditions in our in-house, fixed-bed TPD reactor. This reactor is described in detail in the Mercury Facility Manual. CCRs (mixed with other compounds) will be placed in the fixed bed reactor (about 10 grams). The simulated flue gas will be passed through the fixed-bed that is exposed to a specific time/temperature profile. Detailed description of the simulated flue gas preparation and temperature control of the fixed-bed reactor is also described in the Mercury Facility Manual. This manual also addresses the QA/QC issues regarding the operation of this reactor. The flue gas effluent of the fixed-bed reactor will be sampled for the duration of each test (the time profile) using two standard methods. EPA method 29 (EPA, 1996c) will be used to sample for As, Se, Pb, and Cd. Ontario Hydro Method (ASTM, 2002) will be used to sample for elemental and ionic mercury (inorganic forms of mercury). Since the effluents of the fixed-bed reactor is free of any entrained particulate matter, only the impinger portions of Method 29 and Ontario Hydro will be used (filter box will be eliminated). After each test, the exposed CCR will be recovered and analyzed for Hg, As, Se, Cd, and Pb. The pre- and post-test analysis results of the CCRs together with the Method 29 and Ontario Hydro results will be used to determine mass balances for these five metals. This experiment will also be performed on a sample of the reference fly ash material as a QC check.

4.4.1 Thermal Desorption Test Plan for High Temperature CCR Commercial Processes

<u>A- Cement (Clinker) manufacturing:</u>

In this process, fly ash is used as feed to a cement kiln. Fly ash typically represents a maximum of about 5% (weight) of the typical raw mix to the kiln. Other inputs include limestone (90%), iron ore (3%), and sand (2%), but fly ash can displace other components of cement kiln like limestone and iron ore, so its percentage can go higher. Cement kiln residence time is about one hour, temperature is about 1500°C, and the gas environment is natural gas combustion flue gas. The assumption is that all Hg is vaporized. Thus, the focus of this section will be on As, Cd, Se, and Pb. The test plan is as follow:

1- Mix 5g fly ash, with 5g CaCO3 (limestone), 0.2g iron oxide (Fe_2O_3) and 0.5g sand and place the mixture in the fixed-bed reactor.

2- Inlet flue gas consists of 14% CO_2, 3% O_2, 5.3% H_2O, and 50 ppm NO_X. The total flow rate will be 400 cc/min.

3- Heat the fixed-bed reactor to its maximum temperature (1000°C). With the current system, we will not be able to exceed 1000°C. If no evaporation of these metals is observed at this temperature, we will modify the system to achieve a desorption temperature of 1500°C.

4- Attach a mini-impinger, EPA Method 29 to the outlet of the fixed-bed reactor and sample the whole effluent of the fixed-bed reactor for As, Cd, Pb, and Se for one hour (residence time of cement kilns).

5- Recover the solid residue and the Method 29 train and submit for metal analysis.

6- Close metals' mass balances across all phases (pre-test fixed bed solid, exposed solid, and reactor effluent).

B- Wallboard Manufacturing

This process will be simulated using FGD waste (and not fly ash). Wallboard manufacturing consists of two steps: calcining and drying. FGD waste experiences a higher temperature during calcining, thus only this step will be simulated. The calcining kettle temperature is about 310-370°C; but FGD waste temperature never exceeds 170°C. FGD waste is not mixed with any other compounds, its residence time in the kettle is about 1 hour and it is in contact with natural gas combustion flue gas. The test plan will be as follow:

1- Place 10g of FGD waste in the fixed-bed reactor.

2- Inlet flue gas consists of 14% CO_2, 3% O_2, 5.3% H_2O, and 50 ppm NO_X. The total flow rate will be 400 cc/min.

3- Heat the fixed bed reactor to 170°C.

4- Attach a mini-impinger Method 29 train to the outlet of the fixed-bed reactor and sample for As, Cd, Pb, and Se for one hour (residence time of calcining kettle); recover the solid residue and the Method 29 train and submit for As, Se, Pb, and Cd analysis.

5- Repeat steps 1 thru 3 (new batch of sample) and attach a mini-impinger Ontario Hydro train to the outlet of the reactor and sample for one hour. Recover solid residue and the train and submit for Hg analysis. Ontario Hydro sampling will reveal the amount of total Hg, ionic Hg (inorganic Hg), and elemental Hg evolved from the calcining process simulation.

6- Close metals' mass balances across all phases (pre-test fixed bed solid, exposed solid, and reactor effluent).

C- Asphalt manufacturing

Asphalt manufacturing consists of two steps: a very short residence time mixing process (about one minute) and a long residence time storage process (several hours). The storage process occurs at temperatures of about 5°C higher than the mixing process. Thus, the most important step (in terms of thermal desorption) is the storage step. Hot mix asphalt (HMA) is 95% stone, sand, or gravel bound together with asphalt cement (crude oil); fly ash makes up approximately 5% of this mixture replacing natural fillers such as hydrated lime or stone. This mixture is in contact with natural gas combustion flue gas. Storage temperatures usually range from 130-150°C for binder grade PG46-28 and 160-170°C for binder grade PG82-22. The test plan for asphalt manufacturing simulation will be as follow:

1- Place 1g of fly ash and 9 g sand in the fixed-bed reactor.

2- Inlet flue gas consists of 14% CO_2, 3% O_2, 5.3% H_2O, and 50 ppm NO_X. The total flow rate will be 400 cc/min.

3- Heat the fixed bed reactor to 170°C.

4- Attach a mini-impinger Method 29 train to the outlet of the fixed-bed reactor and sample for As, Cd, Pb, and Se for three hours (assumed residence time of asphalt storage); recover the solid residue and the Method 29 train and submit for As, Se, Pb, and Cd analysis.

5- Repeat steps 1 thru 3 (new batch of sample) and attach a mini-impinger Ontario Hydro train to the outlet of the reactor and sample for three hours. Recover solid residue and the train and submit for Hg analysis. Ontario Hydro sampling will reveal the amount of total Hg, ionic Hg (inorganic Hg), and elemental Hg evolved from the asphalt storage process simulation.

6- Close metals' mass balances across all phases (pre-test fixed bed solid, exposed solid, and reactor effluent).

5.0 TESTING AND MEASUREMENT PROTOCOLS

Whenever possible, standard methods will be used to perform required measurements. Standard methods are cited in each applicable section. Where standard methods are not available, operating procedures will be written to describe activities. In situations where method development is ongoing, activities and method changes will be thoroughly documented in dedicated laboratory notebooks.

5.1 PHYSICAL CHARACTERIZATION

5.1.1 Surface Area and Pore Size Distribution

A Micromeretics ASAP 2400 Surface Area Analyzer will be used to perform Brunauer, Emmett, and Teller (BET) method surface area, pore volume, and pore size distribution analysis on each as-received and size reduced CCR. A 200 mg sample is degassed at 200 C for at least one hour in the sample preparation manifold. Samples are then moved to the analysis manifold, which has a known volume. Total gas volume in the analysis manifold and sample tube is calculated from the pressure change after release of an N_2 and He mixed gas from the analysis manifold known volume. Report forms are automatically generated after each completed analysis. The instrument uses successive dosings of N_2 while measuring pressure. The surface area analyzer is calibrated annually by a Micromeretics service representative. Standards of known surface area are run with each batch of samples as a QC check. Detailed instructions for the operation of this instrument are included in the Mercury Facility Manual.

5.1.2 Density Measurements

The Micromeretics Accupyc 1330, a helium pyncnometer, will be used to determine CCR density. This is a fully automatic gas displacement pycnometer, which measures the volume of solids. Instrument operation is based on the ideal gas law. By measuring the pressure change of He in a calibrated volume, the pycnometer determines sample volume from which density can be derived automatically if sample weight is know. Samples must be free of moisture to obtain true sample weight and to avoid the distorting effect of water vapor on volume measurement. The cell chamber should be kept closed at all times except when actually inserting or removing a sample. The size of the cell and expansion chamber is determined by calibration, which is performed every 10 runs or immediately prior to analysis after two weeks without operation. The density measuring capacity of the Accupyc is calibrated for each run by analyzing two steel balls of known density. Detailed instructions for the operation of this instrument are included in the Mercury Facility Manual.

5.1.3 pH and Conductivity

pH and conductivity will be measured on all aqueous extracts. Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability is dependent upon the presence of ions; on their total concentration, mobility, and variance; and on the temperature of the measurement.

pH of the leachates will be measured using a combined pH electrode. A 2-point calibration will be done using pH buffer solutions. The pH meter will be accurate and reproducible to 0.1 pH units with a range of 0 to 14.

Conductivity of the leachates will be measured using a standard conductivity probe. The conductivity probe will be calibrated using appropriate standard conductivity solutions for the conductivity range of concern. Conductivity meters are typically accurate to ±1% and have a precision of ±1%. The procedure to measure pH and conductivity will be as follow:

Following a gross separation of the solid and liquid phases by centrifugation or settling, a minimum volume of the supernatant to measure the solution pH and conductivity will be taken and poured in a test tube. The remaining liquid will be separated by pressure filtration and filtrates will be accordingly preserved and stored for subsequent chemical analysis.

5.1.4 Moisture Content

Moisture content of the "as received" CCR , the reference fly ash and SRM samples will be determined using ASTM D 2216-92 (ASTM, 1992). This procedure supercedes the method indicated in the leaching procedure (Kosson et al., 2002a). This method, however, is not applicable to the materials containing gypsum (calcium sulfate dihydrate or other compounds having significant amounts of hydrated water), since this material slowly dehydrates at the standard drying temperature (110°C). This slow dehydration results in the formation of another compound (calcium sulfate hemihydrate) which is not normally present in natural material. ASTM method C 22-83 will be used to determine the moisture content of materials containing gypsum (ASTM, 1983).

5.2 CHEMICAL CHARACTERIZATION

5.2.1 Carbon Content (TGA)

A Micromeretics Thermogravimetric Analyzer (TGA) is used to determine weight loss due to thermal decomposition. Through knowledge of chemical components in the sample, composition can be determined based on weight loss, decomposition stoichiometry, and decomposition temperature. This method is used to estimate carbon content of the CCR material. Carbon content corresponds to the weight loss in the temperature range of 400-500°C, when TGA is operated in O_2 or air. The TGA requires temperature and weight calibration. Temperature is calibrated using curie point transistors of nickel and iron. Weight is calibrated with a 100 mg standard weight. Values are entered into the TGA whenever configuration is changed or at least annually. Calcium oxalate monohydrate is analyzed to establish accuracy and is run at least every 20 runs.

It should be noted that an alternative method for the analysis of carbon, nitrogen, and sulfur is also available. This method uses a combustion technique followed by mass spectroscopy. The instrument used in this analysis is a Carlo-Erba NA1500 Series II elemental analyzer. Similar instrumentation is also available from LECO Inc. (www.leco.com).

5.2.2 Mercury (CVAA)

Mercury analysis of each extract and leachate will be carried out by Cold Vapor Atomic Absorption Spectrometry (CVAA) according to EPA SW846 **Method 7470A Mercury in Liquid Waste (Manual Cold Vapor Technique)** (EPA, 1998). Samples are treated with potassium permanganate to reduce possible sulfide interferences. A Perkin Elmer FIMS 100 Flow Injection Mercury System is the instrument to be used for this analysis. The instrument is calibrated with known standards ranging from 0.25 to 10 µg/L mercury. The detection limit for mercury in aqueous samples is 0.05 µg/L.

5.2.3 Other Metals (ICP)

Analysis for arsenic (As), selenium (Se), cadmium (Cd) and lead (Pb) as well as principal constituents such as iron (Fe), calcium (Ca), phosphorus (P) and sulfur (S) will be performed on a ICP-MS using Method 3052 (EPA, 1996a). Metals and estimated instrument detection limits are listed in the method. The ICP will be profiled and calibrated for the target compounds and specific instrument detection limits will be determined. Mixed calibration standards will be prepared at least 5 levels. Each target compound will also be analyzed separately to determine possible spectral interference or the presence of impurities. Two types of blanks will be run with each batch of samples. A calibration blank is used to establish the analytical curve and the method blank is used to identify possible contamination from varying amounts of the acids used in the sample processing. Additional daily QC checks include an Initial Calibration Verification (ICV) and a Continuing Calibration Verification (CCV). The ICV is prepared by combining target elements from a standard source different than that of the calibration standard and at a concentration within the linear working range of the instrument. The CCV is prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve. A calibration blank and a CCV or ICV are analyzed after every tenth sample and at the end of each batch of samples. The CCV and ICV results must verify that the instrument is within 10% of the initial calibration with an RSD < 5% from replicate integrations. Procedures to incorporate the analysis of a MS/MSD for these CCR samples will be evaluated.

These analyses will be performed at two different ICP-MS facilities. The first facility is Severn Trent Laboratories in Savannah, Ga. This laboratory uses a Agilent ICP-MS with octopole reaction system (ORS). The second facility is Vanderbilit University (Department of Civil and Environmental Engineering). This laboratory uses a Perkin Elmer model ELAN DRC II. Standard analysis mode is used for PB and DRC mode is used for analysis of As and Se.

5.2.4 Anions Analysis by IC

Aqueous concentrations of anions (chloride, sulfate, sulfides, carbonate and nitrate) will be determined using ion chromatography (IC). Standard methods (i.e., USEPA guideline SW-846) will be used.

5.2.5 X-Ray Fluorescence (XRF) and Neutron Activation Analysis (NAA)

For the five target metals, XRF analysis will be performed on each CCR to provide additional information on the CCR material. This information will be useful in supplementing and/or validating CVAA and ICP results and calculating mass balances. XRF is capable of detection limits in the µg range. If levels are in the ng range, XRF analysis will not be useful. Considering the high detection limit of the XRF, this method will be used only as a second validation method or a "referee" method. Details of XRF analysis are included in the Mercury Facility Manual.

Neutron activation analysis (NAA) is an established analytical technique with elemental analysis applications. This method will be considered in this test program. NAA is different than AA or inductively coupled plasma mass spectrometry (ICP-MS) because it is based on nuclear instead of electronic properties. Neutron activation analysis is a sensitive multielement analytical method for the accurate and precise determination of elemental concentrations in unknown materials. Sensitivities are sufficient to measure certain elements at the nanogram level and below, although the method is well suited for the determination of major and minor elemental components as well. The method is based on the detection and measurement of characteristic gamma rays emitted from radioactive isotopes produced in the sample upon irradiation with neutrons. Depending on the source of the neutrons, their energies and the treatment of the samples, the technique takes on several differing forms. It is generally referred to as INAA (instrumental neutron activation analysis) for the purely instrumental version of the technique. RNAA (radiochemical neutron activation analysis) is the acronym used if radiochemistry is used to separate the isotope of interest before counting. FNAA (fast neutron activation analysis) is the form of the technique if higher energy neutrons, usually from an accelerator based neutron generator, are used.

6.0 QA/QC CHECKS

6.1 DATA QUALITY INDICATOR GOALS

Data quality indicator goals for critical measurements in terms of accuracy, precision and completeness are shown in Table 6-1.

TABLE 6-1. DATA QUALITY INDICATOR GOALS

Measurement	Method	Accuracy	Precision	Completeness
As, Se, Pb, Cd, Fe, P, S, and Ca Concentration	ICP/6010B	10%	10%	>90%
Hg Concentration	CVAA/7470A	10%	10%	>90%
Anions, Sulfate, Carbonates, Chlorides	IC/SW-846	10%	10%	>90%
PH	Electrode	2%	2%	100%
Carbon Content	TGA	10%	10%	>90%
Surface Area	BET	5%	5%	>90%
Density	Pycnometer	2%	2%	100%
Moisture	ASTM D2216-92 ASTM C22-83	N/A	10%	N/A

N/A: Not Applicable (see Appendix B)

Accuracy will be determined by calculating the percent bias from a known standard. Precision will be calculated as relative percent difference (RPD) between duplicate values and relative standard deviation (RSD) for parameters that have more than two replicates. Completeness is defined as the percentage of measurements that meet DQI goals of the total number measurements taken.

Mass balance calculations will also be used as a data quality indicator. Different mass balance recovery methods will be examined. The reference fly ash sample will be used to develop and validate an appropriate mass balance recovery method. Mass balance will be determined by using the metals concentrations determined by analysis of the "as-received" reference fly ash as the total. Results from successive leaching samples and analysis of any solid residues will be combined to determine recoveries.

One approach that will be considered is the use of either total digestion (Method 3052) or Neutron Activation Analysis (NAA) for the analysis of solid residues.

The mass balance recovery will be only performed on 3 pH points and one low LS ratio. Uncertainty analysis will be considered for each mass balance. The selection of the target pH values will be dependent on the natural pH of the material. If the natural pH is <5, then natural pH, 7 and 9 will be selected as the target pH values. If the natural pH ranges between 5 and 9, then 5, 7 and 9 will be selected as the target pH values, and if the natural pH is >9, then 5, 7 and natural pH will selected as the target pH values. In addition, an extraction at the natural pH of the material and an LS ratio of 1mL/g will be carried out. At least 4 replicates per extract will be run. In the case where the mass balance will be performed using total digestion or NAA, at least 3 representative samples per residue will be analyzed.

6.2 QC SAMPLE TYPES

Types of QC samples used in this project will include blanks, spiked samples, replicates, and mass balance tests on the reference fly ash and the SRM. For physical characterization testing, duplicate samples of the CCR, reference fly ash and SRM will be processed through each analysis. Duplicates must agree within ±10% to be considered acceptable. For the leaching studies, an objective of this project is to determine the appropriate types of QC samples to incorporate in the proposed leaching methods. This will be accomplished by subjecting the reference fly ash to the leaching procedure and determining the metals' mass balances by analyzing the leaching solution and the post-leachate solids. Initially, mass balances of 70-130% will be considered as an acceptable QC of the leaching procedure. Further statistical analysis on available data will be performed to narrow down the range of acceptable mass balances. This method development will be thoroughly documented in a dedicated laboratory notebook. Leaching of the reference fly ash samples may also be used as method controls during testing of CCR samples. For the fixed-bed reactor testing, one in every five tests will be run in duplicate. Duplicate results from the reactor testing are expected to agree within 20% to be considered valid. Identical to the leaching procedure, the use of the reference fly ash as a baseline QC sample will also be implemented during TPD tests (initial mass balances of 70-130%). Required QC samples for metals and mercury sampling trains are detailed in EPA Method 29 (EPA, 1996c) and the Ontario Hydro Methods (ASTM, 2002). QC samples required for ICP, CVAA, IC analysis are detailed in Methods 3052, 7470A, and SW-864 respectively.

