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Assessment of Hazardous Air Pollutants for Advanced Power Systems

Topical Report

David W. Brekke
Thomas A. Erickson

December 1995

Work Performed Under Contract No.: DE-AC21-92MC28016

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of North Dakota
Grand Forks, North Dakota

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P.O. Box 880
Morgantown, West Virginia 26507-0880

By
University of North Dakota
Energy and Environmental Center
P.O. Box 9018
Grand Forks, North Dakota 58202-9018

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ASSESSMENT OF HAZARDOUS AIR POLLUTANTS FOR ADVANCED POWER SYSTEMS

EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments (CAAA) identified 189 substances as air toxics or hazardous air pollutants (HAPs). Under the CAAA, the U.S. Environmental Protection Agency (EPA) must regulate emissions of these HAPs at their sources, including advanced power systems used for the production of electricity. Eleven trace elements are included in the CAAA list of HAPs, as shown in Table ES-1. The EPA will define those sources that require regulation and limit their emissions according to regulatory directives. This project focused on evaluating and manipulating the advanced power systems HAP data currently available for presentation to the U.S. Department of Energy (DOE).

TABLE ES-1

Trace Components Included in the 189 HAPs of the 1990 CAAA

Antimony Compounds	Arsenic Compounds	Beryllium Compounds
Cadmium Compounds	Chromium Compounds	Cobalt Compounds
Lead Compounds	Manganese Compounds	Mercury Compounds
Nickel Compounds	Selenium Compounds	

Systems Reviewed

The review of trace element emissions from advanced power systems and hot-gas cleanup systems included data from Tidd Station, General Electric hot-gas cleanup (GE HGCU), Louisiana Gasification Technology Incorporated (LGTI), and the Cool Water plant. Very few other sources of information were located, and those that were contained significantly flawed information that was not of value to this project. To offset the shortage of information, thermochemical equilibrium predictions were used in evaluating advanced control systems. An outline of the systems reviewed is given in Table ES-2. In addition to the four demonstration and full-scale systems reviewed, nine conventional systems were also reviewed for comparison with the advanced systems.

Review of Sampling and Analysis Procedures

The sampling procedures used at all of the plant sites generally conformed to established sampling methods. At all four of the sites, the contractor for sampling and testing was Radian Corporation. Sampling strategy at the sites was normally consistent with the DOE programs under which these plants were studied. Since each plant has a unique system and configuration, however, the methods were slightly different for each plant. Modifications or adaptations were necessary in some instances because of product gas compositions, temperatures, and trace metal content in the apparatus disposables.

TABLE ES-2

Advanced Power Systems and Cleanup Technologies

Plant Name	System Type	System Description	Particulate Control	Sulfur Control
Tidd	PFBC[1]	Bubbling-bed PFBC	Two-stage cyclone/ ESP[2]	Dolomite bed
Tidd	APF[3]	Barrier filter	Cyclone/ceramic barrier APF	None
LGTI	IGCC[4]	Entrained-flow, oxygen-blown, two-stage, slagging gasifier	Venturi scrubber	Selectamine® absorber
GE HGCU	IGCC, turbine simulator	Pressurized, air-blown, fixed-bed gasifier	Cyclones	Zn titanate sorbent with regenerator
Cool Water	IGCC	Entrained-flow, oxygen-blown, slagging gasifier	Water scrubber	Selexol absorber

[1] Pressurized fluidized-bed combustor.
[2] Electrostatic precipitator.
[3] Advanced particle filter.
[4] Integrated gasification combined cycle.

The primary methods used to obtain samples from flue gas streams were EPA Method 5 and Method 29. Particulate emissions were normally measured using Method 5. The major modification to this method was the use of a quartz filter, which reduced the amount of trace metals in the collection medium. The multimetals sampling train technique, Method 29, was used to collect trace metal samples in the flue and product gases. This technique involves a filter and a series of impingers. However, the procedure is designed for oxidizing conditions and has not been validated for use in reducing environments. Gases such as H_2S, CO, and H_2 rapidly deplete the oxidizing capacity of the impingers, and the train fails to retain the vapor-phase metals. None of the vapor-phase trace element samples taken in any of the systems from reduced gas streams are believed accurate.

Effect of Conversion Technology

The type of coal conversion technology can affect the total plant emissions by reducing the amount of emissions that the hot-gas cleanup system must encounter. The Tidd pressurized fluidized bed combustor (PFBC) showed a lower release of most trace elements to the cleanup device than did the neighboring Cardinal station, a pulverized coal (pc)-fired system. The lower operating temperature of the PFBC and the primary cyclone are the principal causes of this. Figure ES-1 displays the partitioning of species as the ratio of the element mass in the flue gas to that leaving the system in the slag. Mercury emission was about the same for both systems, as expected.