7.0 DATA REDUCTION, VALIDATION, AND REPORTING

Chemical (ICP, CVAA, TGA, XRF, IC, NAA) and physical (surface area, pore size distribution and density) characterization data are reduced and reports are generated automatically by the instrument software. The primary analyst will review 100% of the report for completeness and to ensure that quality control checks meet established criteria. If QC checks do not meet acceptance criteria, sample analysis must be repeated. A secondary review will be performed by the Inorganic Laboratory Manager to validate the analytical report. If appropriate, certain chemical characterization data will be compared to the XRF and NAA analyses. In addition, the designated QA Officer will review at least 10% of the raw data for completeness. Analytical data will be summarized in periodic reports to the ARCADIS WAL. The procedure for reduction, validation and reporting of the leaching experiments Task II) are outlined in Appendix A. ARCADIS WAL is responsible for the implementation of these procedures. Data reduction and interpretation for the TPD experiments (Task III) is included in the Mercury Facility Manual. ARCADIS WAL is responsible for implementing those procedures. ARCADIS WAL is also responsible for ensuring that mass balance criteria have been met. Mass balance for task II will be calculated as:

[(metal in leachate + metal in residue)/metal in "as received" CCR]*100

Mass balance for Task III will be calculated as:

[(metal in off gas + metal in thermally exposed sample)/metal in "as received" CCR]*100

Hg control benefit calculation for each metal or other parameters (such as carbon content, surface area, and so on) is:

[(content in CCR, leachate, or residue)$_{\text{w Hg control}}$/(content in CCR, leachate, or residue)$_{\text{w/o Hg control}}$]*100

Values greater than 100% indicate an increase in that parameter due to implementation of the Hg control technology. In summary, the ARCADIS WAL checks to ensure that the duplicates meet the precision limits and the QC-checks for each run are within documented data quality indicators. Progress of the research conducted under this QAPP is reported in written monthly reports by ARCADIS WAL. Weekly verbal and written progress reports are submitted to the EPA WAM. Efforts will be made to publish and present results. QA/QC activities will be mentioned in any published materials. A data quality report will be provided in the final report of this investigation.

8.0 ASSESSMENTS

Assessments and audits are an integral part of a quality system. This project is assigned a QA Category III and, while desirable, doest not require planned technical systems and performance evaluation audits. EPA will determine external or third-party audit activities. Internal assessments will be performed by project personnel to ensure acquired data meets data quality indicator goals established in Section 6. The ARCADIS Designated QA Officer will perform at least one internal technical systems audit (TSA) to ensure that this QAPP is implemented and methods are performed according to the documented procedures. This audit will occur during the early stages of the project to ensure any necessary corrective actions are implemented before large amounts of data are collected.

There are currently not planned performance evaluation audits but Table 8-1 lists the measurement parameters and expected ranges should EPA determine a PEA should be provided.

8-1. PEA PARAMETERS AND RANGES

Analyte or Measurement	Method	Expected Range
As, Se, Pb and Cd	ICP/3052	1-100 ug/mL
Hg	CVAA/7470A	0.25 to 10 ug/L
PH	Electrode	0-14

In addition to the TSA, the ARCADIS Designated QA Officer will perform an internal data quality audit on at least 10% of the reported data. Reported results will be verified by performing calculations using raw data and information recorded in laboratory notebooks.

9.0 REFERENCES

ASTM, 1983. Method C 22-83, "Standard Specification for Gypsum"

ASTM, 1992. Method D 2216-92, "Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock"

ASTM, 2002. Method D 6784-02, "Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario-Hydro Method)"

EPA, 1996a. Method 3052 "Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices". Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

EPA, 1996b. Method 6010 "Inductively Coupled Plasma-Atomic Emission Spectrometry". Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

EPA, 1996c . Method 29 "Determination of Metals Emissions from Stationary Sources." *Code of Federal Regulations*, Title 40, Part 60, Appendix A, April 1996.

EPA, 1998. Method 7470A "Mercury in Liquid Waste (Manual Cold-Vapor Technique)". Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

EPA, 2002a. Characterization and Management of Residues from Coal-Fired Power Plants, Interim Report. EPA-600/R-02, 083, December 2002.

EPA, 2002b. Reply to comments on EPA/OSW's Proposed Approach to Environmental Assessment of CCRs. Discussed March 5, 2002.

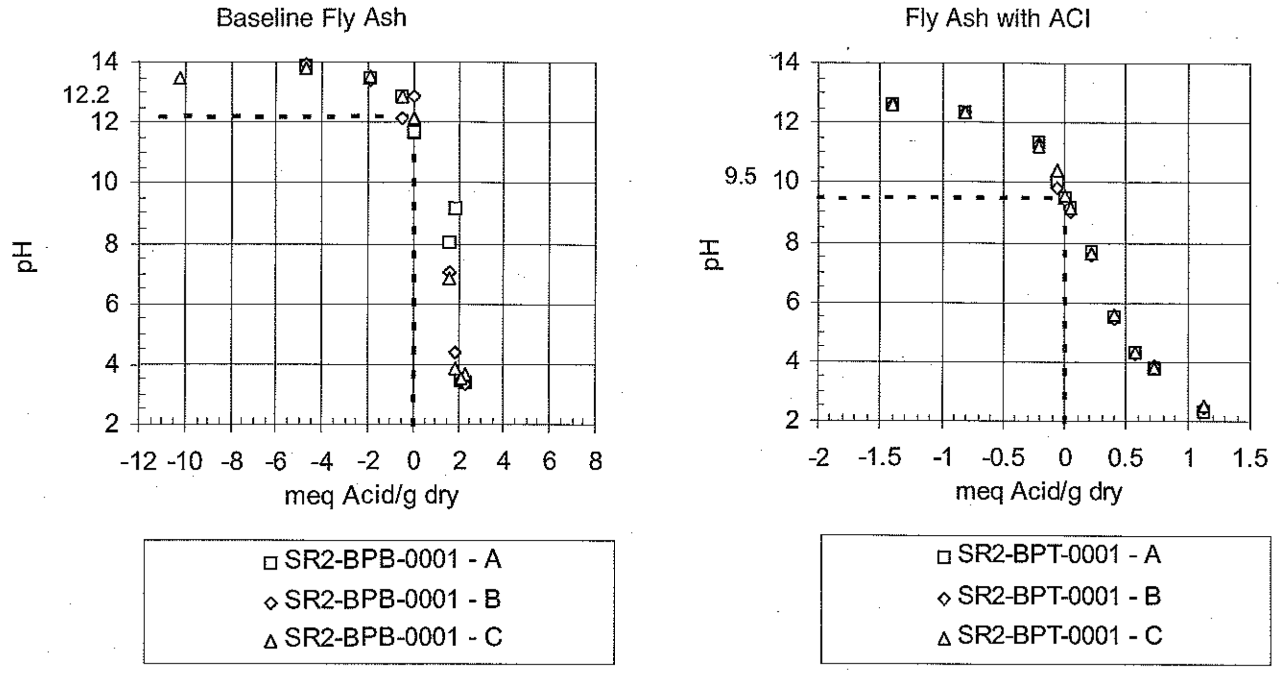
Kosson, D.S., van der Sloot, H.A., Sanchez, F. and Garrabrants, A.C., 2002a. An Integrated Framework for Evaluating Leaching in Waste management and Utilization of Secondary materials. *Environmental Engineering Science* 19(3):159-204.

Kosson, D.S., and Sanchez, F., 2002b. Draft (Revision #2), Sampling and Characterization Plan for Coal Combustion Residues from Facilities with Enhanced Mercury Emissions Reduction Technology. May 2002.

Appendix D
Brayton Point Fly Ashes

List of Figures

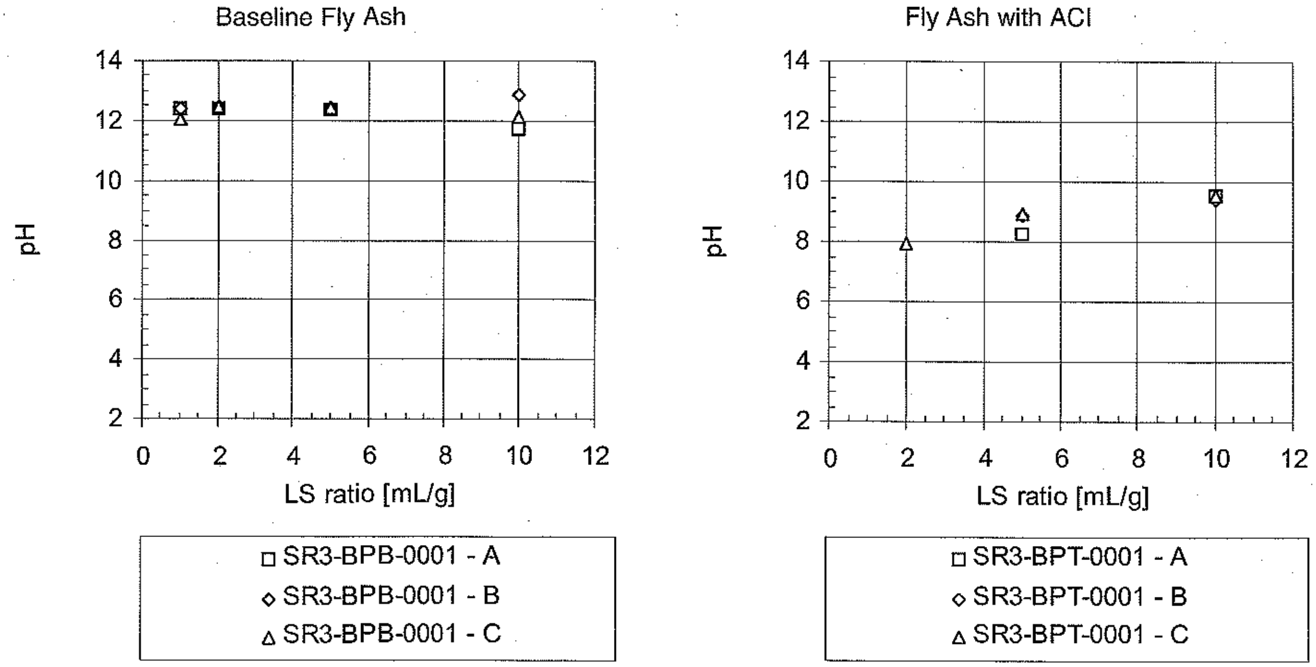
pH Titration Curves


Baseline Fly Ash

Fly Ash with ACI

Figure D-1. pH Titration Curves for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

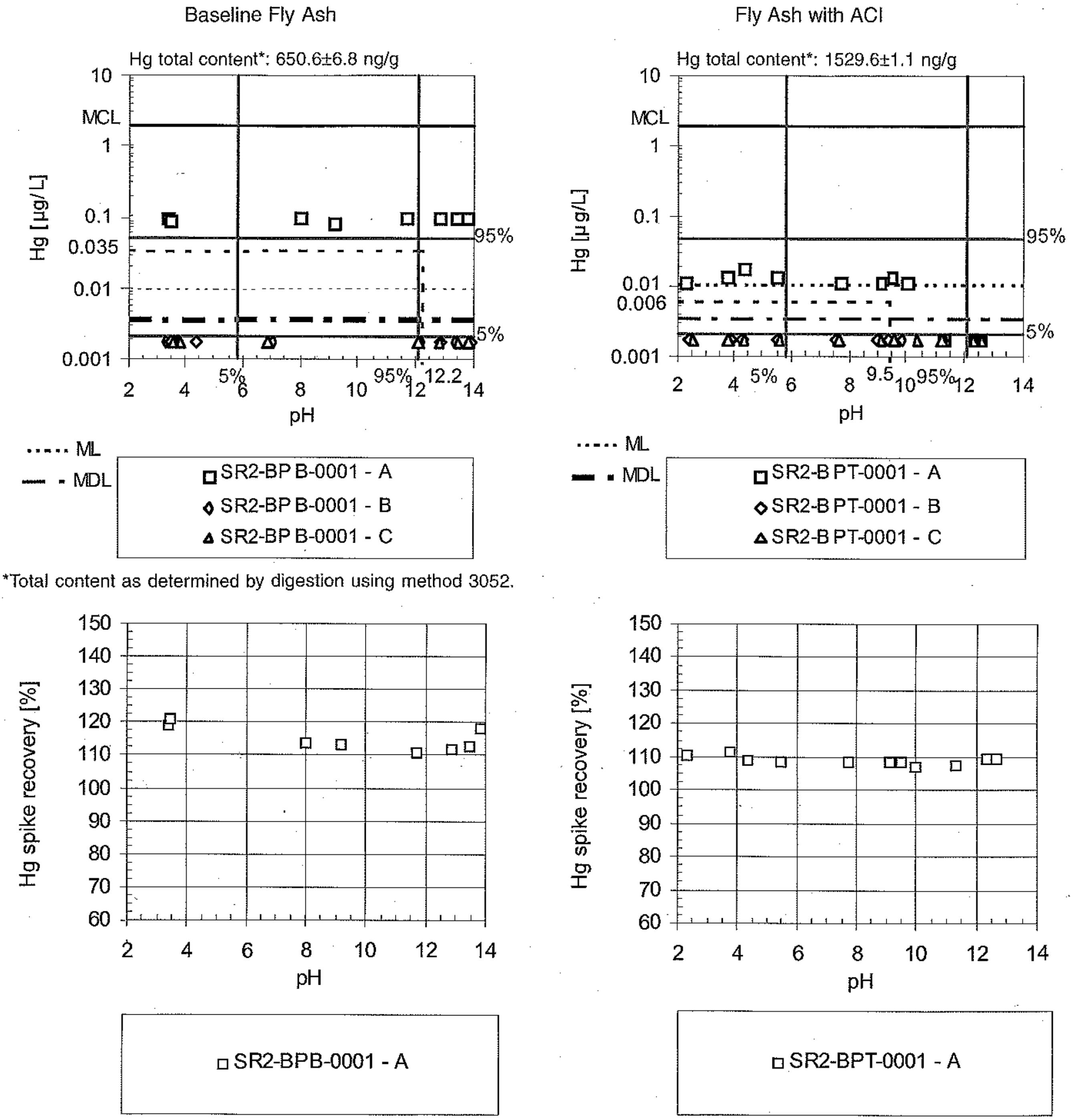
pH as a Function of LS Ratio


Baseline Fly Ash

Fly Ash with ACI

Figure D-2. pH as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Mercury Release as a Function of pH



*Total content as determined by digestion using method 3052.

Figure D-3. Mercury Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of mercury concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Mercury Release as a Function of LS Ratio

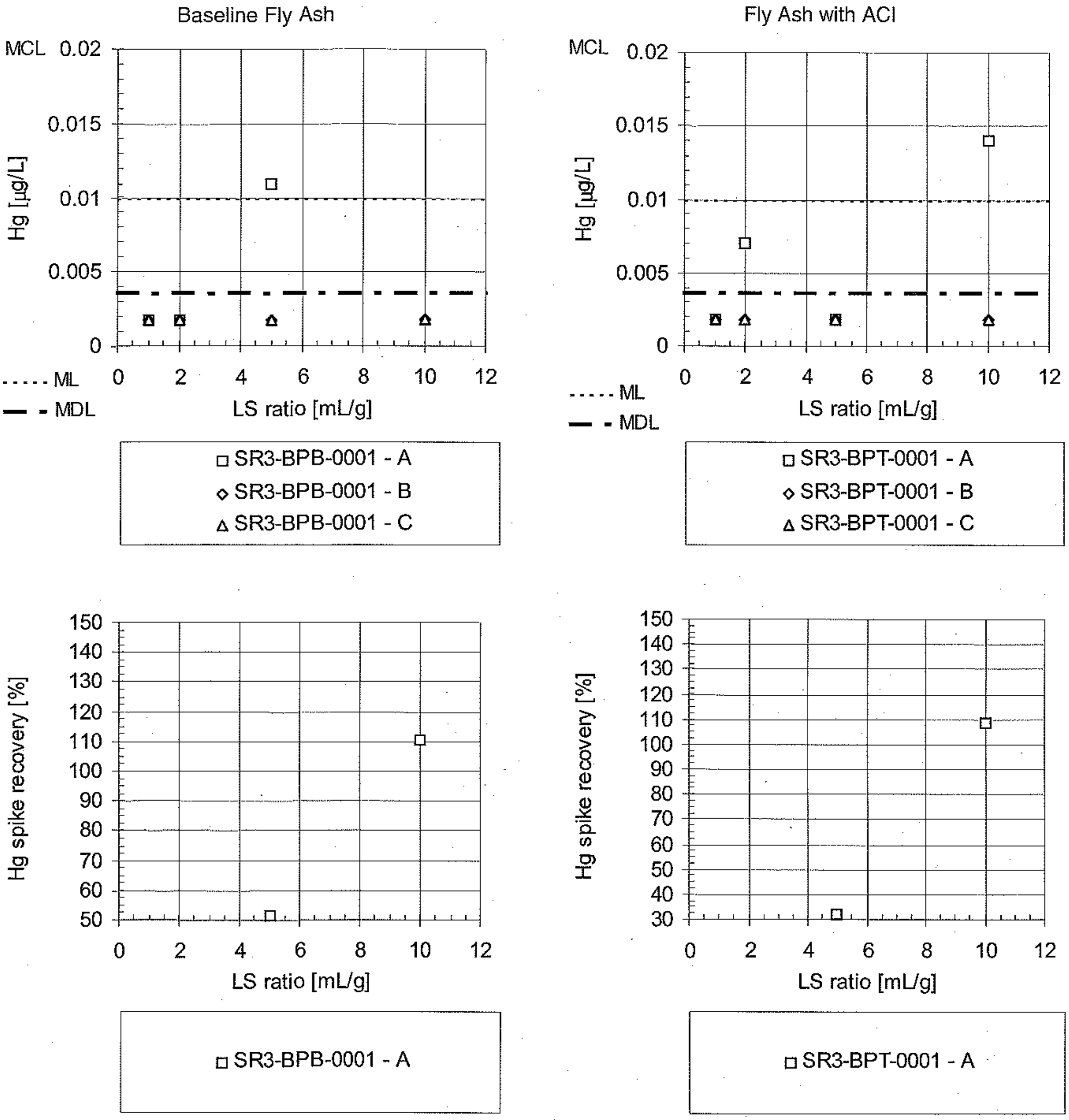
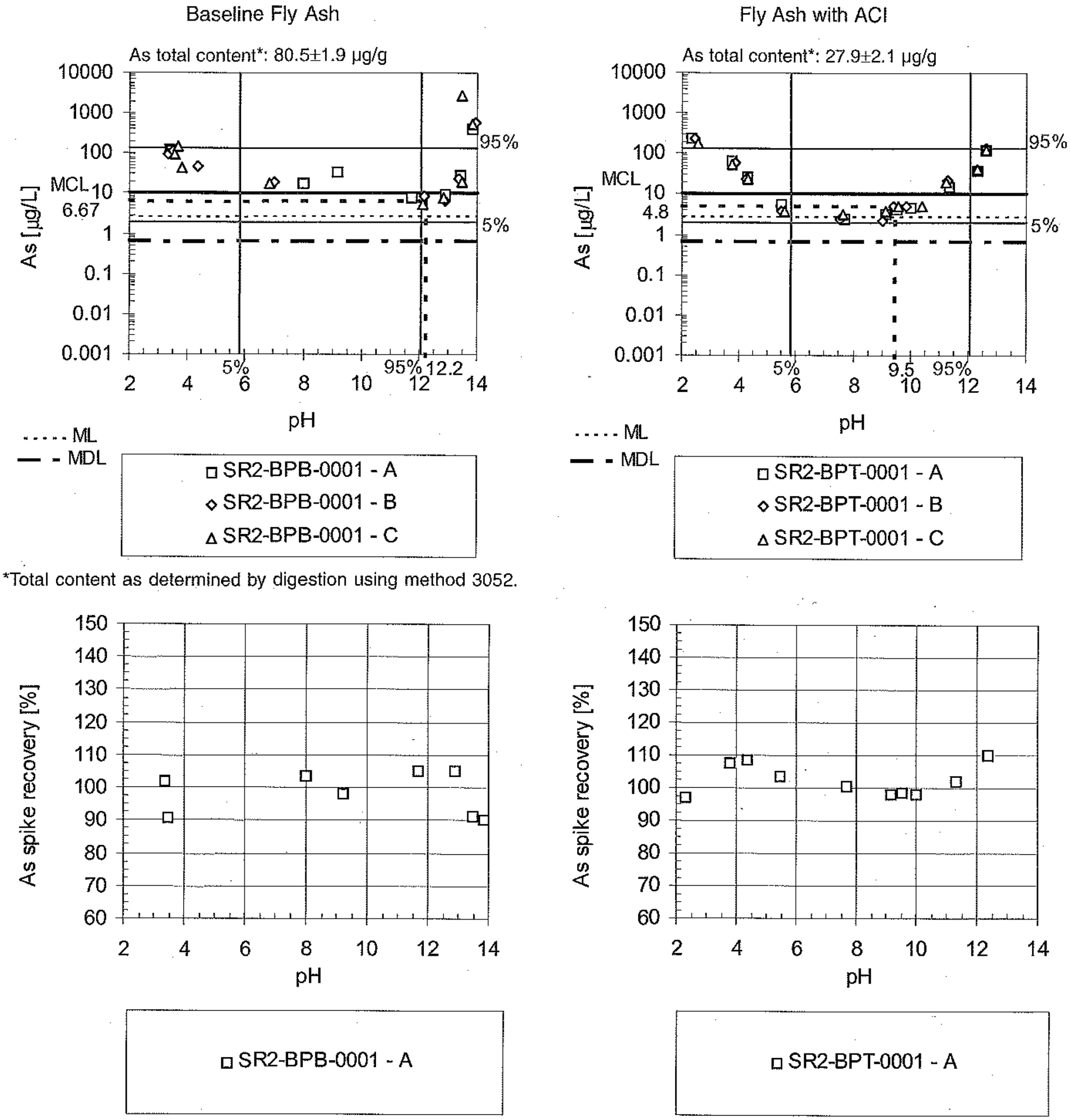


Figure D-4. Mercury Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Arsenic Release as a Function of pH



*Total content as determined by digestion using method 3052.

Figure D-5. Arsenic Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of arsenic concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Arsenic Release as a Function of LS Ratio

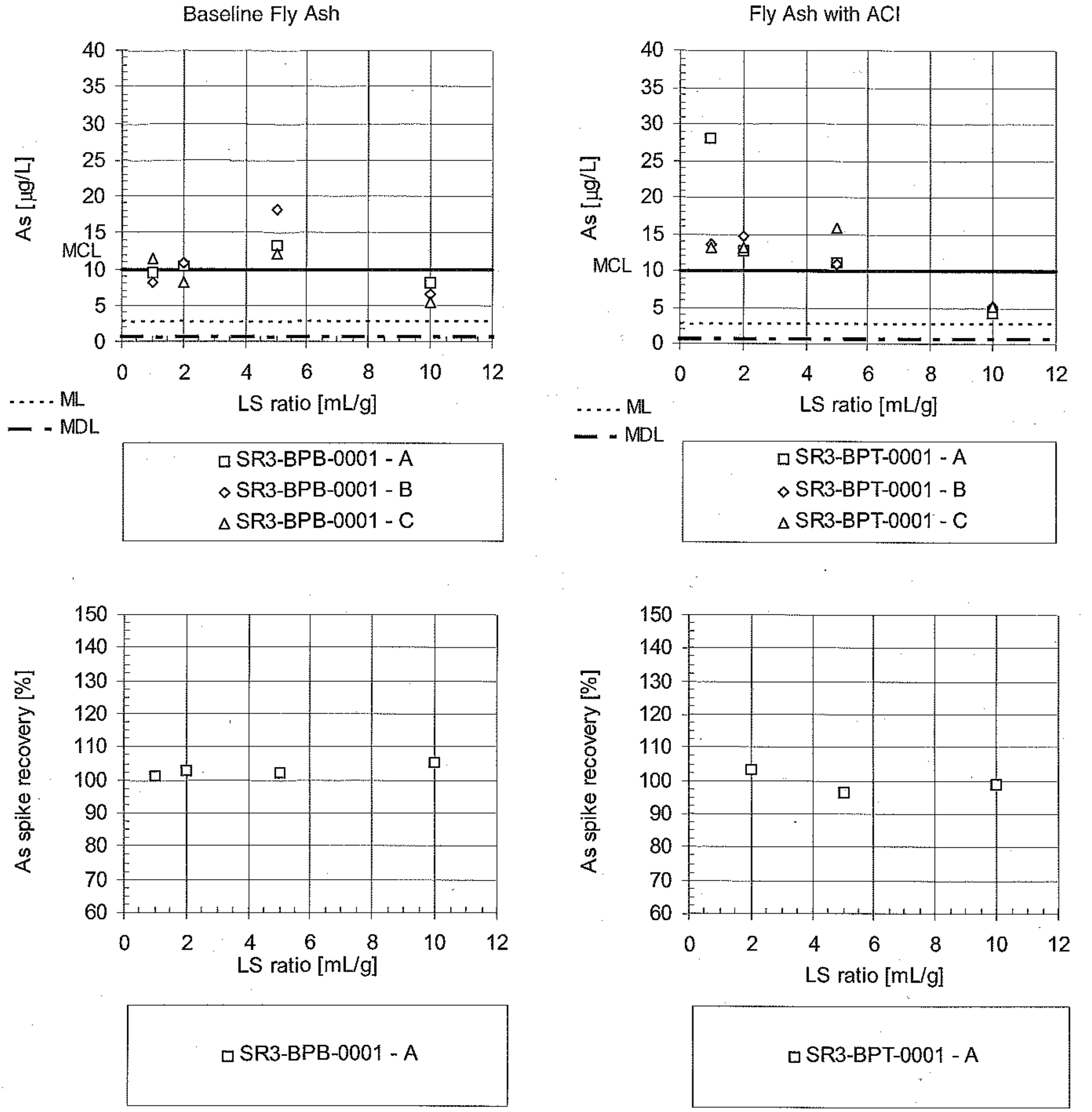
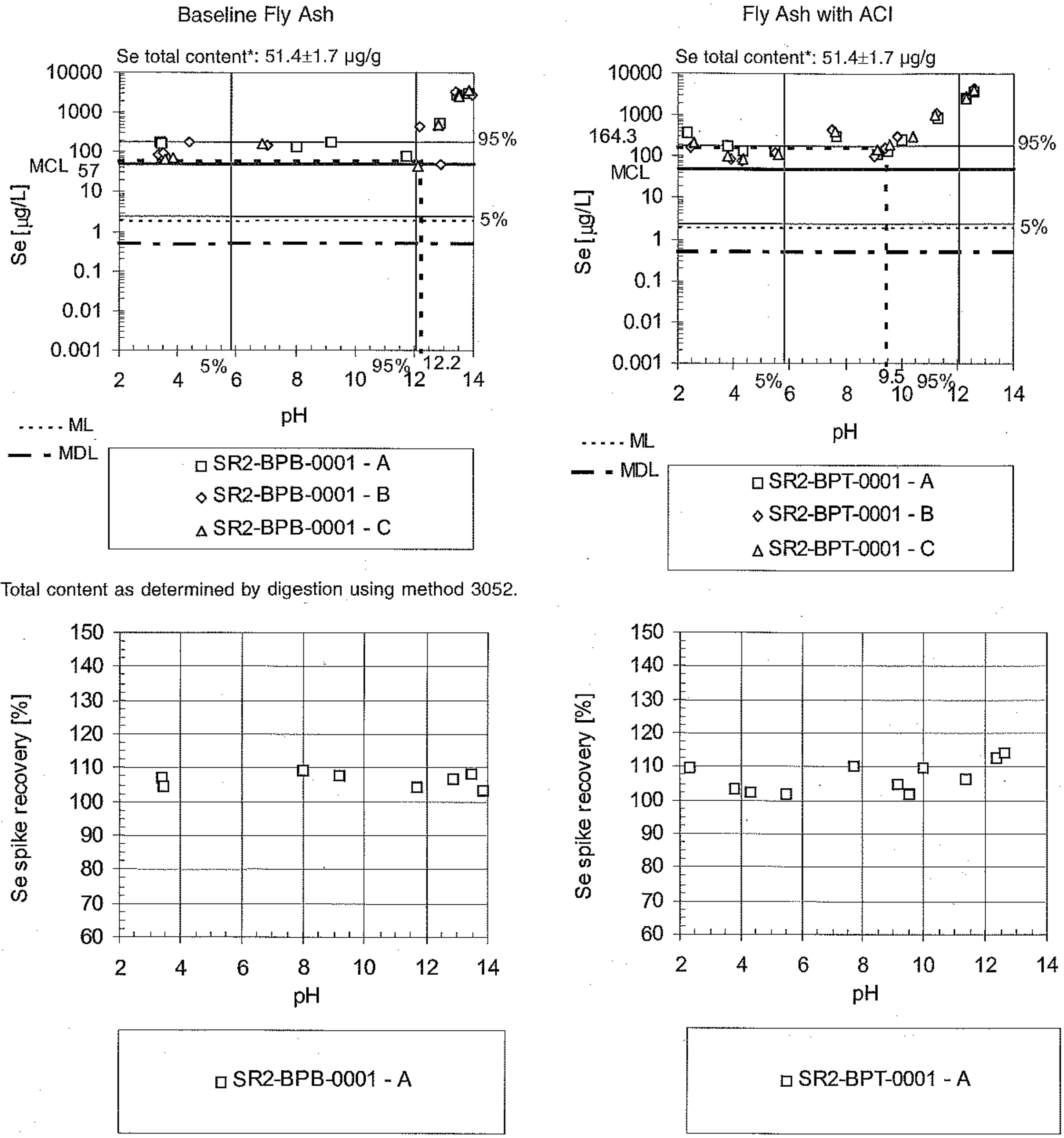


Figure D-6. Arsenic Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Selenium Release as a Function of pH



*Total content as determined by digestion using method 3052.

Figure D-7. Selenium Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of selenium concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Selenium Release as a Function of LS Ratio

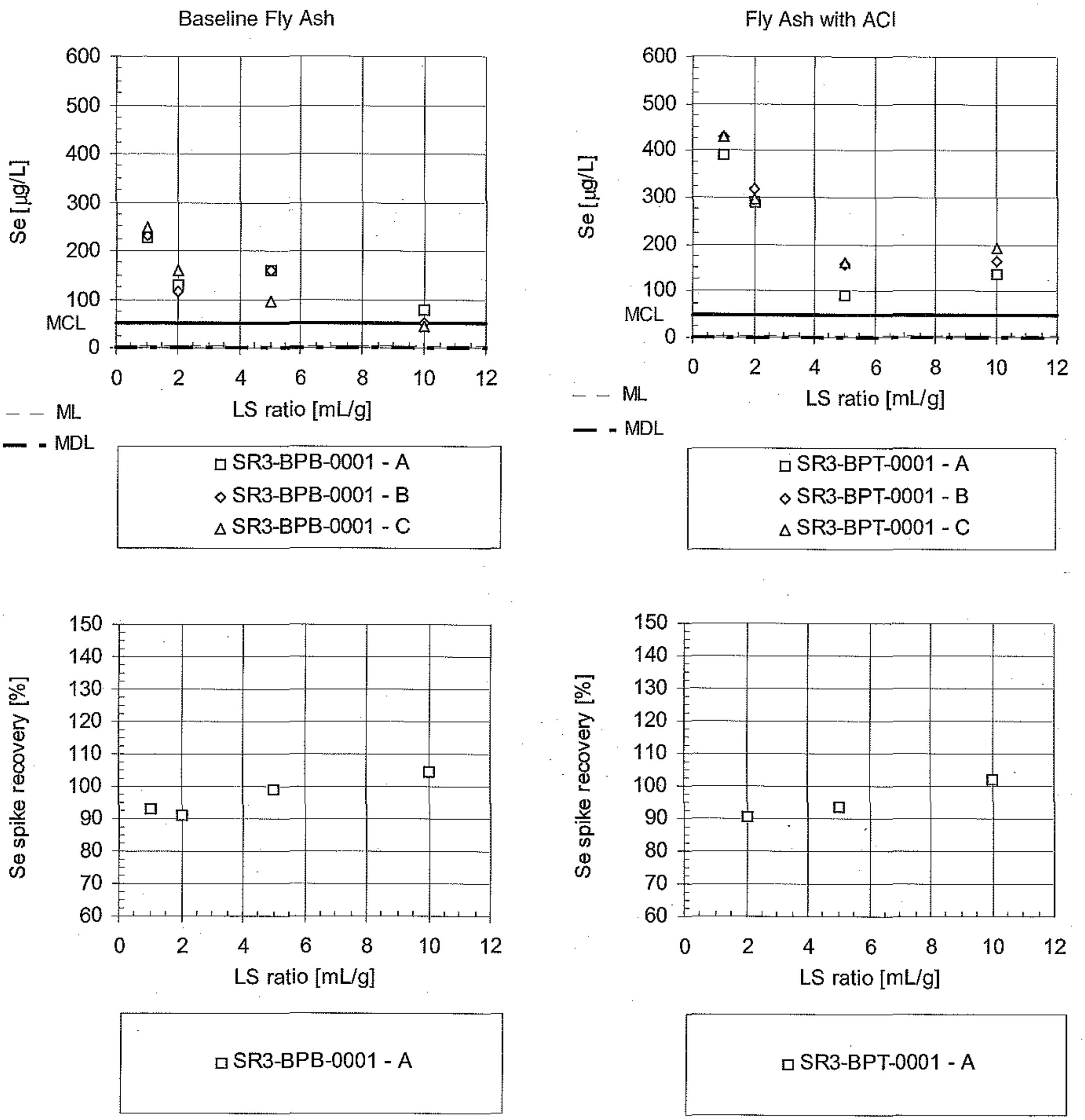
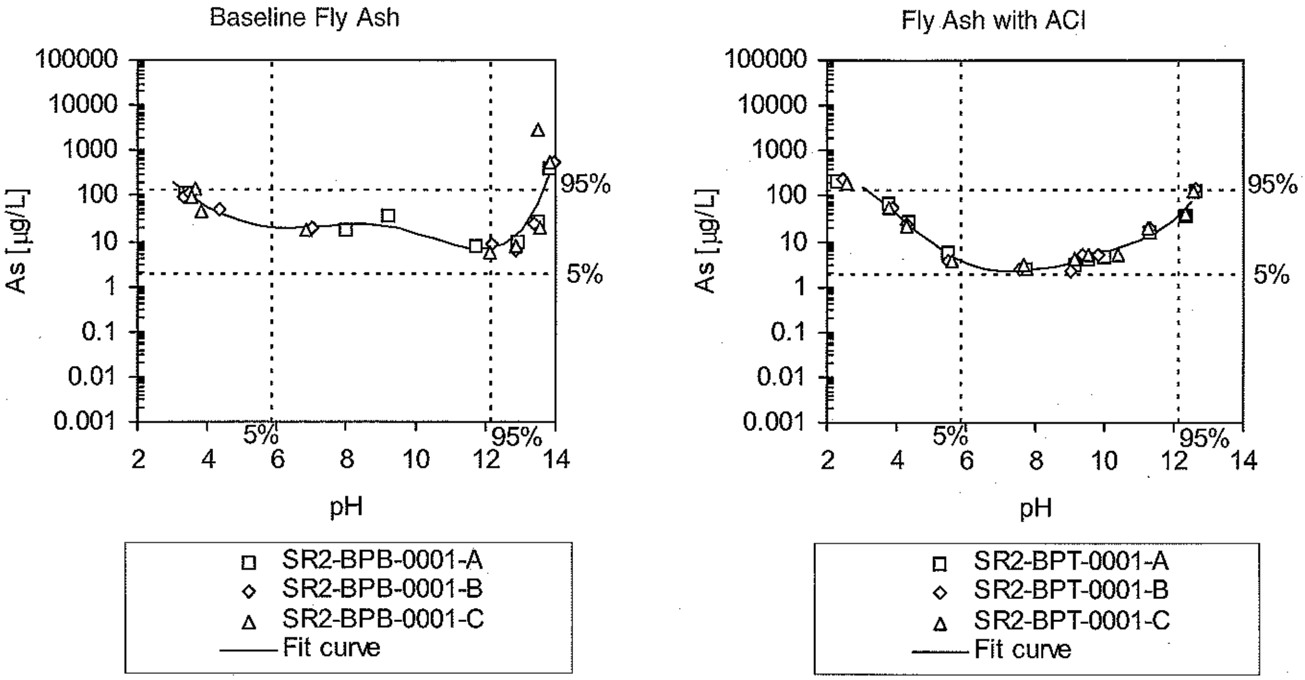