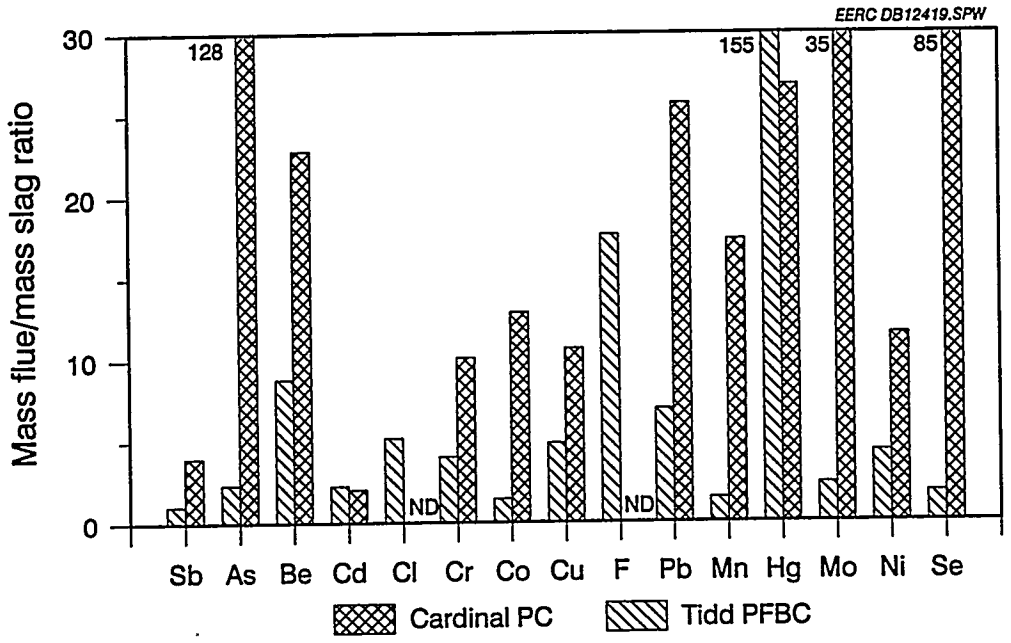


Figure ES-1. Partitioning of trace elements in ash within the "boiler" for the Tidd PFBC and the Cardinal pc-fired units. Partitioning factor is equal to the ratio of the mass of the element leaving the system in the flue gas to the mass in the slag/bottom ash. ND - Not detected.

The emission of trace elements from the gasifier section of gasification systems was not adequately measured in the studies reviewed. The commonly held view that everything is forced into the slag within a gasification system is readily apparent upon inspection of the gasification data. However, samples taken exiting gasifiers were subject to very low closure because of inappropriate sampling techniques. It is more likely that a significant amount of trace elements do indeed exit the gasifier, but these elements are removed during the cooling and sulfur removal stages, processes that were not investigated in this project. Since these particular sulfur removal processes will not be used in the newer technologies, trace metal emission may still present a problem, although insufficient data were available to support this assessment.

Total Plant Emissions

Figure ES-2a summarizes the emissions data for the 11 elements listed in the CAAA for both advanced and conventional systems. Also shown are the two most commonly volatile elements, Hg and Se. The CAAA trace element emissions for the GE HGCU and the Cool Water plant are significantly higher than for the other systems. The GE HGCU and Cool Water data are highly suspect and should not be considered valid for these comparisons. The Tidd advanced particle filter (APF) data indicate the third highest emitter. However, most of these emissions are from Cr

and Ni, which are believed to be contamination from the sampling probe. Thermochemical equilibrium calculations also suggest that this is contamination. By assuming that the Cr and Ni values are from contamination and that they are present in the system primarily as particulate, a new estimate for the CAAA emissions can be calculated. Removing 99% of their values (which allows 1% for breakthrough, a high estimate) gives the new results shown in Figure ES-2b. Considering this assumption, both the Tidd APF and the LGTI systems show emission as low or lower than conventional systems.

The emissions of Hg and Se appear to be higher in the Tidd APF, likely because of the high operation temperature of the system. Since the Hg mass balance around the APF is very close to 100 with only a small deviation, it is assumed that the elevated mercury emissions are real and warrant future attention. The GE HGCU and Cool Water systems also show slightly elevated mercury emission values. However, since sampling errors occurred, the true extent of the emissions is not clear.

Evaluation of Control Technologies

The average control efficiency for total particulate, total CAAA trace elements, and Hg and Se are shown in Figure ES-3. The LGTI and Cool Water plants are included as a total plant efficiency value, not as a control technology efficiency. The poor performance of the GE HGCU system was expected because of sampling errors, and the poor performance of the APF is due to Cr and Ni contamination in the APF data.

Thermochemical Equilibrium Predictions

The efficiency and environmental friendliness of emerging advanced power systems largely depends upon the effective removal of particulates from the gas stream at temperatures higher than those in conventional systems. These higher temperatures result in a change between the equilibrium abundances of inorganics present in the solid and vapor state, as compared to conventional systems. The ability to physically collect inorganic species depends largely upon their existence as particulate. Thermochemical equilibrium programs are an effective tool to aid in the determination of trace metal partitioning between vapor and solid species.

In using the thermochemical equilibrium programs to aid in the design and operation of higher-temperature cleanup systems, predictions must be made using exact parameters. However, to generalize, the lower the pressure, the lower the temperature needed for effective collection. At atmospheric pressure, systems should be run below approximately 900°F, while under higher pressures, temperatures can be extended to 1100°F (at 20 atm), as shown in Figures ES-4 and ES-5. The presence of vapor-phase lead at lower temperatures is an unresolved problem in predicting lead species; it is assumed that the lead is primarily particulate up to 1000°F.

Potential Regulatory Impact

The potential for the regulation of advanced power systems is currently being driven by the 1990 CAAA. The CAAA list 189 compounds considered HAPs that must be minimized. The current form of the regulations would allow only 10 tons/year of any single HAP and 25 tons/year of all HAPs combined. Any major source exceeding these limits will be required to apply the

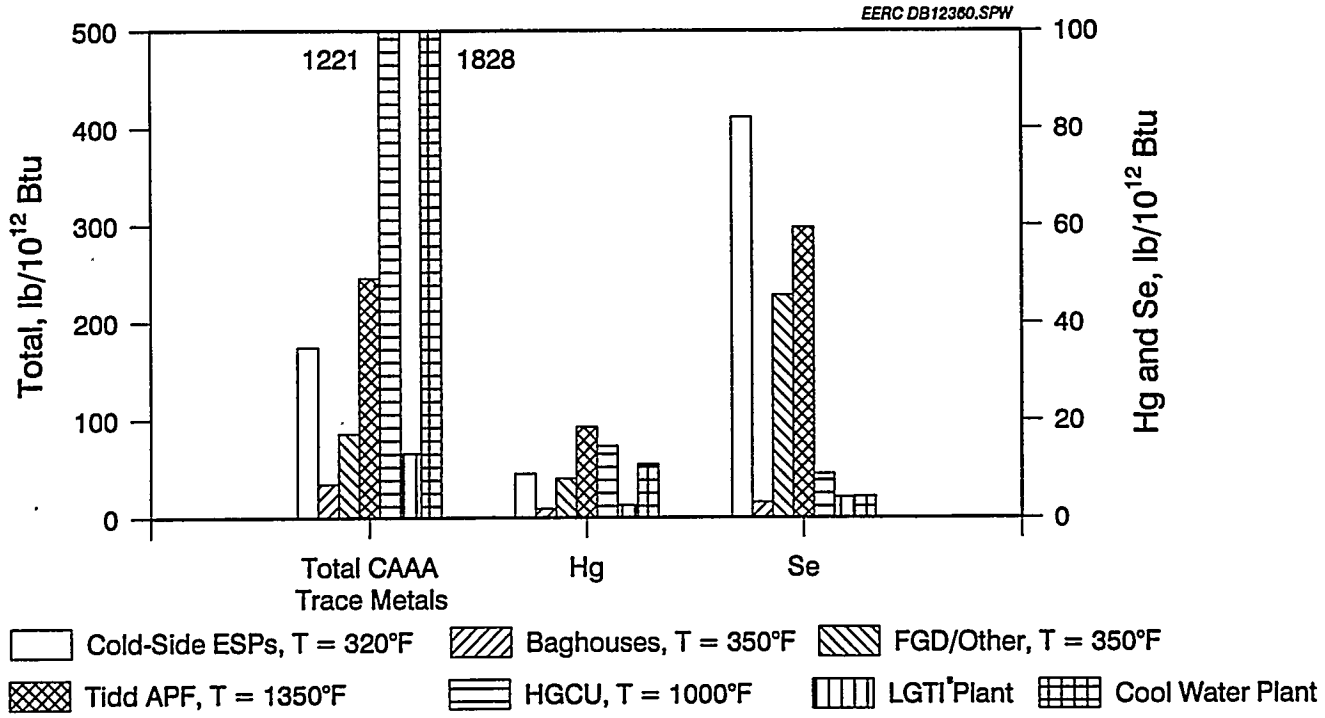


Figure ES-2a. Summarized emission factors of total CAAA trace elements, Hg, and Se. Note that contamination of Cr and Ni in the Tidd APF outlet samples is suspected. Results from both GE HGCU and Cool Water were subject to sampling error.