Figure D-8. Selenium Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

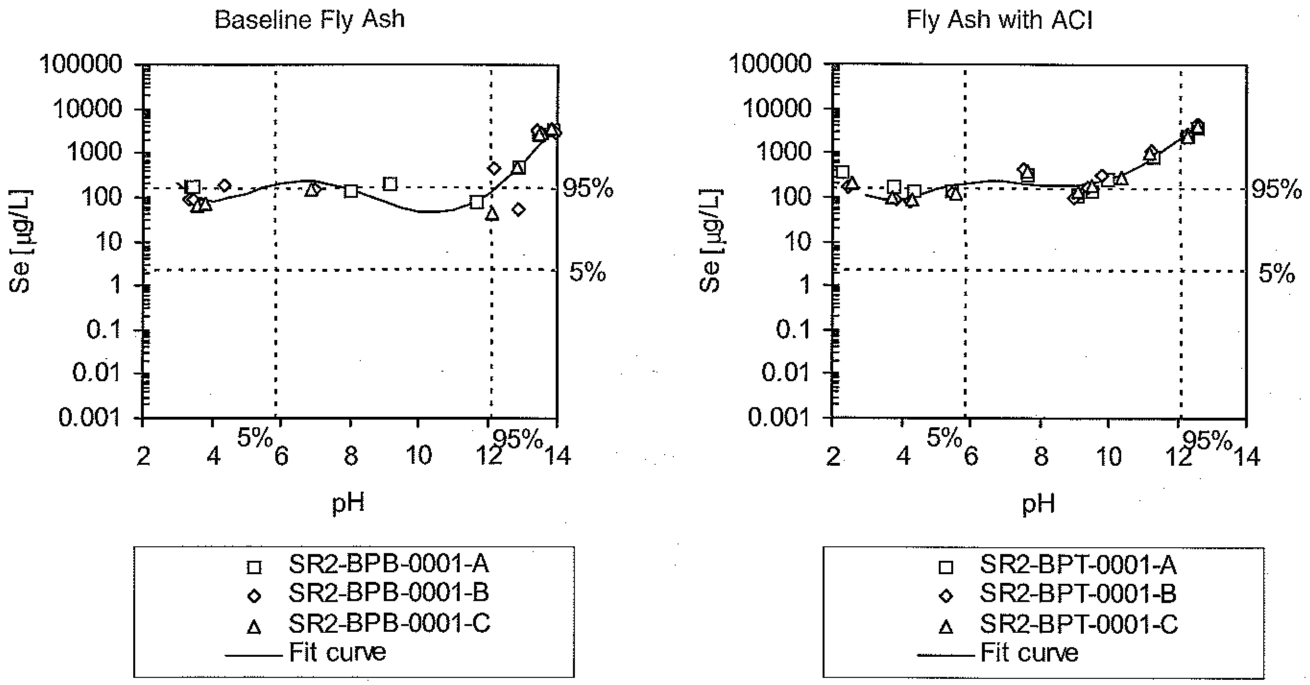
Arsenic Solubility



Material	log As (µg/L)			pH range of validity	R^2	Number of points
BPB	0.0004 pH^5	-0.0135 pH^4	0.1634 pH^3	3-14	0.77	27
	-0.8130 pH^2	1.1609 pH	2.7085			
BPT	0.0005 pH^5	-0.0207 pH^4	0.3035 pH^3	3-12.5	0.98	33
	-2.0113 pH^2	5.4552 pH	-2.7126			

Figure D-9. Regression Curves of Experimental Data of Arsenic Solubility as a Function of pH.

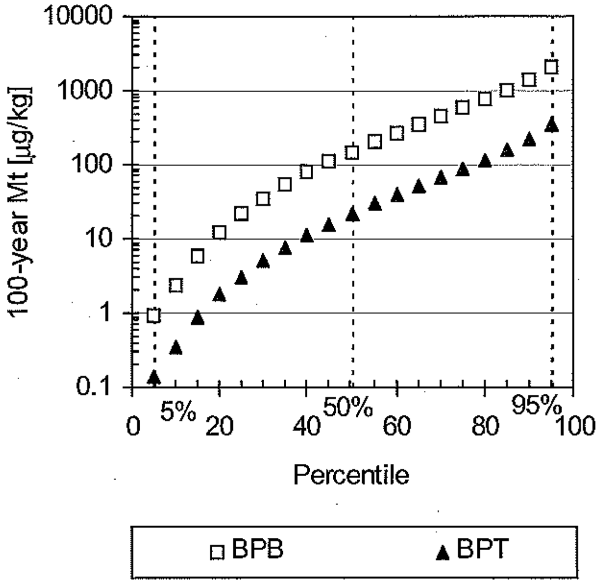
Selenium Solubility



Material	log Se (µg/L)			pH range of validity	R^2	Number of points
BPB	$-0.0006\ pH^5$	$0.0262\ pH^4$	$-0.4379\ pH^3$	3-14	0.81	27
	$3.3856\ pH^2$	-12.0291 pH	17.7907			
BPT	$-0.0006\ pH^5$	$0.0229\ pH^4$	$-0.3475\ pH^3$	3-12.5	0.93	33
	$2.4521\ pH^2$	-7.9388 pH	11.4439			

Figure D-10. Regression Curves of Experimental Data of Selenium Solubility as a Function of pH.

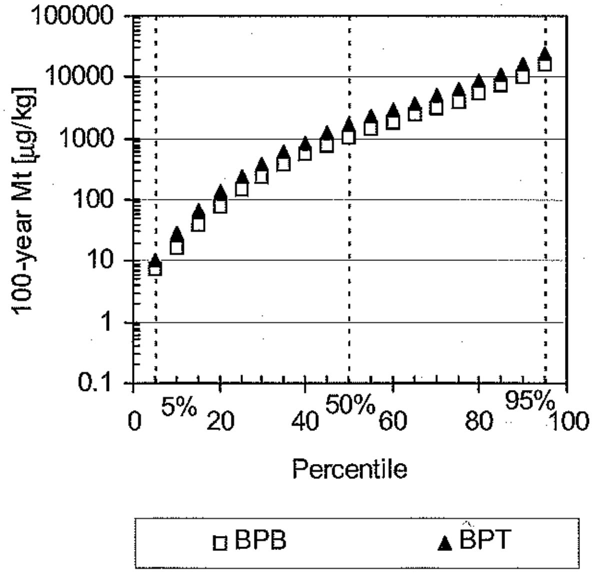
100-Year Arsenic Release Estimates



	BPB		BPT	
	µg/kg	%	µg/kg	%
Mt min	0.2	0.0003	0.1	0.0003
Mt - 5%	0.9	0.0011	0.1	0.0005
Mt - 50%	152	0.2	22	0.0772
Mt - 95%	2095	2.6	338	1.2
Mean Mt	468	0.6	90	0.3
Mt max	4693	5.8	10157	36.4

Figure D-11. 100-Year Arsenic Release Estimates as a Function of the Cumulative Probability for the Scenario of Disposal in a Combustion Waste Landfill.

100-Year Selenium Release Estimates



	BPB		BPT	
	µg/kg	%	µg/kg	%
Mt min	1.5	0.003	5.9	0.004
Mt - 5%	7.6	0.015	10.0	0.007
Mt - 50%	1031	2.0	1661	1.1
Mt - 95%	16681	32.5	23931	15.8
Mean Mt	3573	7.0	6038	4.0
Mt max	45169	87.9	151900	100.0

Figure D-12. 100-Year Selenium Release Estimates as a Function of the Cumulative Probability for the Scenario of Disposal in a Combustion Waste Landfill.

100-Year Arsenic Release Estimates

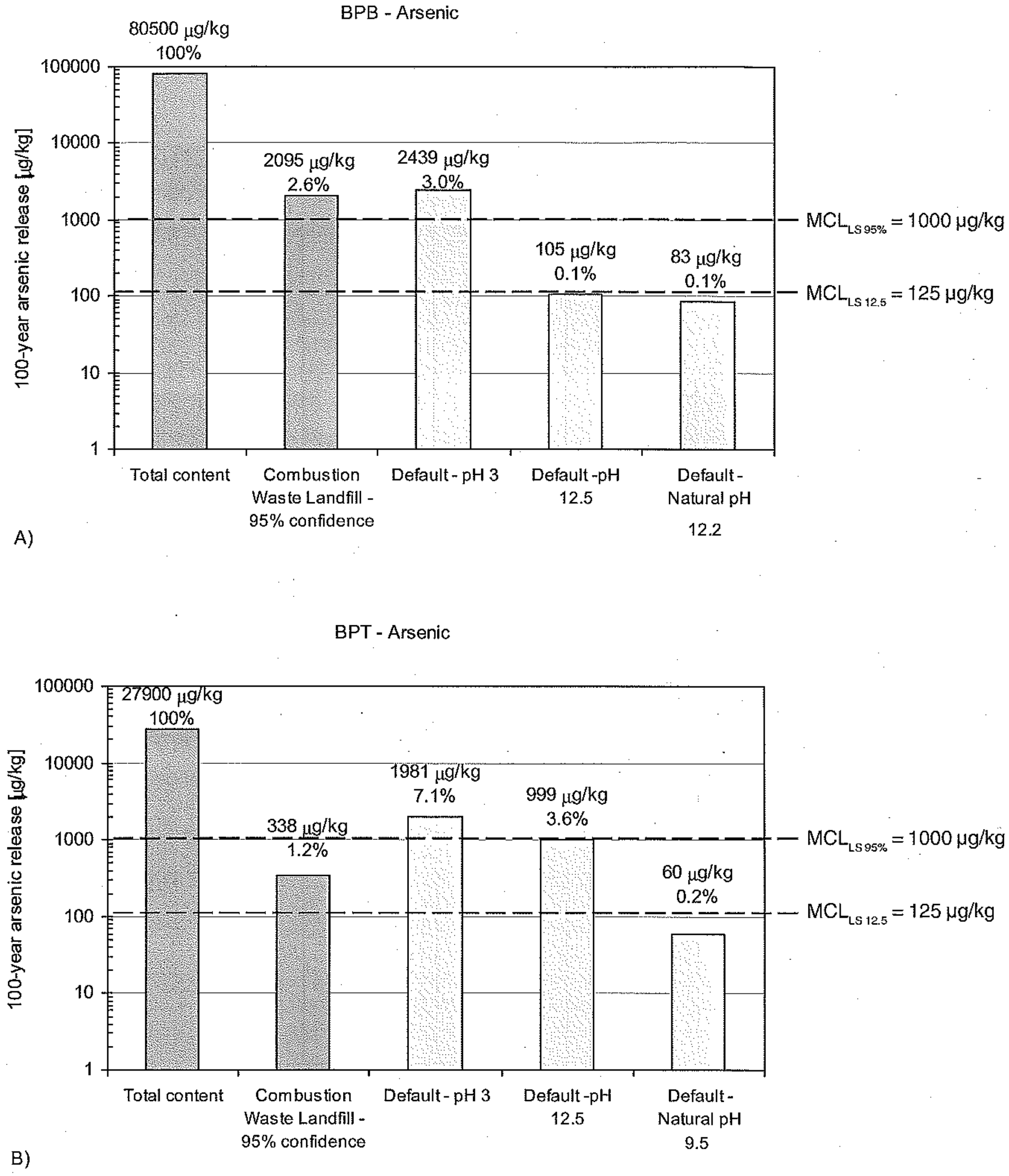


Figure D-13. 100-Year Arsenic Release Estimates from A) Baseline Fly Ash and B) Fly Ash with ACI. Release estimates for percolation controlled scenario are compared to release estimate based on total content. The amount of the arsenic that would be released if the release concentration was at the MCL is also shown for comparison ($LS_{default\ scenario}$ = 12.5 L/kg and $LS_{95\%}$ = 100 L/kg).

100-Year Selenium Release Estimates

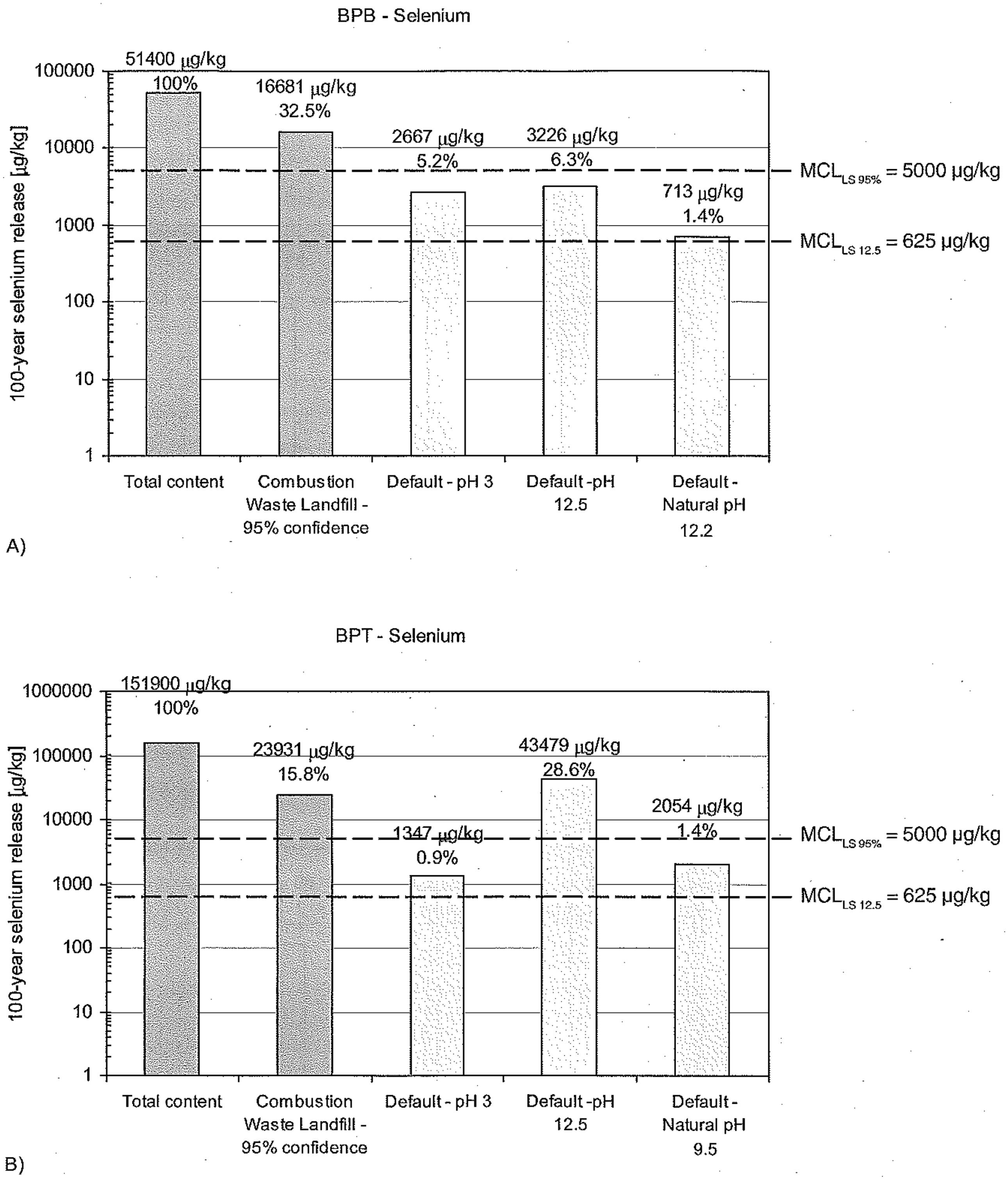


Figure D-14. 100-year Selenium Release Estimates from A) Baseline Fly Ash and B) Fly Ash with ACI. Release estimates for percolation controlled scenario are compared to release estimate based on total content. The amount of the selenium that would be released if the release concentration was at the MCL is also shown for comparison ($LS_{default\,scenario}$ = 12.5 L/kg and $LS_{95\%}$ = 100 L/kg).

Comments

Figure D-3:

- The fly ash from the test case had greater total Hg content than the fly ash from the baseline case (by about 2.5 times).
- Hg release is low (but poor replication) for both baseline and test cases.

Figure D-5:

- The fly ash from the test case had lower total As content than the fly ash from the baseline case (by about a factor of 3).
- The laboratory measurements fit within the 5-95% confidence intervals of the field observations.
- As release is most frequently worse in baseline case than test case and exceeds MCL for many possible conditions.

Figure D-7:

- The fly ash from the test case had greater total Se content than the fly ash from the baseline case (by about a factor of 3).
- The laboratory measurements fit within the 5% to 95% confidence intervals of the field observations.
- Se release substantially exceeds MCL for both baseline and test cases and is generally worse for test cases.
- The fly ash from the test case resulted in greater Se concentration at the natural pH of the material than the baseline case (by about 3 times).

Figures D-11. and D-12:

- The fly ash from the test case would result in As release less than expected from the baseline case, with a 95% probability to be less than 338 and 2095 μg/kg, respectively.
- No significant difference in Se release is expected from both baseline and test cases.

Figure D-13:

- For the 95% probability scenario, arsenic release from the baseline case would be greater than the amount that would be released if the release concentration was at the MCL.
- For the 95% probability scenario, a lower arsenic release would be expected from the test case. However, the fly ash from the test case had lower total As content than the fly ash from the baseline case (by about a factor of 3).
- For the default scenario corresponding to disposal in a monofill (leachate pH controlled by the material being disposed), no significant difference in arsenic release between the baseline and the test cases would be expected. Additionally, arsenic release would be less than the amount that would be released if the release concentration was at the MCL.
- For the default scenario corresponding to the "extreme" pH of 3, arsenic release would be greater than the amount that would be released if the release concentration was at the MCL, for both the baseline and the test cases.
- For the default scenario corresponding to the "extreme" pH of 12.5, arsenic release is expected to be greater for the test case than the baseline case.

Figure D-14:

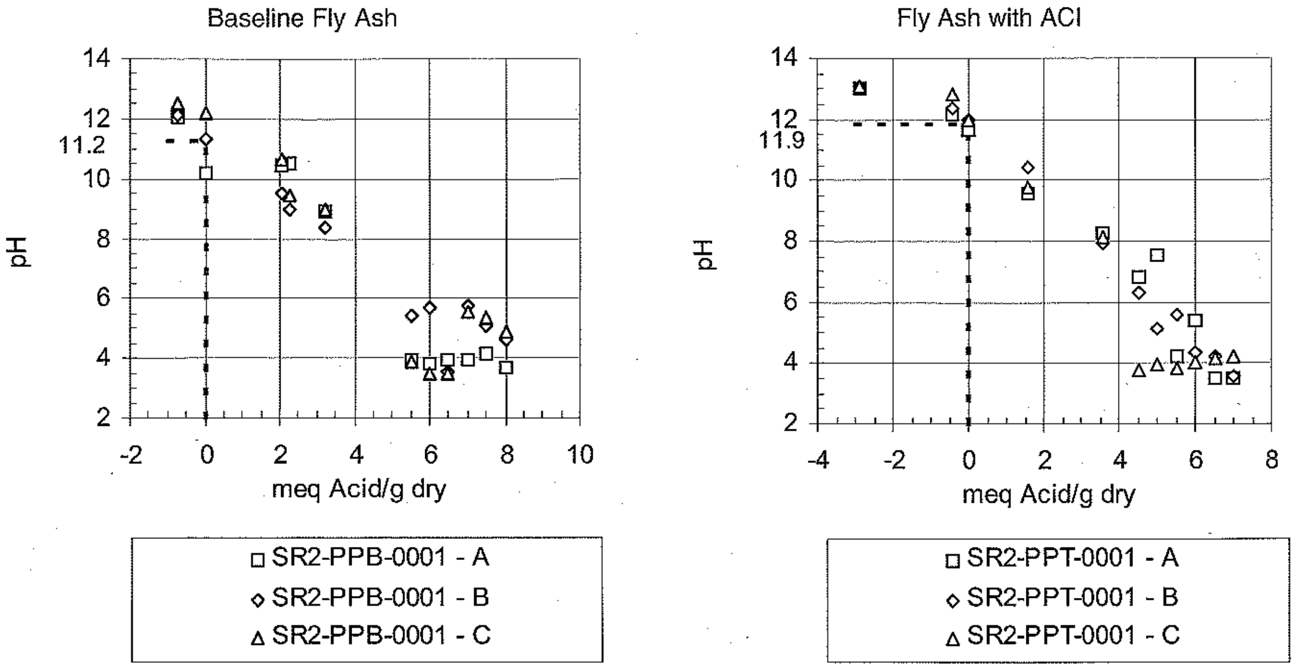
- For the 95% probability case, selenium release would be greater than the amount that would be released if the release concentration was at the MCL for both the baseline and the test cases.
- For the default scenario corresponding to disposal in a monofill (leachate pH controlled by the material being disposed), a greater selenium release would be expected from the test case.
- For the default scenario corresponding to the "extreme" pH of 12.5, selenium release is expected to be greater for the test case than the baseline case. Selenium release from the test case would be greater than the amount that would be released if the release concentration was at the MCL.

Appendix E
Pleasant Prairie Fly Ashes

List of Figures

Figure **Page**

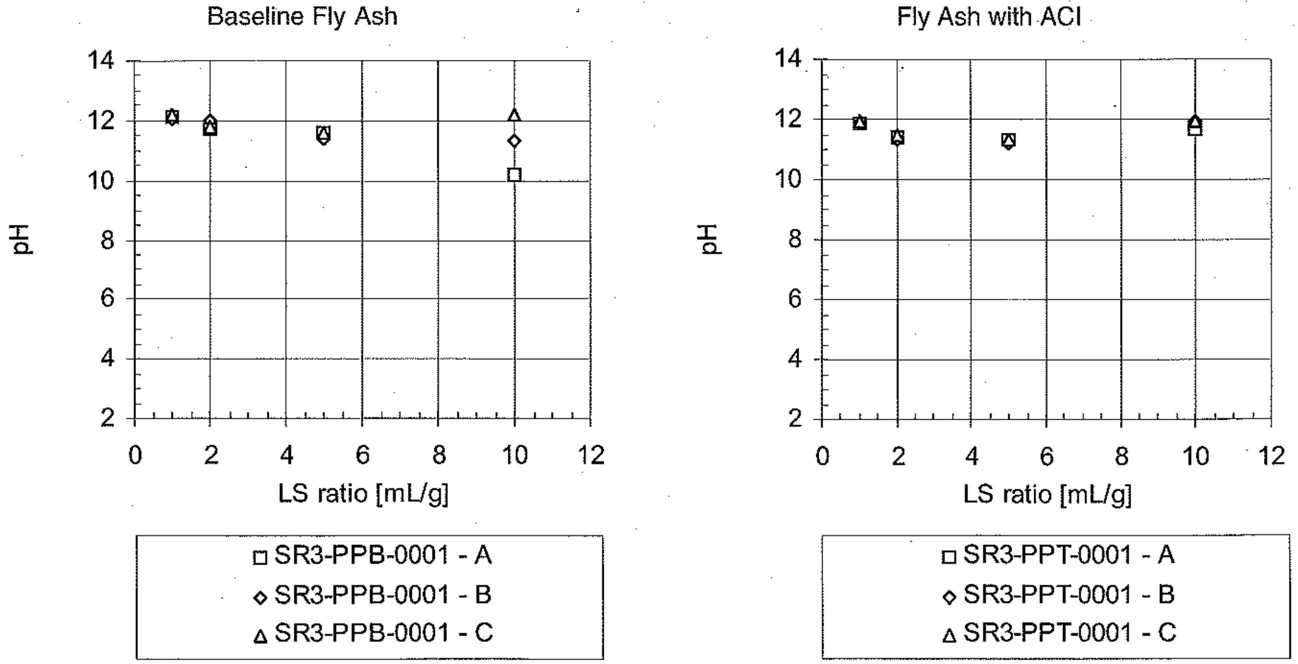
pH Titration Curves


Baseline Fly Ash

Fly Ash with ACI

Figure E-1. pH Titration Curves for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

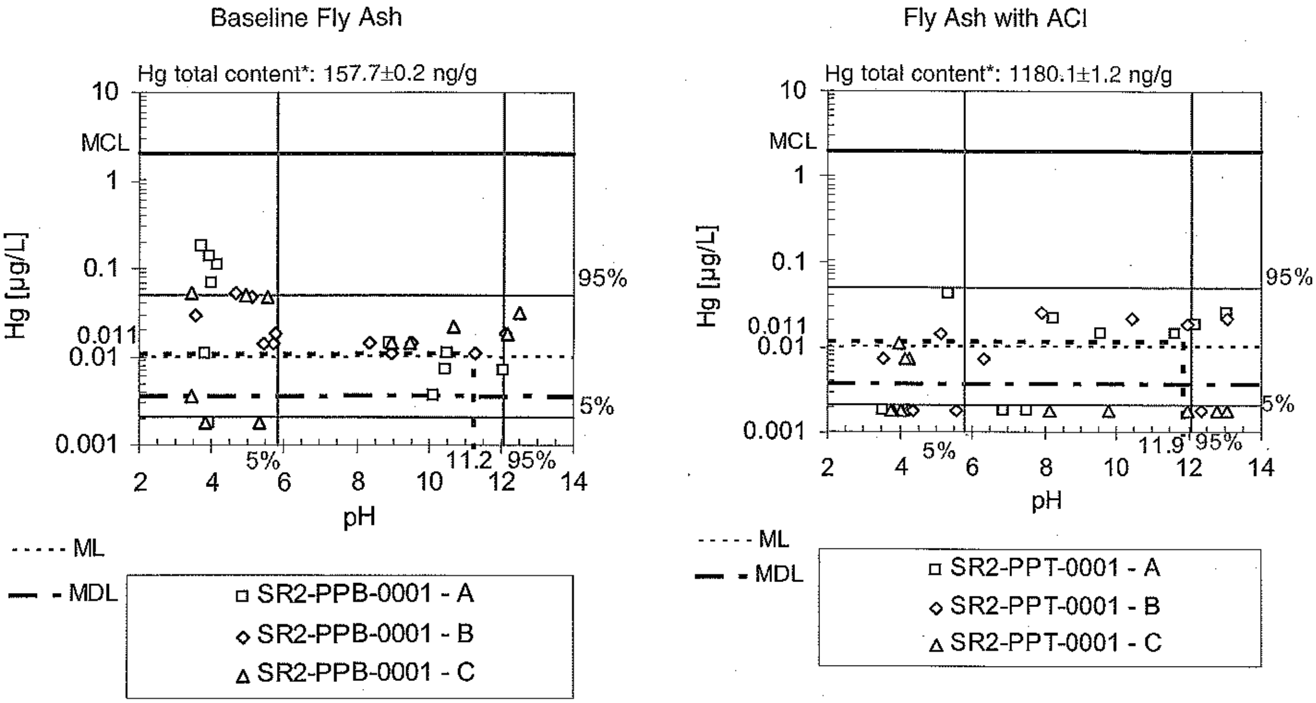
pH as a Function of LS Ratio


Baseline Fly Ash

Fly Ash with ACI

Figure E-2. pH as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Mercury Release as a Function of pH



*Total content as determined by digestion using method 3052.

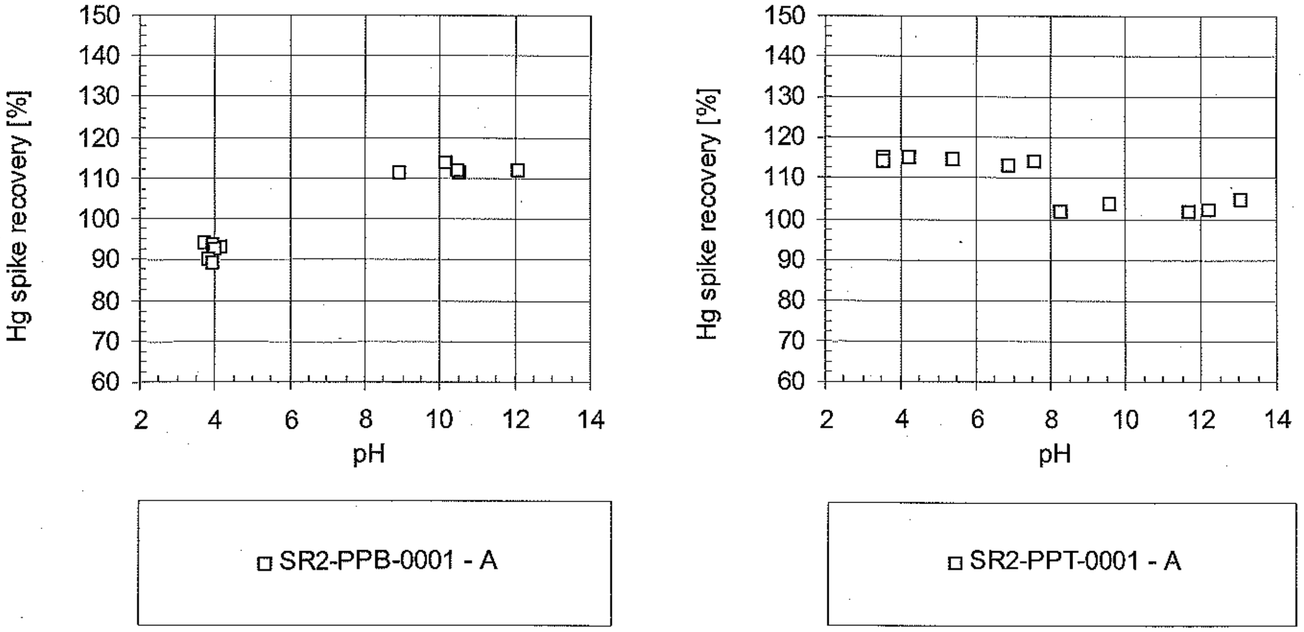


Figure E-3. Mercury Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of mercury concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Mercury Release as a Function of LS Ratio

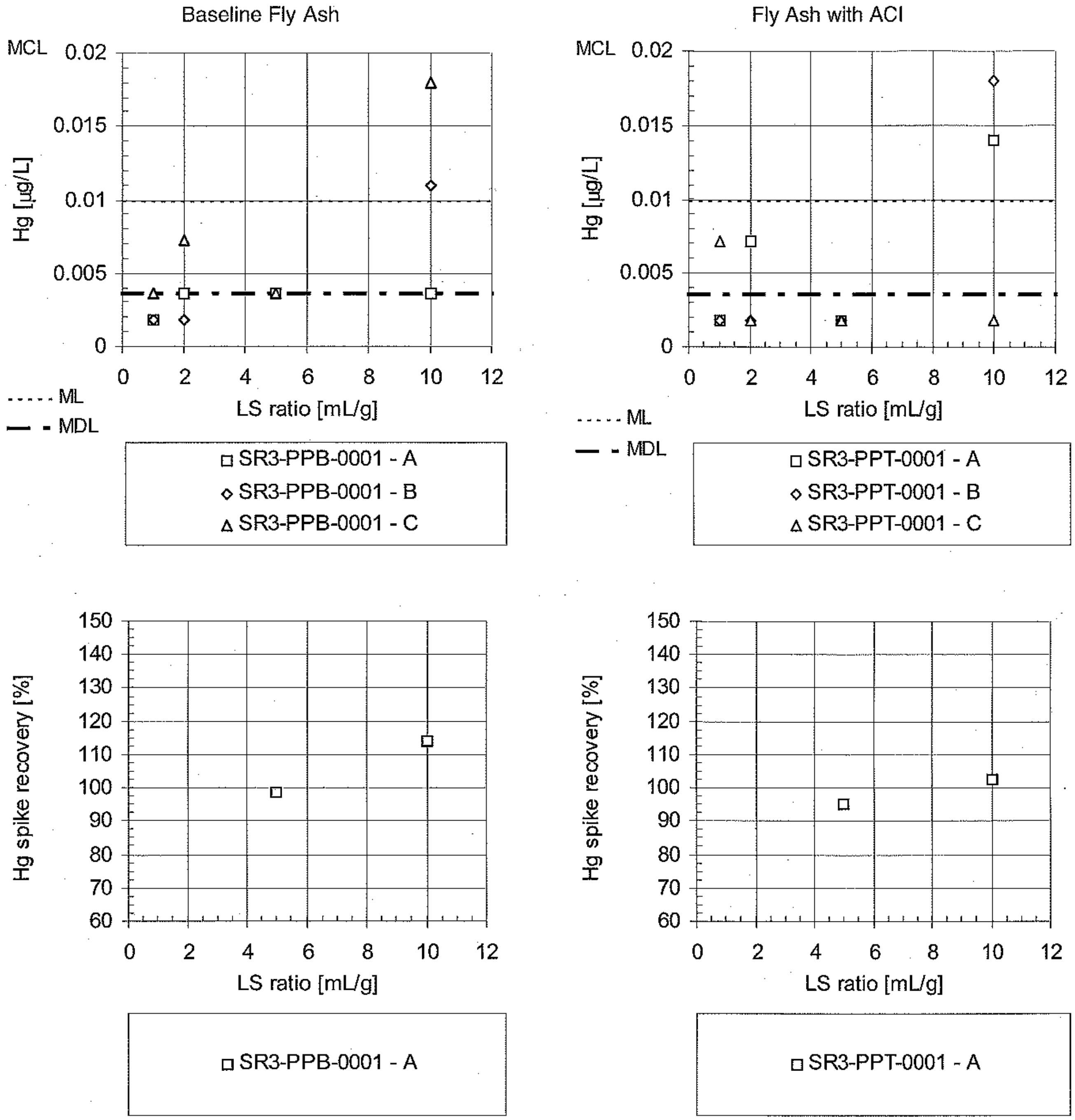
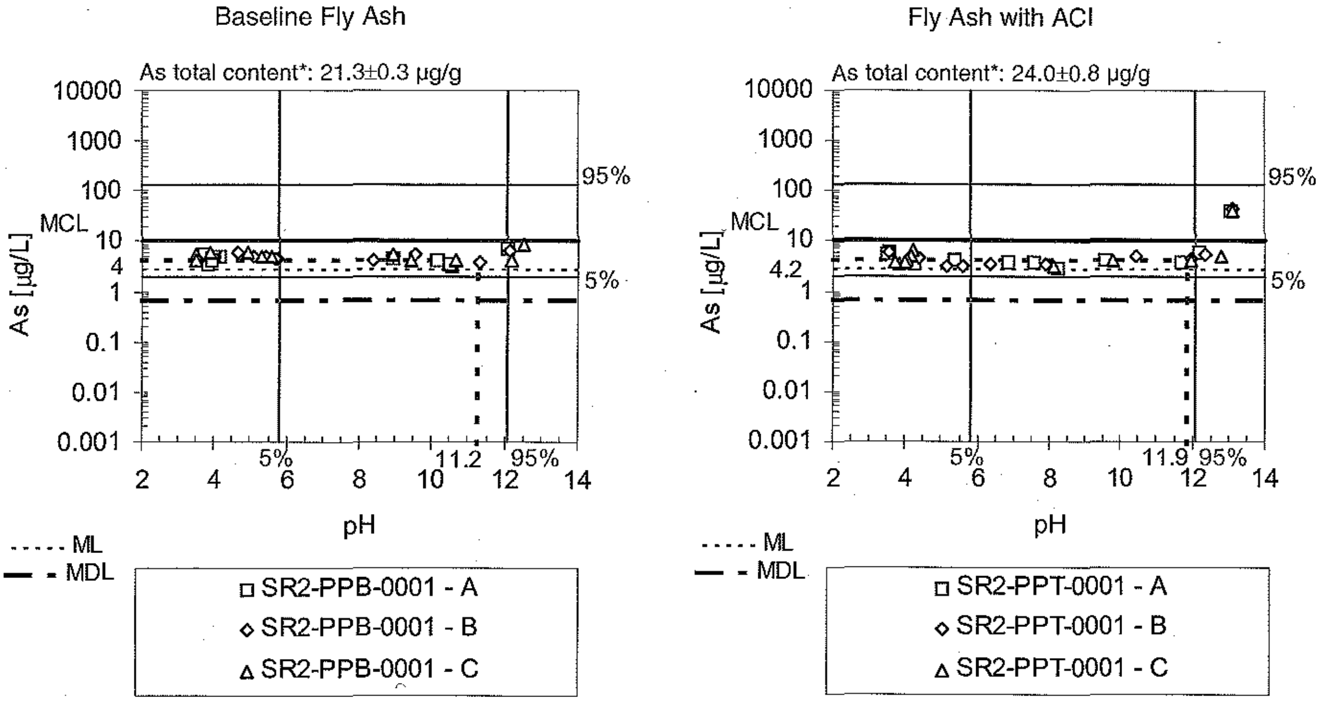


Figure E-4. Mercury Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Arsenic Release as a Function of pH



*Total content as determined by digestion using method 3052.