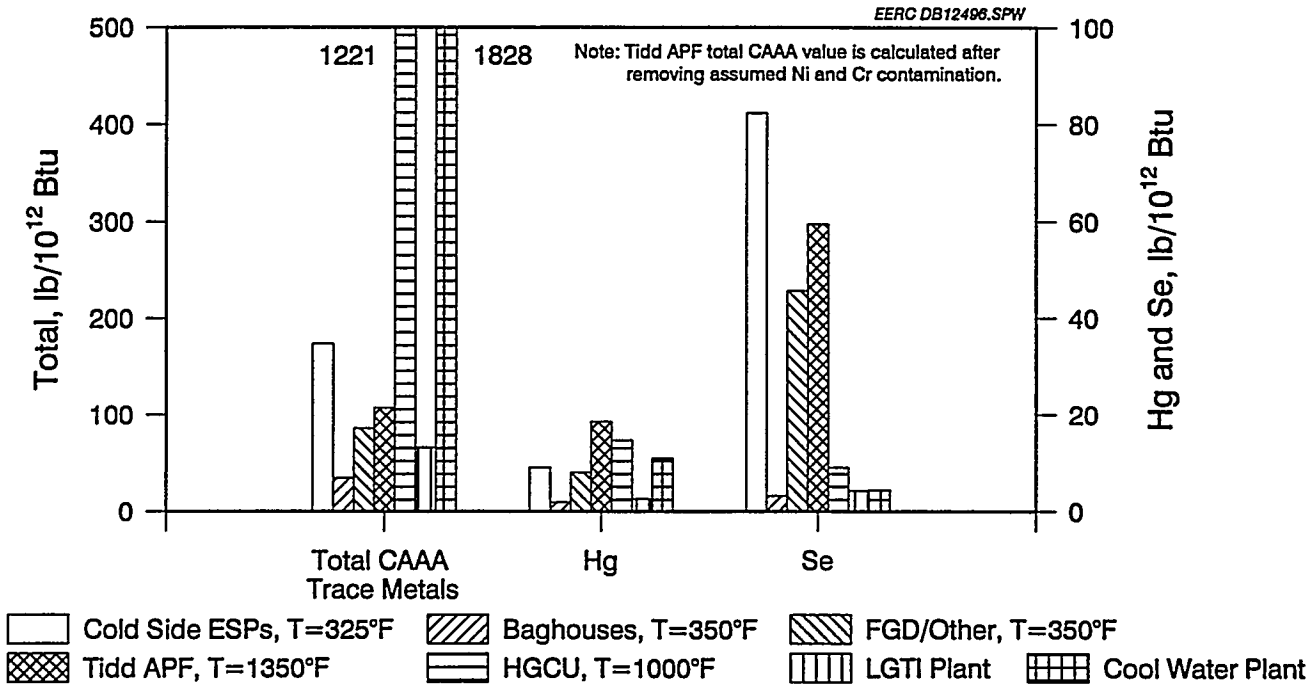


Figure ES-2b. Summarized emission factors for all 11 CAAA trace elements, Hg, and Se with the Tidd APF total CAAA value corrected for contamination of Cr and Ni.

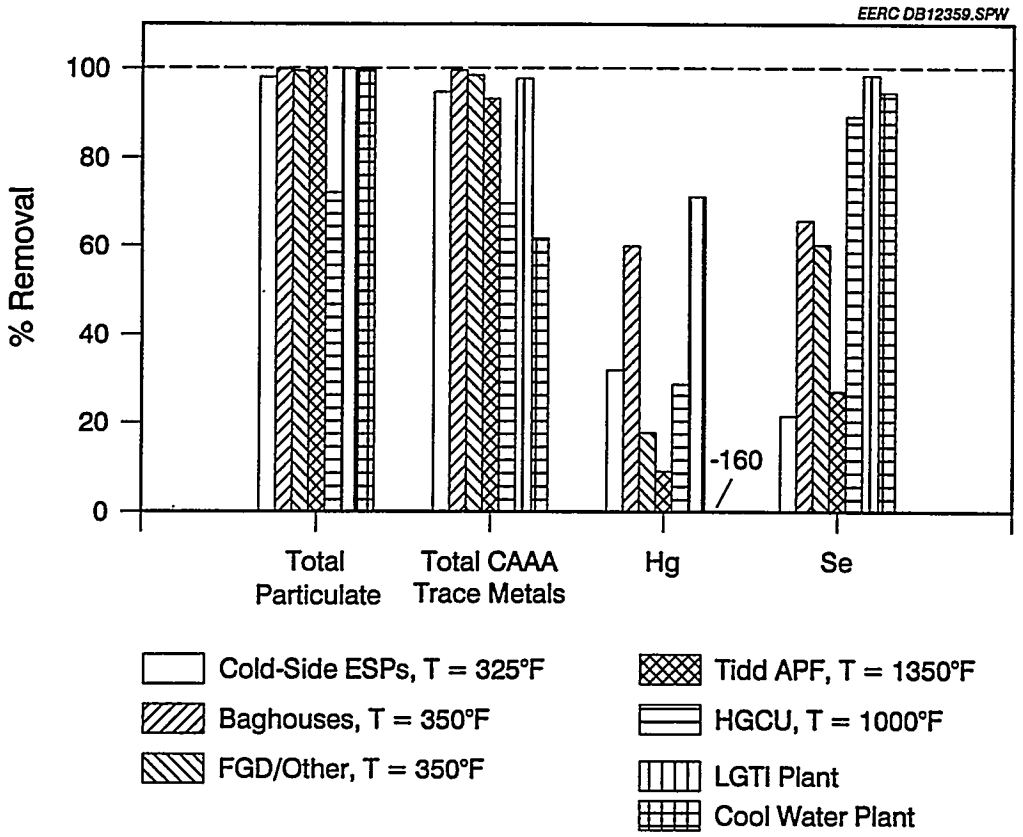


Figure ES-3. Average collection efficiency for all 11 CAAA trace elements, Hg, and Se for both conventional and advanced control systems.