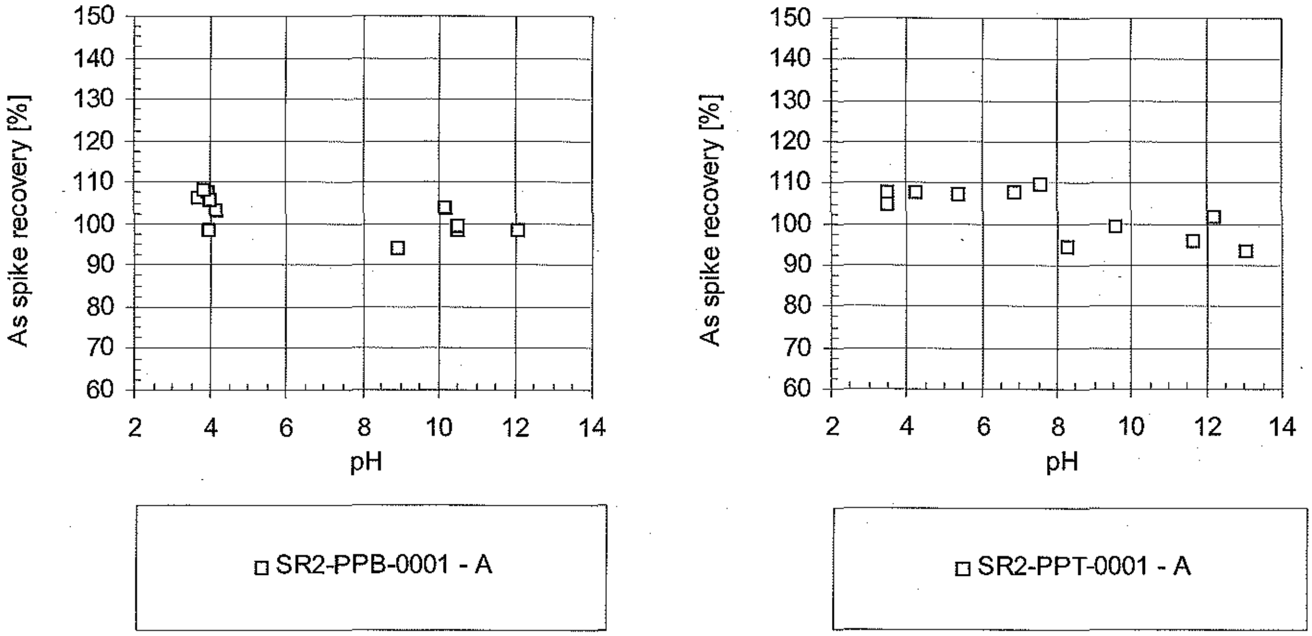


Figure E-5. Arsenic Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of arsenic concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Arsenic Release as a Function of LS Ratio

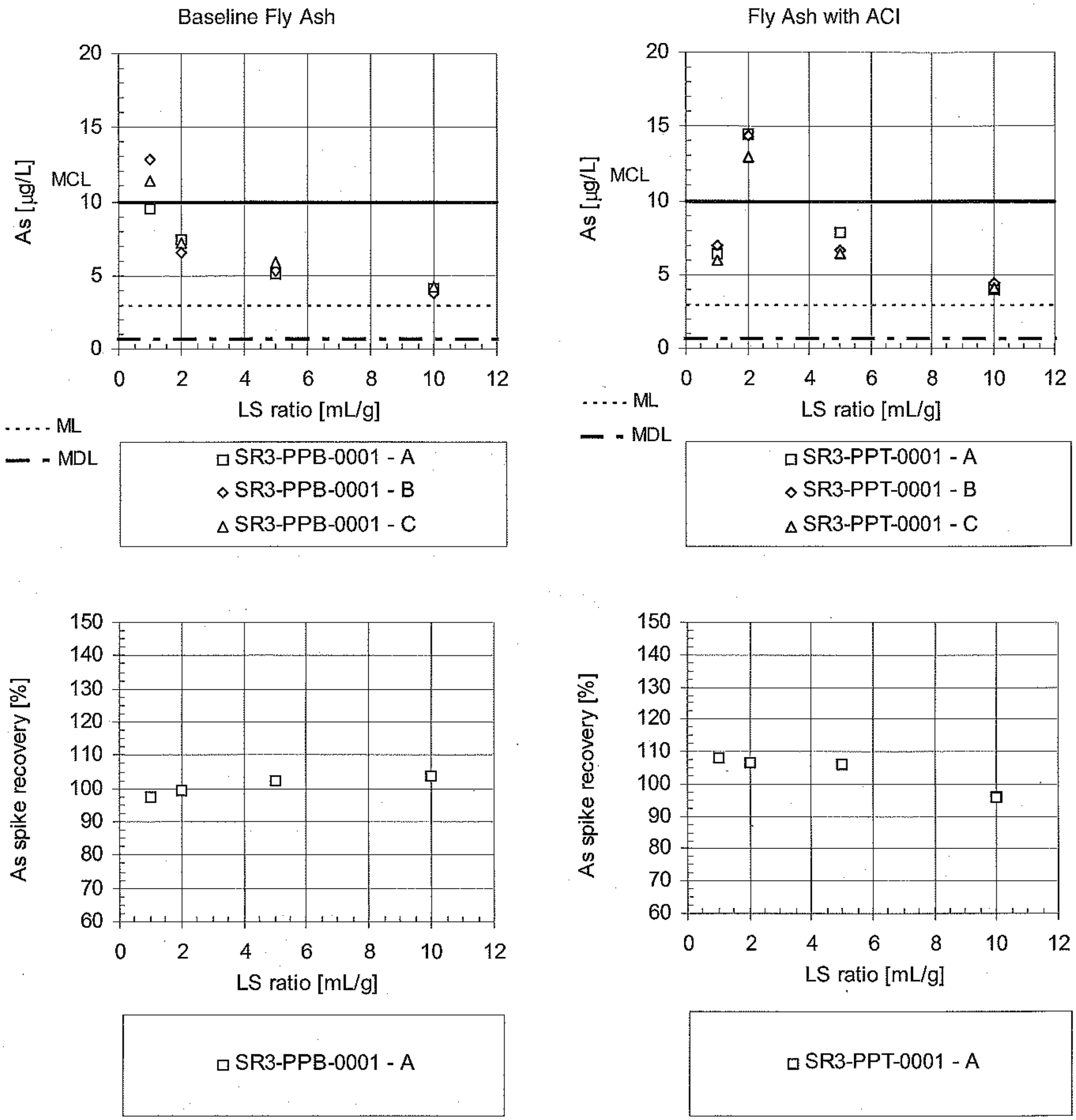
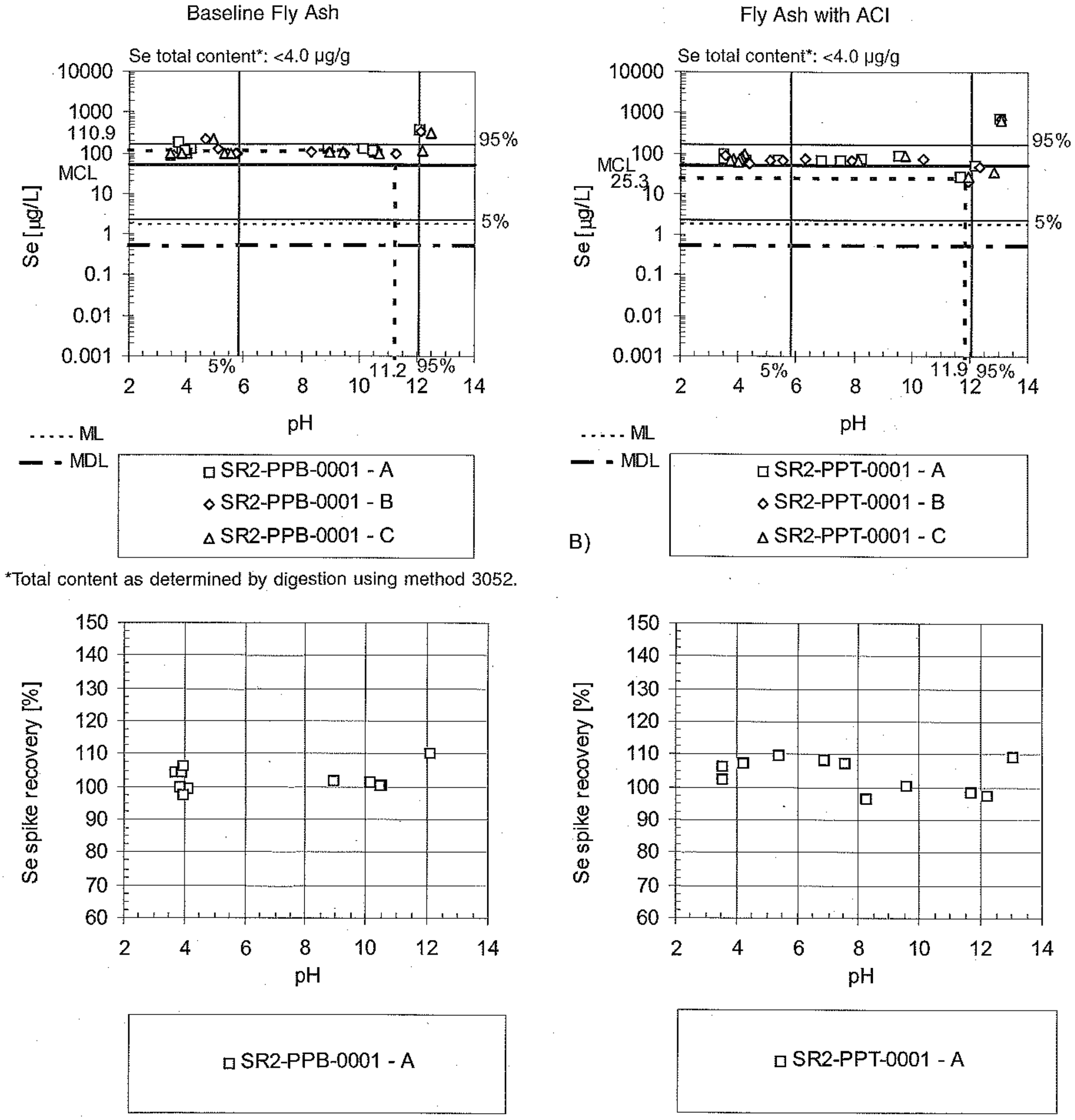


Figure E-6. Arsenic Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Selenium Release as a Function of pH



*Total content as determined by digestion using method 3052.

Figure E-7. Selenium Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of selenium concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Selenium Release as a Function of LS Ratio

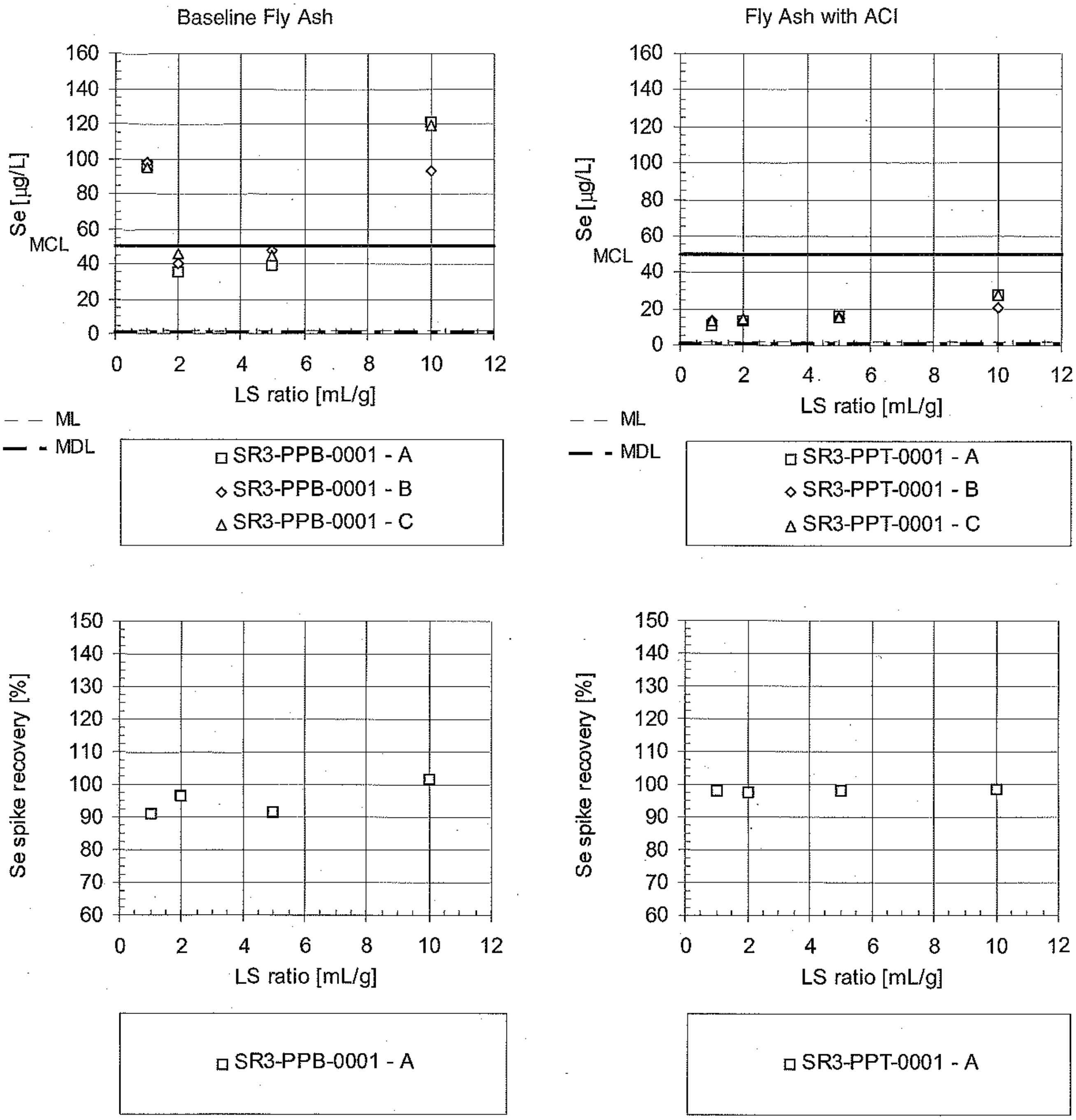
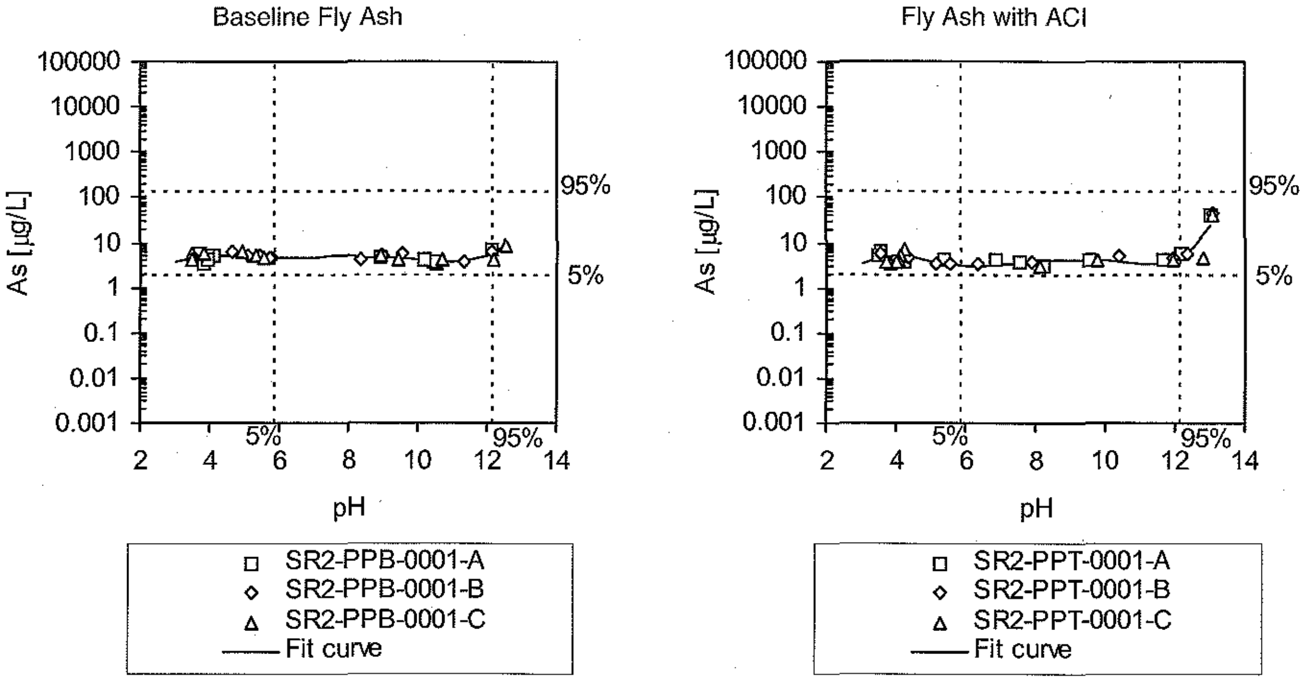


Figure E-8. Selenium Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

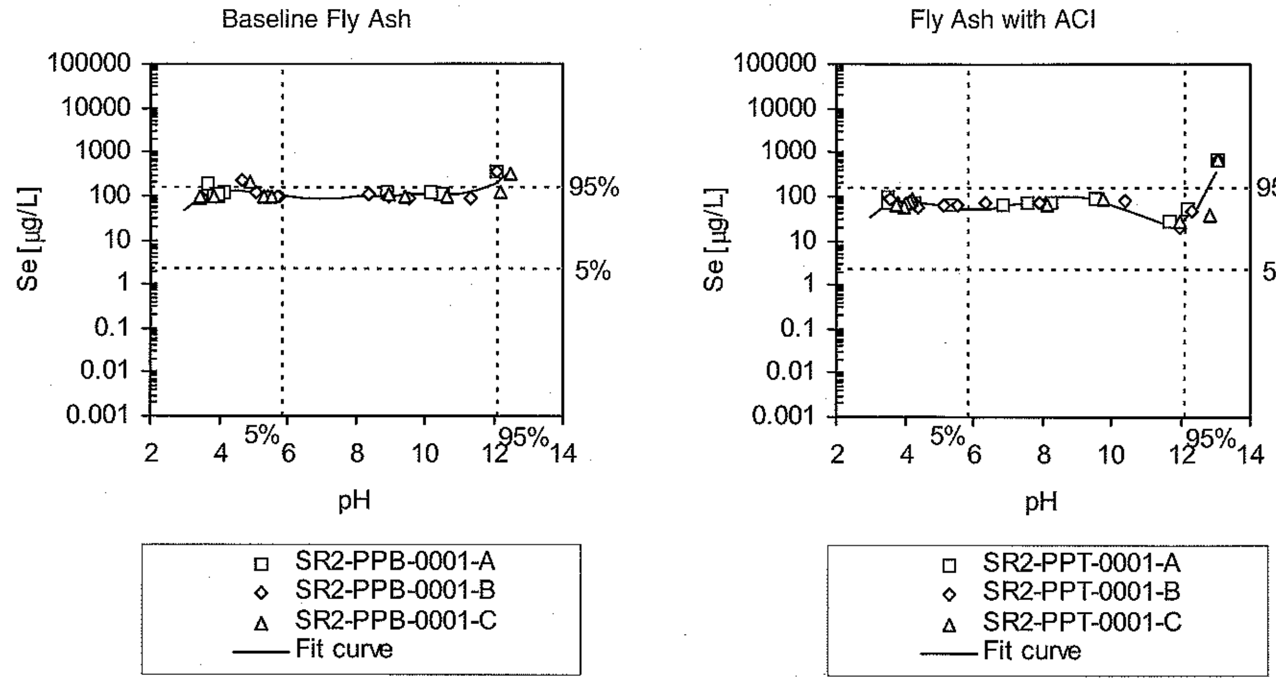
Arsenic Solubility



Material	log As (µg/L)			pH range of validity	R^2	Number of points
PPB	$0.0003\ pH^5$	$-0.0117\ pH^4$	$0.1674\ pH^3$	3-12.5	0.47	33
	$-1.1600\ pH^2$	$3.8716\ pH$	-4.2743			
PPT	$0.0006\ pH^5$	$-0.0238\ pH^4$	$0.3460\ pH^3$	3-13	0.84	33
	$-2.3840\ pH^2$	$7.7036\ pH$	-8.6786			

Figure E-9. Regression Curves of Experimental Data of Arsenic Solubility as a Function of pH.

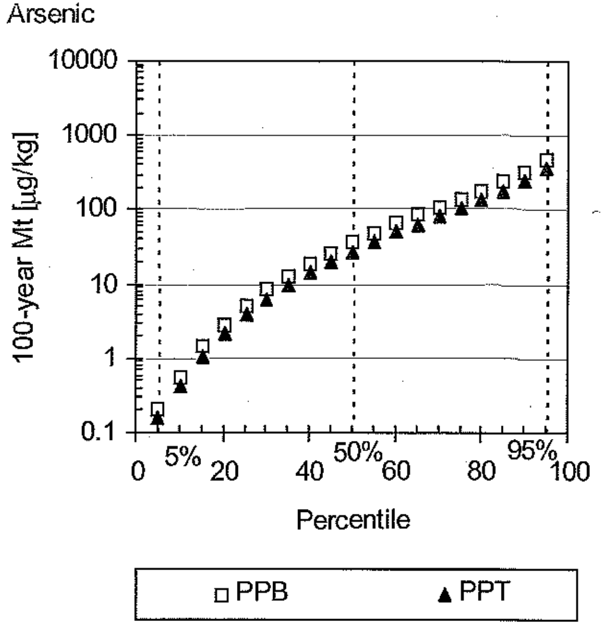
Selenium Solubility



Material	log Se (µg/L)			pH range of validity	R^2	Number of points
PPB	0.0006 pH^5	-0.0234 pH^4	0.3605 pH^3	3-12.5	0.54	33
	-2.6711 pH^2	9.4536 pH	-10.6432			
PPT	0.0012 pH^5	-0.0440 pH^4	0.6379 pH^3	3-13	0.81	33
	-4.3855 pH^2	14.2483 pH	-15.6626			

Figure E-10. Regression Curves of Experimental Data of Selenium Solubility as a Function of pH.

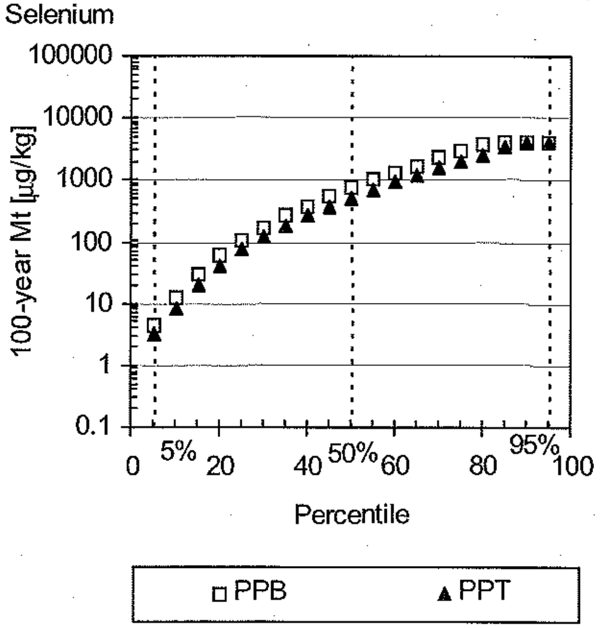
100-Year Arsenic Release Estimates



	PPB		PPT	
	µg/kg	%	µg/kg	%
Mt min	0.1	0.0006	0.1	0.0004
Mt - 5%	0.2	0.0010	0.2	0.0007
Mt - 50%	36	0.2	27	0.1
Mt - 95%	473	2.2	358	1.5
Mean Mt	107	0.5	81	0.3
Mt max	1188	5.6	1049	4.4

Figure E-11. 100-Year Arsenic Release Estimates as a Function of the Cumulative Probability for the Scenario of Disposal in a Combustion Waste Landfill.

100-Year Selenium Release Estimates



	PPB		PPT	
	µg/kg	%	µg/kg	%
Mt min	3.0	0.1	0.9	0.0
Mt - 5%	4.4	0.1	3.3	0.1
Mt - 50%	733	18.3	516	12.9
Mt - 95%	4000	100.0	4000	100.0
Mean Mt	2254	56.4	1599	40.0
Mt max	4000	100.0	4000	100.0

Figure E-12. 100-Year Selenium Release Estimates as a Function of the Cumulative Probability for the Scenario of Disposal in a Combustion Waste Landfill.

100-Year Arsenic Release Estimates

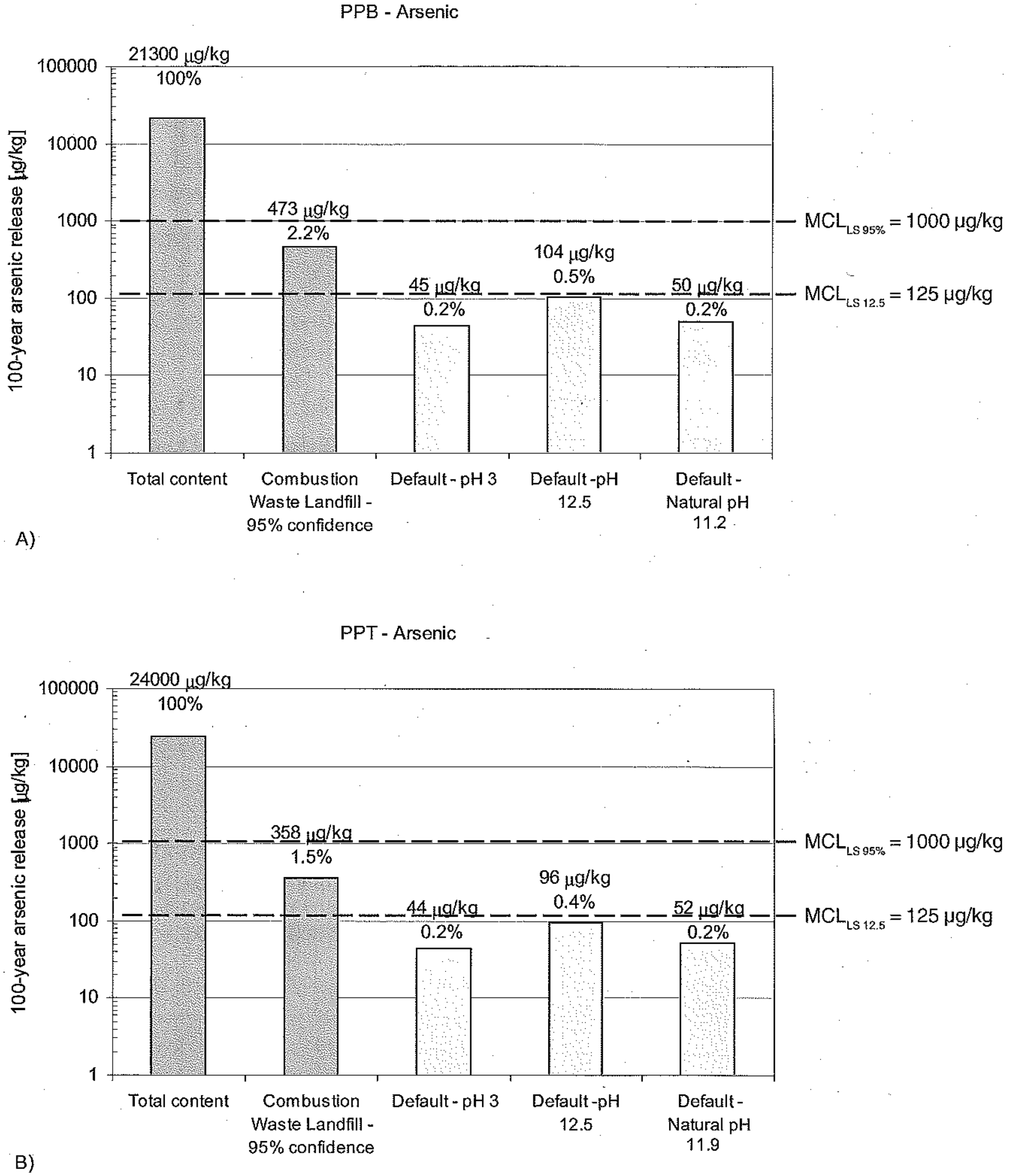
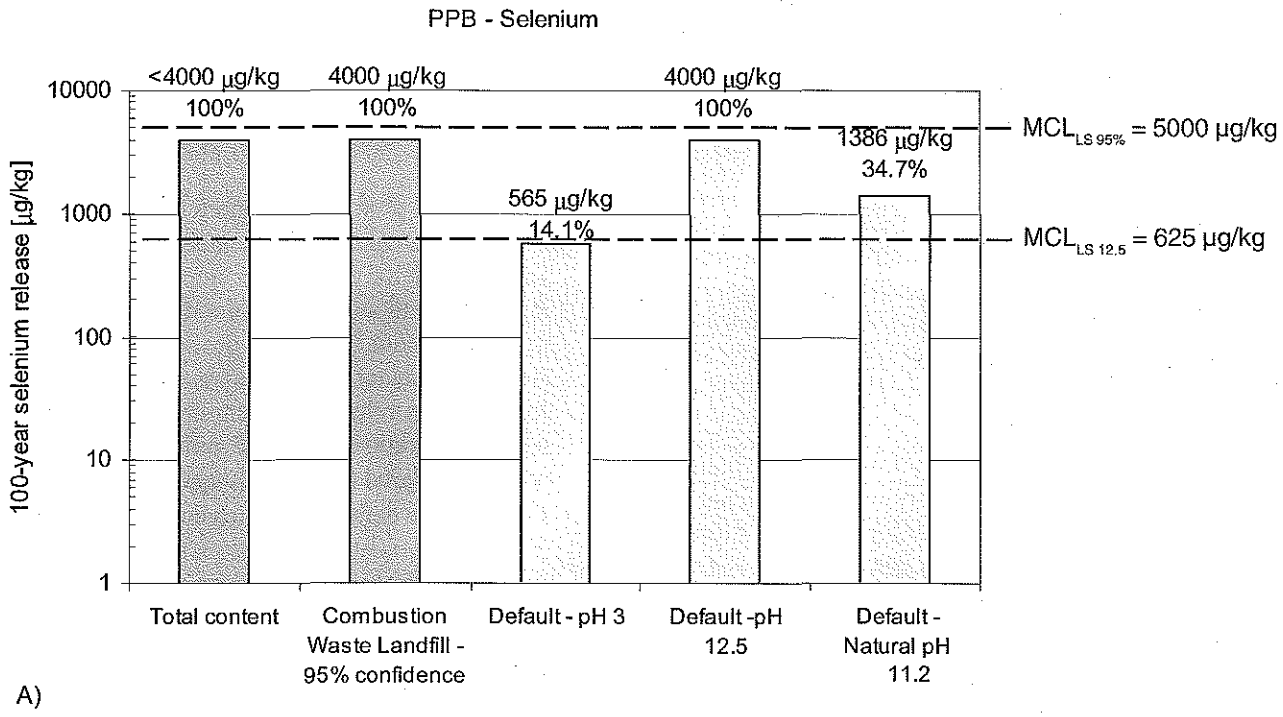


Figure E-13. 100-Year Arsenic Release Estimates from A) Baseline Fly Ash and B) Fly Ash with ACI. Release estimates for percolation controlled scenario are compared to release estimate based on total content. The amount of the arsenic that would be released if the release concentration was at the MCL is also shown for comparison ($LS_{default\ scenario}$ = 12.5 L/kg and $LS_{95\%}$ = 100 L/kg).

100-Year Selenium Release Estimates



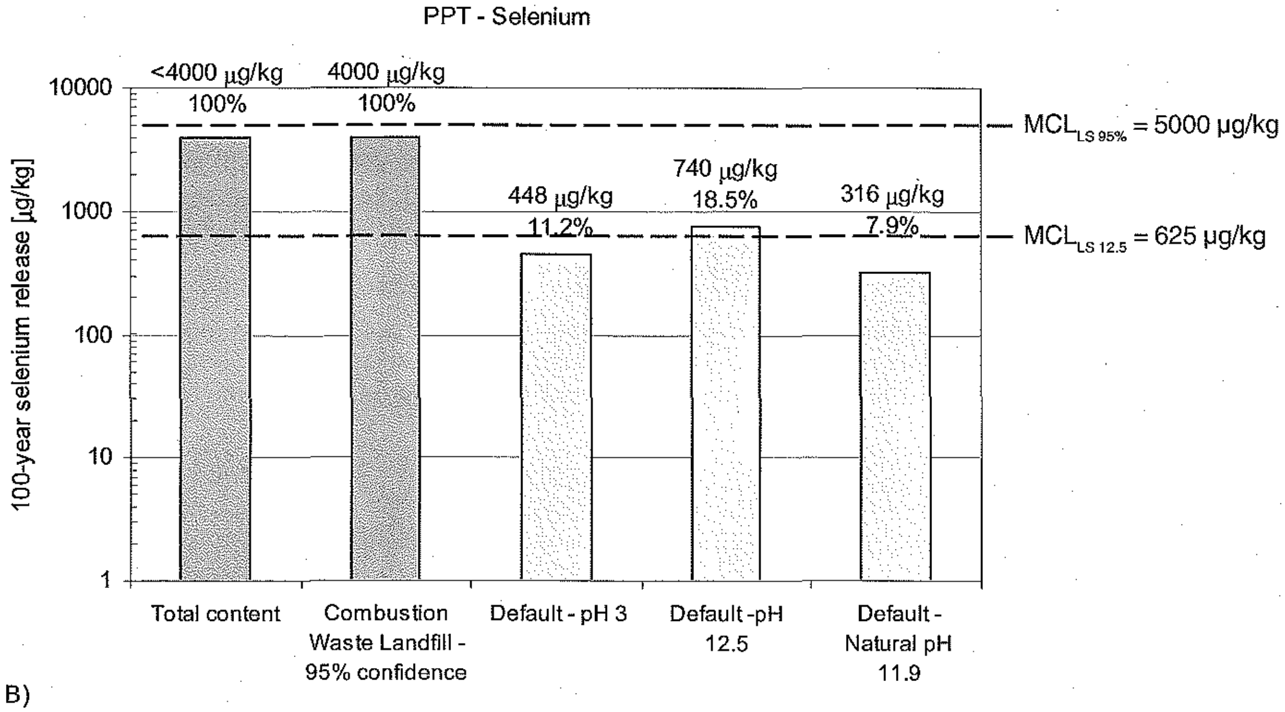


Figure E-14. 100-year Selenium Release Estimates from A) Baseline Fly Ash and B) Fly Ash with ACI. Release estimates for percolation controlled scenario are compared to release estimate based on total content. The amount of the selenium that would be released if the release concentration was at the MCL is also shown for comparison ($LS_{default\ scenario}$ = 12.5 L/kg and $LS_{95\%}$ = 100 L/kg).

Comments

Figure E-3:

- Fly ash from the test case had greater total Hg content than the fly ash from the baseline case (by about 7.5 times).
- Hg release is well below levels of potential concern (but poor replication) for both baseline and test cases.

Figure E-5:

- The fly ash from the test case had similar total As content than that from the baseline case.
- As release was below the MCL for both the baseline and the test cases for most pH conditions.

Figure E-7:

- Total selenium content was below detection limits for Method 3052 for both fly ashes while significant selenium release (ranging from around 30 µg/L to around 1000 µg/L) as a function of pH was observed. This result is a consequence of the dilution effects of the digestion method and analytical requirements.
- Selenium release from both the baseline and the test cases was close to or exceeded the MCL (50 µg/L) for most pH conditions.

Figures E-11 and E-12:

- The fly ash from the test case would result in As release slightly less than expected from the baseline case, with a 95% probability to be less than 358 and 473 µg/kg, respectively.
- The fly ash from the test case would result in Se release less than expected from the baseline case, with a 95% probability to be less than 4000 µg/kg (total content) in both cases and a 5% possibility that the total content will be released.

Figure E-13:

- For all scenarios examined, no significant difference in arsenic release would be observed between the fly ash from the baseline case and the fly ash from the test case.
- For the 95% probability scenario, arsenic release from both cases would be less than the amount that would be released if the release concentration was at the MCL and the LS ratio was the resultant LS ratio for the 95% case (i.e., about 100 L/kg). However, arsenic release would be greater than the amount that would be released if the release concentration was at the MCL and the LS ratio was the LS ratio of the default scenario considered (i.e., 12.5 L/kg).
- For the three default scenarios considered, arsenic release would most likely be less than the amount that would be released if the release concentration was at the MCL.

Figure E-14:

- For scenarios at alkaline pH, lower Se release would be expected for the test case compared to the baseline case.
- For the 95% probability scenario, selenium release from both cases would be greater than the amount that would be released if the release concentration was at the MCL.
- In conclusion, Se release will most likely be greater than the MCL based on solubility and cumulative release. Without controls appears worse than with controls.