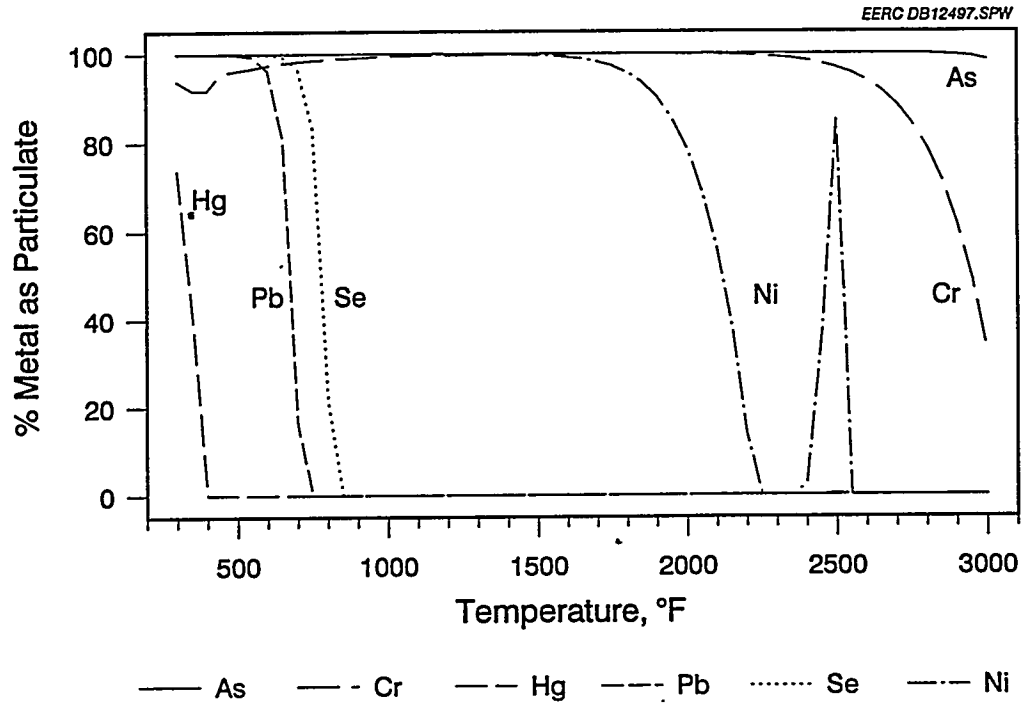


Figure ES-4. Amount of each element present as particulate as a function of temperature under typical combustion conditions as simulated for the Tidd PFBC system at 20 atm.

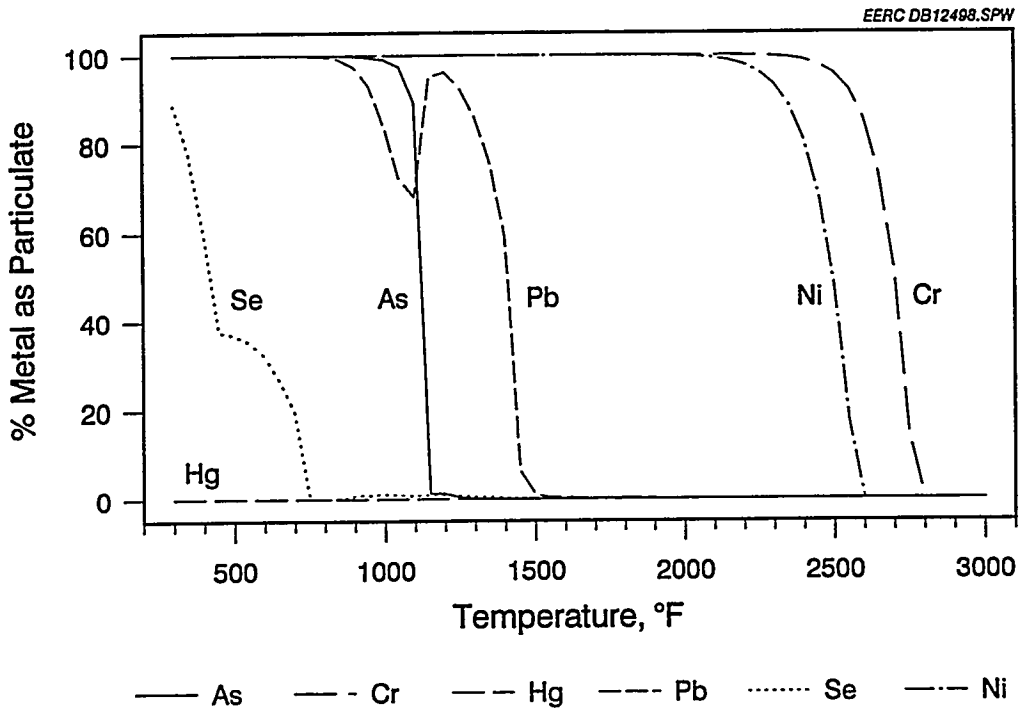


Figure ES-5. Amount of each element present as particulate as a function of temperature under typical combustion conditions as simulated for an entrained-flow gasifier at 20 atm.

maximum achievable control technology to their system to meet the regulations. It is assumed that advanced systems will be governed under regulations derived from the results of conventional system testing.

Assuming that only the Tidd APF and LGTI data sets are valid, the overall emission of trace elements from advanced power systems appears to be equal to or lower than that of conventional systems, on average. All systems fall below one ton of emission per year. The only area of concern is likely the emission of mercury from the advanced power systems. Regulation of mercury is to be expected because of its environmental and health risks. Informal reports indicate that the EPA believes there is significant mercury contamination of lakes from air deposition and that coal-burning power plants are one of the major sources. Since the Tidd APF and other future advanced technologies will operate at temperatures exceeding conventional technologies, it is anticipated that mercury emissions will be an issue.

Recommendations for Future Work

The following is a list of recommendations for future work involving the evolution of advanced power systems into proven, environmentally safe coal conversion systems. These recommendations are given in order of importance as determined by the authors of this report.

- **Control of Mercury in Advanced Combustion Systems.** Since mercury is likely to be regulated, notwithstanding its low concentration, a suitable method of control must be

identified for advanced power systems. For the current gasification systems using low-temperature cleanup devices, this does not appear to be a problem. As systems switch to high-temperature cleanup technologies, this will become a problem. In PFBC systems, this problem is evident from the sampling around the APF. Research should focus on the use of high-temperature mercury sorbents (possibly scrap metals) in both oxidizing and reducing environments and on the economics of placing low-temperature mercury cleaning systems prior to stack emission (now being developed for conventional combustion systems).

- **Development of Sampling Techniques for Use in Reducing Environments.** To fully research the impacts of cleanup technologies on trace elements, an effective technique to quantitatively sample trace elements is needed. The technique may be either a modification to the existing EPA Method 29 technique or a completely new one. Until such a technique is found, all gasification system sampling for trace metals should be limited to the fully oxidized gas streams (flue gas exiting turbines and incinerators). The most near-term solution to this sampling problem may be to oxidize the gas stream after particulate removal and prior to impinger sampling. A second filter should be located just prior to the impingers to capture any metals that condense during the oxidation. The overall gas-phase concentration can then be calculated from the second filter and the impingers. Optional methods of oxidizing the gas stream include installing a burner or passing the gas over/through an oxidizing catalyst (platinum) with excess oxygen.

- **Need for More Data.** Much of the information presented within this report is based on a limited amount of data, of which a large part is significantly flawed. Considering the imminent arrival of clean coal technologies, it is recommended that an initiative be undertaken to sample emissions from numerous advanced power systems. Internal process measurements should also be mandated, but only if the appropriate sampling techniques exist. The use of ceramic filters should be monitored closely for mercury control as noted in the first recommendation. All sampling projects should be very structured including validation of sampling and analysis prior to initiation.

- **Use of Modeling to Aid in Research.** In cases where data do not exist or sampling methods are not yet appropriate, thermochemical equilibrium modeling can be performed to aid in research. Thermochemical equilibrium predictions can support the development of sampling techniques by identifying species present and can assist in the design of hot-gas cleanup systems where it can be used to predict points of condensation and particulate capture. Models do not replace advanced research, but rather help focus the research to provide answers at a lower cost.

ASSESSMENT OF HAZARDOUS AIR POLLUTANTS FOR ADVANCED POWER SYSTEMS

1.0 INTRODUCTION

1.1 Background

The 1990 Clean Air Act Amendments (CAAA) identified 189 substances as air toxics or hazardous air pollutants (HAPs). Under the CAAA, the U.S. Environmental Protection Agency (EPA) must regulate emissions of these HAPs at their sources, including advanced power systems used for the production of electricity. Eleven trace elements are listed in the CAAA list of HAPs (shown in Table 1-1). Under the CAAA, the EPA will define those sources that require regulation and limit their emissions according to regulatory directives.

This project focused on evaluating and manipulating the advanced power systems HAP data currently available for presentation to the U.S. Department of Energy (DOE). The data were analyzed for trends associated with emission control systems and operating conditions. This project was an addition to an existing DOE program entitled Trace Element Emissions (TEE), which is being conducted by the Energy & Environmental Research Center (EERC). The purpose of this addition is to evaluate the current results of HAP emissions sampling from full-scale and demonstration units employing advanced power or hot-gas cleanup systems.

TABLE 1-1

Trace Components Included in the 189 HAPs of the 1990 CAAA

Antimony Compounds	Arsenic Compounds	Beryllium Compounds
Cadmium Compounds	Chromium Compounds	Cobalt Compounds
Lead Compounds	Manganese Compounds	Mercury Compounds
Nickel Compounds	Selenium Compounds	

1.2 Goal and Objectives

The goal of this project was to assess the fate of HAPs in advanced power generation systems and make recommendations regarding potential control approaches based on available information.

The specific objectives of this program are to 1) perform a technical review and assessment of the data accumulated on the fate of trace metals in advanced coal power systems and compare them to emissions from conventional coal-fired power plants, and 2) assess the effectiveness of conventional and innovative control technologies relative to potential regulation requirements.