Appendix F
Salem Harbor Fly Ashes

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pH Titration Curves

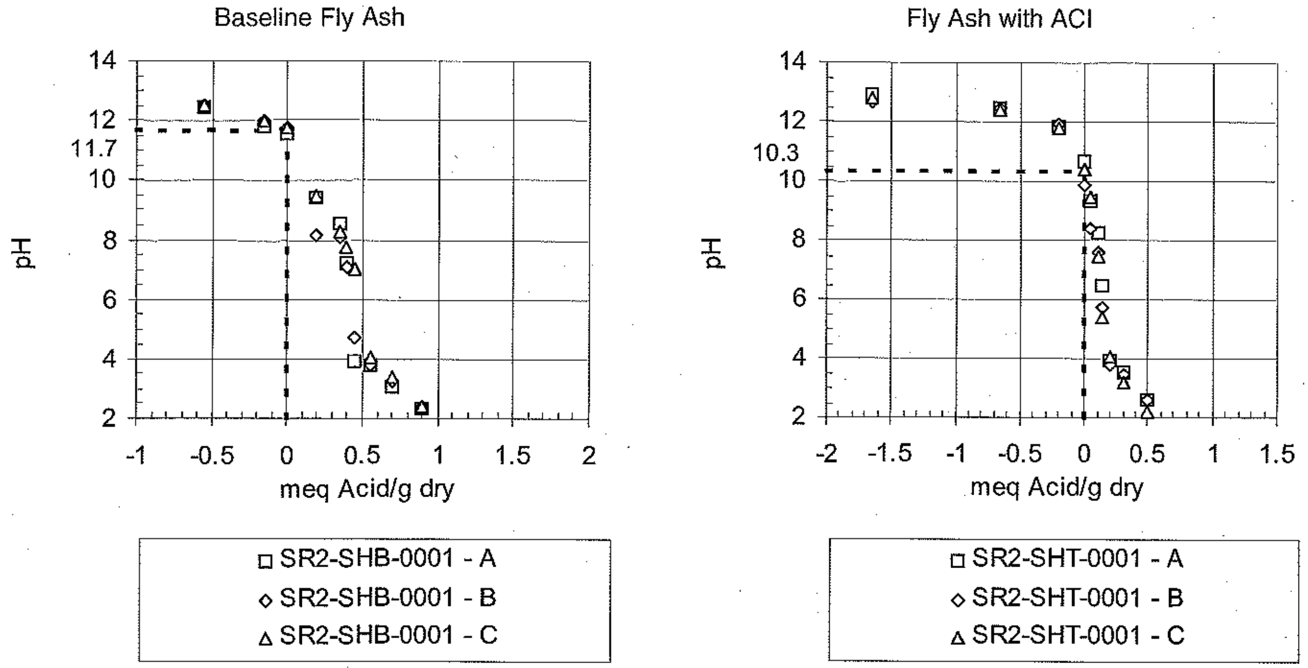


Figure F-1. pH Titration Curves for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

pH as a Function of LS Ratio

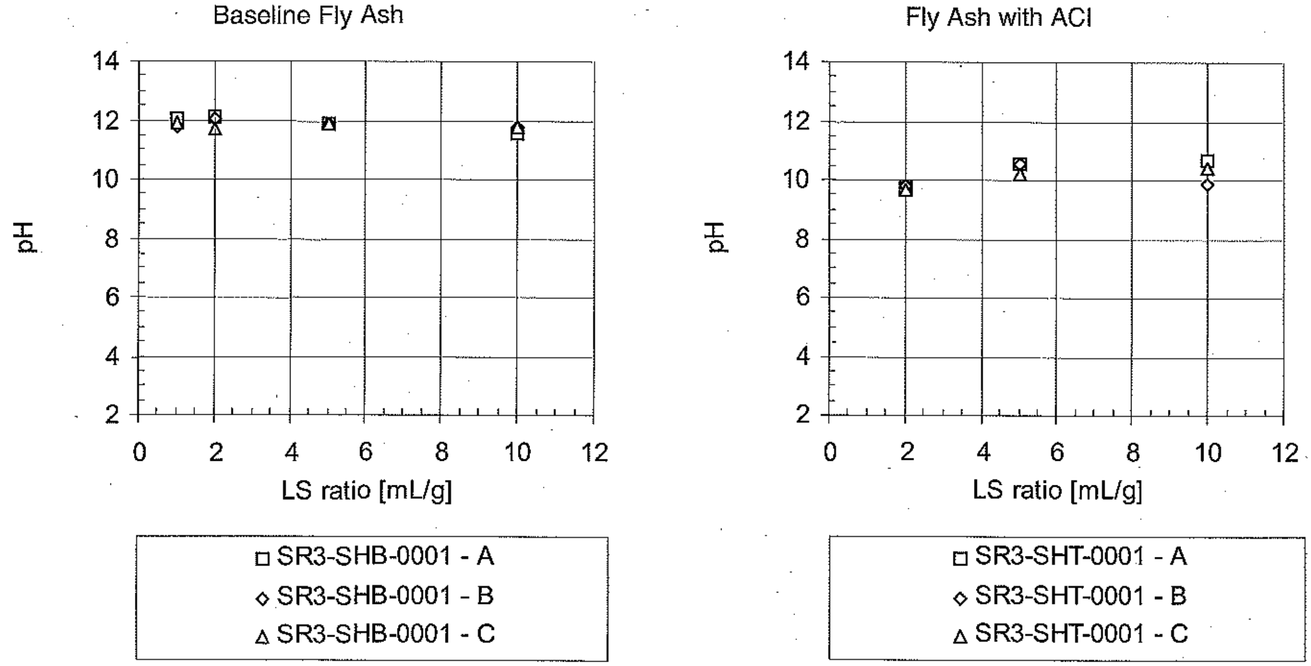
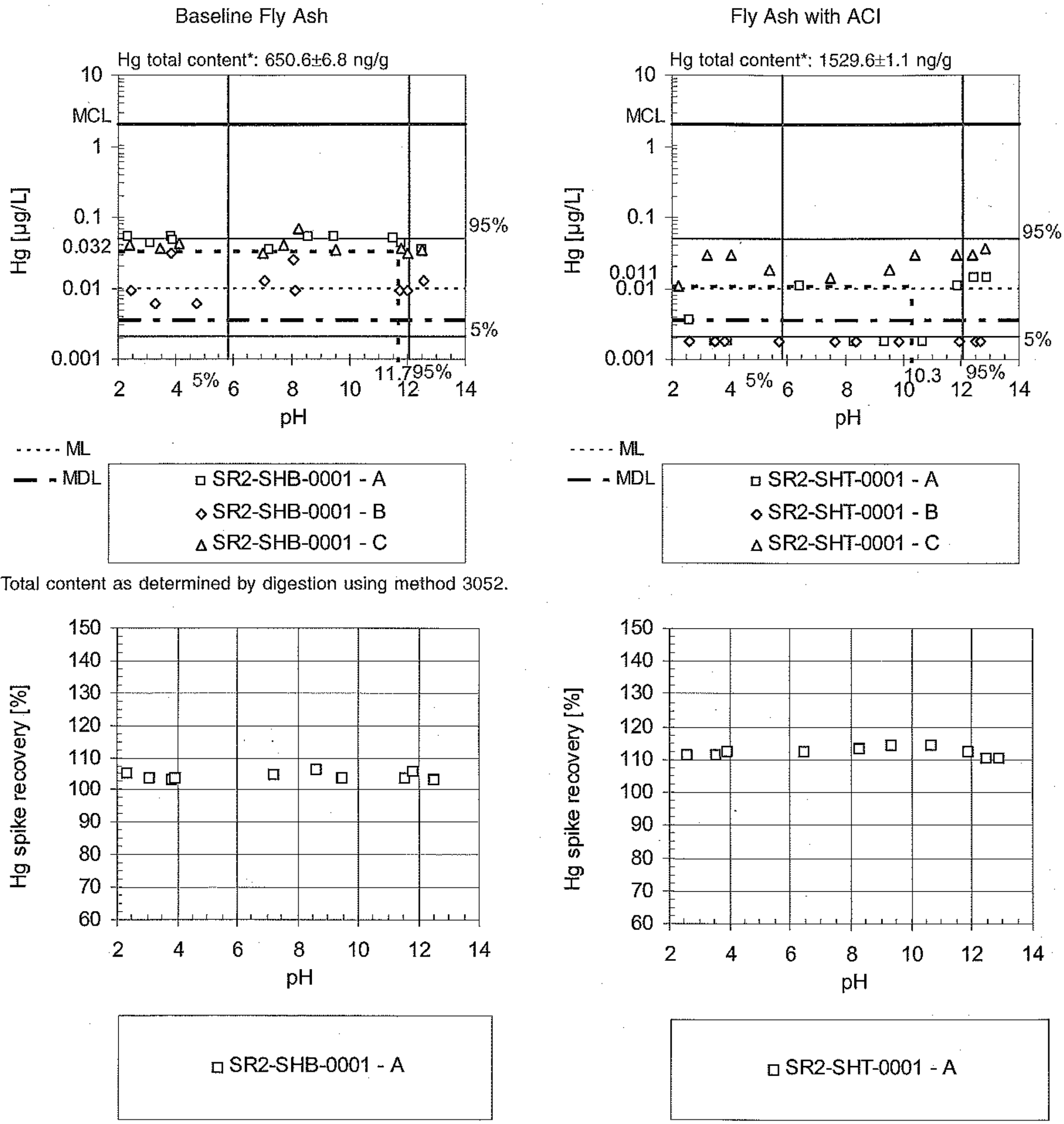


Figure F-2. pH as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Mercury Release as a Function of pH



*Total content as determined by digestion using method 3052.

Figure F-3. Mercury Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of mercury concentrations observed in typical combustion waste landfill leachate are shown for comparison.

Mercury Release as a Function of LS Ratio

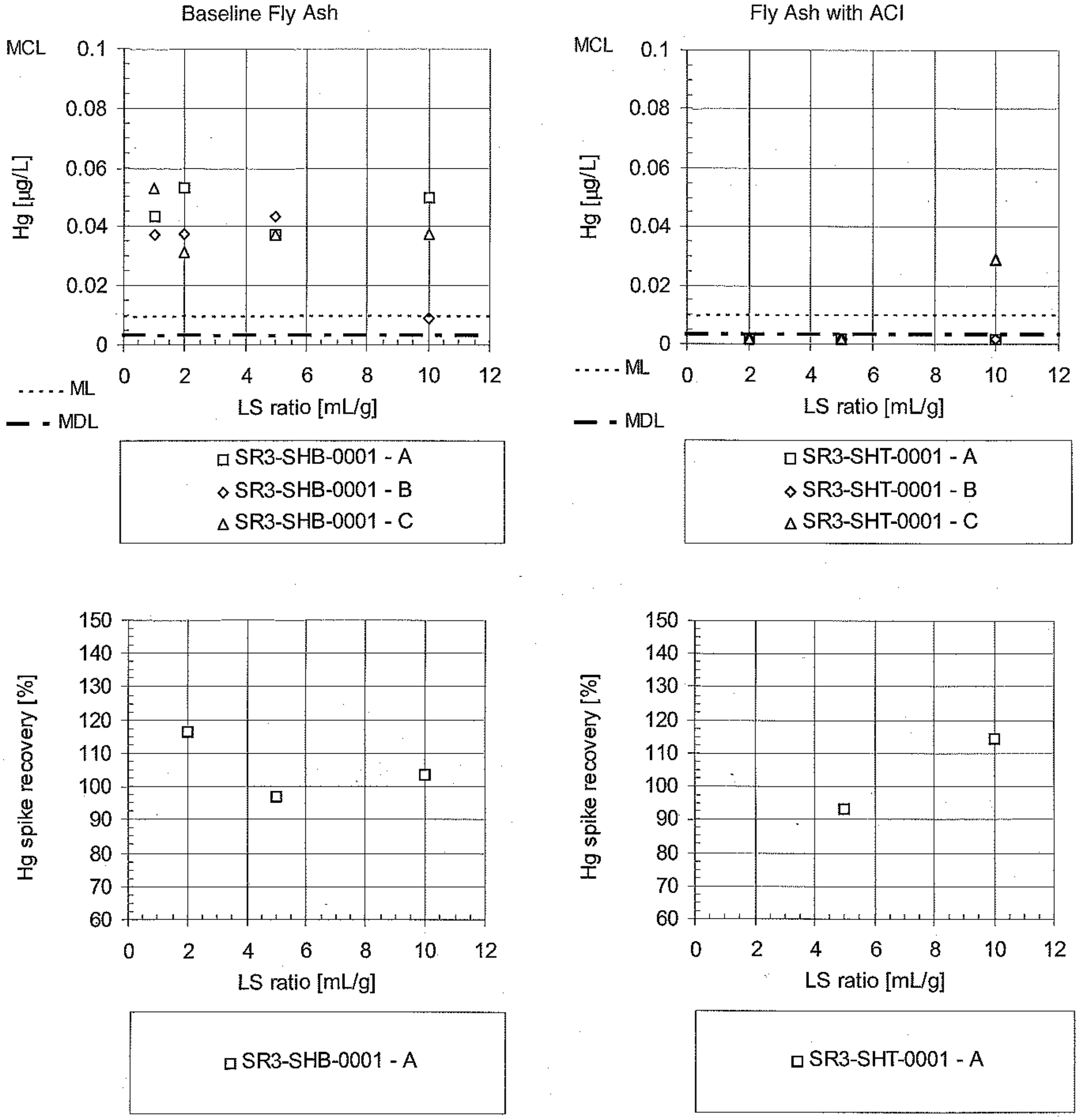
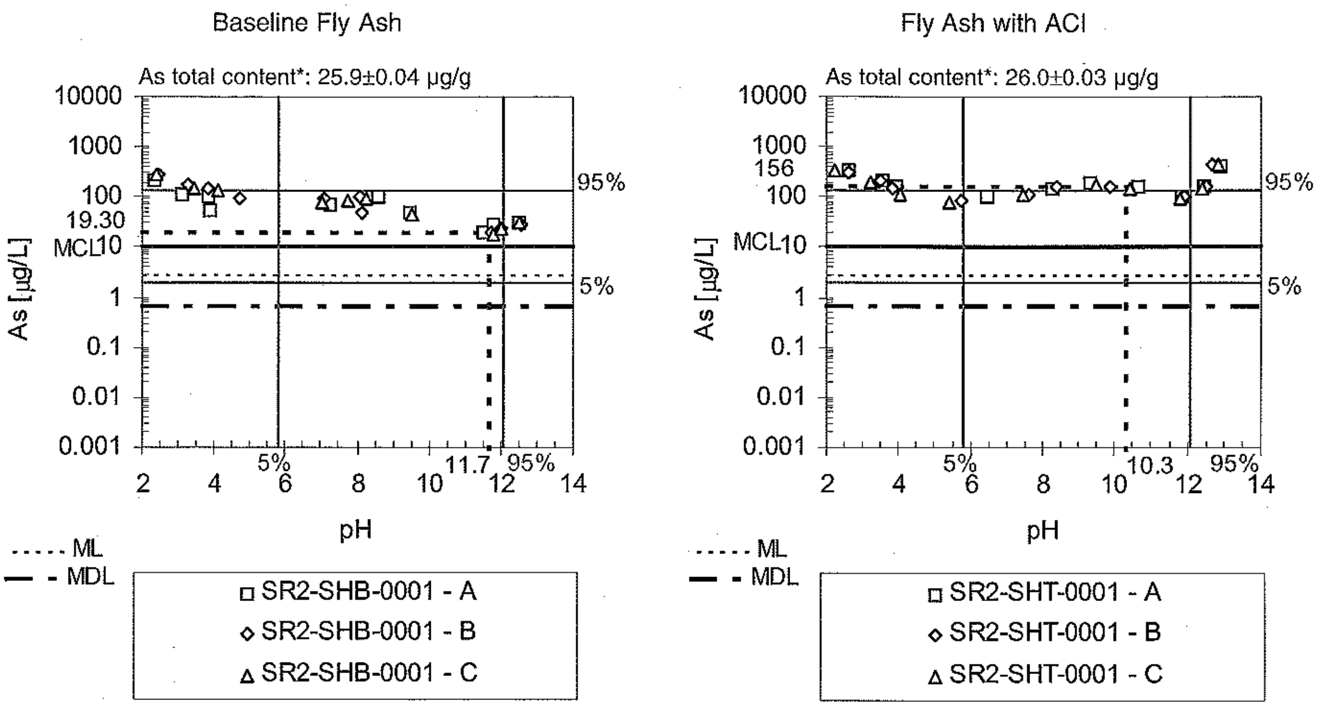


Figure F-4. Mercury Release (top) and Spike Recoveries (bottom) as a Function of LS Ratio for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control.

Arsenic Release as a Function of pH



*Total content as determined by digestion using method 3052.

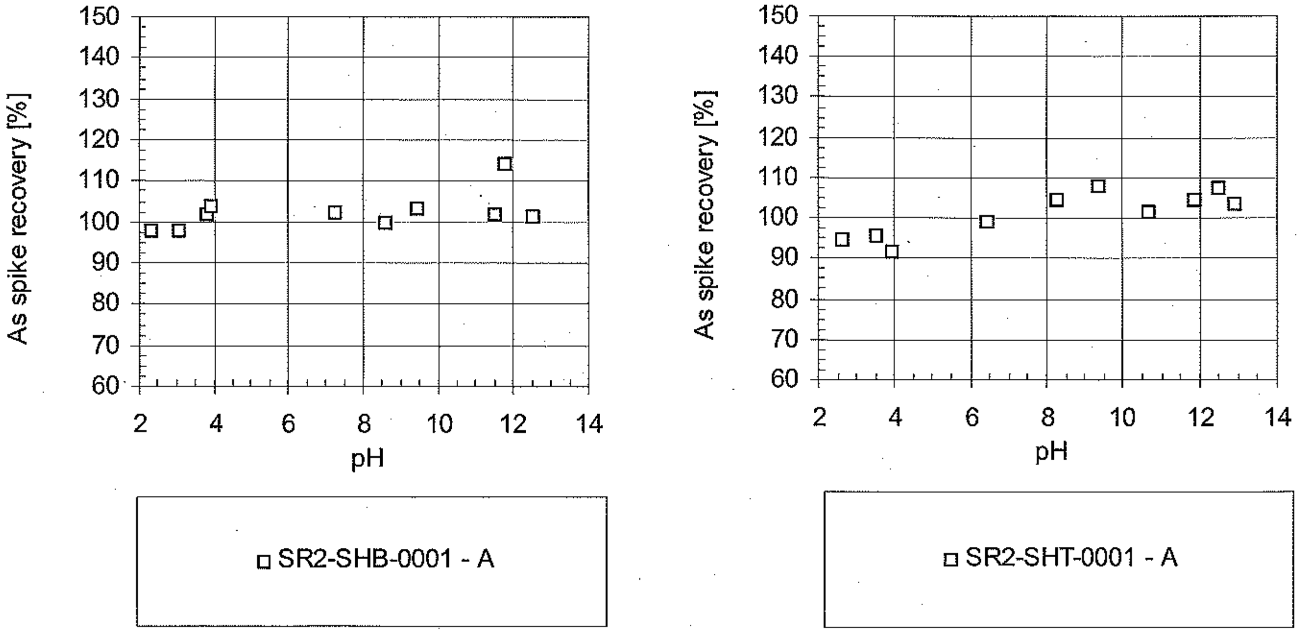


Figure F-5. Arsenic Release (top) and Spike Recoveries (bottom) as a Function of pH for the Baseline Fly Ash and the Fly Ash with Enhanced Hg Control. 5th and 95th percentiles of arsenic concentrations observed in typical combustion waste landfill leachate are shown for comparison.