1.3 Description of Systems

Data from three advanced power systems and two advanced cleanup technologies were evaluated. The power systems include the Tidd Station pressurized fluidized-bed combustion (PFBC) system (American Electric Power Service Corporation),[1] the Louisiana Gasification Technology Incorporated (LGTI) entrained-flow gasifier (Destec),[2] and the Cool Water entrained-flow gasifier (Texaco).[3] The cleanup technologies include the Tidd advanced particle filter (APF)[1] and the General Electric hot-gas cleanup (HGCU) zinc titanate system.[4] Table 1-2 lists these plant-site configurations. Trace metal data were compared between the various technologies and compared to data from conventional coal-fired power systems. Table 1-3 lists configurations of the nine conventional coal-fired power plants that were used for comparison, as well as the operational information for the advanced control systems. Additional information for the conventional power systems can be found in the site reports[5-13] or within the project review materials for the entire conventional systems sampling effort.[14, 15]

TABLE 1-2

Advanced Power Systems and Cleanup Technologies

Name	System Type	System Description	Particulate Control	Sulfur Control
Tidd	PFBC[1]	Bubbling-bed PFBC	Two-stage cyclone/ ESP[2]	Dolomite bed
Tidd	APF[3]	Barrier filter	Cyclone/ceramic barrier APF	None
LGTI	IGCC[4]	Entrained-flow, oxygen-blown, two-stage, slagging gasifier	Venturi scrubber	Selectamine® absorber
GE HGCU	IGCC, turbine simulator	Pressurized, air-blown, fixed-bed gasifier	Cyclones	Zn titanate sorbent with regenerator
Cool Water	IGCC	Entrained-flow, oxygen-blown, slagging gasifier	Water scrubber	Selexol absorber

[1] Pressurized fluidized-bed combustor.
[2] Electrostatic precipitator.
[3] Advanced particle filter.
[4] Integrated gasification combined cycle.

TABLE 1-3

Operational Information and System Design for Conventional and Advanced Systems

Plant:	Yates Plant Unit No. 1	Cardinal Plant Unit No. 1	Boswell Energy Center Unit No. 2	Baldwin Power Station Unit No. 2	Coal Creek Station Unit No. 1	Niles Station Unit No. 2	Niles/SNOX	Springerville Generating Station Unit No. 2	Bailly Station Units No. 7 and 8	Tidd Station ESP Unit	Tidd Station APF Unit	General Electric HGCU
Location	Newnan, GA	Brilliant, OH	Cohasset, MN	Baldwin, IL	Underwood, ND	Niles, OH	Niles, OH	Springerville, AZ	Chesterton, IN	Brilliant, OH	Brilliant, OH	Schenectady, NY
Furnace Type	Tangentially fired, dry-bottom	Opposed wall-fired, dry-bottom	Front-fired, dry-bottom	Cyclone-fired	Tangentially fired divided, dry-bottom	Cyclone-fired	Cyclone-fired	Tangentially fired, dry-bottom	Cyclone-fired	PFBC	PFBC	PFBC
Fuel	Illinois No. 5–Illinois No. 6 bituminous blend	Pittsburgh No. 8 bituminous	Powder River Basin subbituminous	Illinois bituminous	North Dakota lignite	Pennsylvania–Ohio bituminous blend	Pennsylvania–Ohio bituminous blend	New Mexico subbituminous	Illinois–Indiana bituminous	Pittsburgh No. 8 bituminous	Pittsburgh No. 8 bituminous	
Particulate Control	ESP	ESP	Baghouse	ESP	ESP	ESP	Baghouse	Baghouse	ESP	ESP	Advanced particle filter	Primary and secondary cyclones
Particulate Control Unit Operating Temperature	280°F	300°F	350°F	335°F	320°F	300°F	390°F	180°F	310°F	400°F	1350°F	1000°F
SO_2 Control	Jet-bubbling reactor (JBR)	None	None	None	Wet flue gas desulfurization	None	Wet-gas sulfuric acid (WSA)–selective catalytic reduction of NO_x (SNOX)	Spray dryer absorbers	Advanced flue gas desulfurization (AFGD)	None	None	HGCU
NO_x Control	Tangential-firing	None	None	None	Tangential-firing–overfire air	None	WSA–SNOX	Tangential-firing–overfire air	None	None	None	None

2.0 REVIEW OF SAMPLING PROCEDURES

2.1 Plant Sampling

The sampling procedures used at all of the plant sites generally conformed to established sampling methods. At all four of the sites, the contractor for sampling and testing was Radian Corporation. Sampling strategy at the sites was normally consistent with the DOE programs under which these plants were studied. Since each plant has a unique system and configuration, the methods were slightly different for each plant. Modifications or adaptations to the methods were necessary in some instances because of product gas compositions, temperatures, and trace metal content in the apparatus disposables. Each contractor described the particular methods and modifications applied to a plant in individual reports. Specifics of the primary methods used in the sampling are discussed below. Process stream flow rates in volumetric or mass units were determined at sampling points where possible. Limitations on system access or low accumulation problems prevented the furnishing of several measured rates in the reports. Determination by estimation or by difference was necessary in order to calculate mass balances, removal efficiencies, and emission factors. This necessarily introduces error in some of the calculations in this report.

Solid-, liquid-, and gas-phase samples were collected at various points in the systems. The locations of individual sampling points varied somewhat among the plants according to site-specific characteristics. The solid-phase samples were generally periodic grab samples taken so as to obtain a composite. Other samples were taken as filters from flue gas sampling trains. Solid samples included various coals, boiler-related ash and slag, and cleanup device ash, sorbents, and by-products. Liquid samples included slurry and sluice streams. Unless no other data were available, this report usually ignores liquid composition and instead uses the slurry/sluice solids values in calculations. Gas samples were generally limited to flue gas at the particulate control inlet and outlet, in the stack, and at an incinerator, if applicable. The gas phase was typically sampled using isokinetic techniques and both the vapor phase and the entrained particulate were collected.

The primary methods used to obtain samples from flue gas streams were EPA Method 5[16] and Method 29.[17] Particulate emissions were normally measured using Method 5. The major modification to this method was the use of a quartz filter instead of borosilicate glass, which reduced the amount of trace metals in the collection medium. The multimetals sampling train technique, Method 29, was used to collect trace metal samples of the flue gas. This technique involves a filter and a series of impingers. However, the procedure is designed for oxidizing conditions and has not been validated for use in reducing environments. Gases such as H_2S, CO, and H_2 rapidly deplete the oxidizing capacity of the impingers, and the train fails to retain the vapor-phase metals. Sampling procedures for reducing environments are discussed in more detail in Section 2.2. The poor mass balances calculated around system units under reducing conditions can largely be attributed to this.

The sampling portion of each project is critical to the success of the systems evaluation. Every project and project site in the various studies under consideration had a problem somewhere in the sampling process that either produced data that was of poor quality or simply failed to collect data at all. Part of the problem can be attributed to sampling point access at the plant sites where relevant data can be collected free of difficulties due to temperature, moisture, duct cross-sectional area and turbulence, low mass flow, or uncontrolled mass flow. The poor data quality from the

reports is in part attributable to the previously mentioned reducing gas problem with Method 29 and in part to particulate filter breakthrough, vapor condensing in sampling lines, use of stainless steel sampling lines, impinger train breakage, incomplete cleaning of sampling devices between runs, and plant system unit excursions and breakdowns. Problems associated with the overall approach to the sampling activities at each site are discussed separately below. Detailed sample-to-sample information is found in the original site reports.

Tidd Station – The sampling performed at the Tidd site followed all of the standard techniques used for conventional combustion systems. No significant sampling problems were found, with the exception of potential stainless steel contamination at the outlet of the APF. The Tidd plant was one of the more simply configured systems and that is reflected in the data quality.

GE HGCU – This sampling effort was flawed in three different manners: 1) the modified Method 29 sampling train used for vapor-phase species was not designed for reducing gases, and the results are extremely suspect, indicating poor metals capture in the impingers; 2) the sampling activity involved numerous mechanical errors, including breakdown of filters and contamination from sample to sample from insufficient cleaning; and 3) only two sets of data were taken and the results between them varied significantly. In addition, no samples were taken within the sorbent regeneration stage, which did not allow any assumptions of concentrations by difference. Appendix A contains correspondence from Dr. Feitelberg of General Electric discussing the problems. Results for this system are included within this report, though great caution must be used in evaluating this data.

LGTI – Sampling of the few available oxidized streams within the LGTI plant were conducted by standardized techniques and the results were favorable. Reducing atmosphere sampling was done primarily with a modified version of Method 29. This modified Method 29 technique is highly suspect with regard to satisfactory results for reducing gases; thus all internal stream measurements are suspect. Radian performed comparisons of Method 29 with packed charcoal tube absorption and direct measurement with a modified atomic absorption spectrometer. The results between the techniques vary widely. Some additional (Phase 2) testing was done with these techniques that showed more favorable results, but still produced discrepancies.

Cool Water – The IGCC system at Cool Water is very complex. Throughout the life of the plant, many modifications were made to the configuration of the internal streams. Extracting data from sampling points with the same plant configuration was not possible in all cases. Evaluation of internal system units was also hampered by incomplete sampling. Either particulate values or flue gas values were missing from element concentration data in a few key sampling points. Gasifier flue gas flow rates were not taken at the sampling point where analytical data existed. There was some indication of material accumulations in individual process units. All of these factors tend to make calculations of mass balance and gas partitioning unreliable. The report also

showed no data quality indicators, and calculation of these was not possible since only mean value results were given and run data was unavailable. No indication of sampling technique quality assurance/quality control (QA/QC) was given in the report.

2.2 Sampling in Reducing Environments

Most of the methods currently employed to analyze HAPs within coal conversion systems were developed for use in combustion systems, that is, under oxidizing conditions. EPA Method 29 is the technique most commonly used to sample for vapor-phase trace elements. The trace metals are normally found in the oxidized form in combustion gases, but in gasifier systems the metals could be in the form of hydrides or carbonyls or conceivably in elemental form. Because of the reducing potential and caustic nature of the gas within a gasification system, the impinger solutions do not effectively capture the trace elements. The inferior quality of mass balances and other performance factors calculated around internal system units that operate under reducing conditions can largely be attributed to this.

In sampling the LGTI facility, Radian attempted to compensate for the problem associated with reducing atmospheres by increasing impinger solution concentrations, adding a caustic scrubber, and trying two completely different sampling techniques. The basic Method 29 was modified by increasing the hydrogen peroxide concentration in the first two impingers to 30% from 10%. Also, the permanganate impingers were not used in streams with high H_2S, since mercury was to be determined by either of the two new experimental methods. Radian experimented with sampling by using charcoal traps and on-line atomic absorption spectroscopy (AAS). The traps consisted of a quartz tube packed with aggressively cleaned coconut-based charcoal. Two of the units were connected to a particle-free slipstream. Relevant species targeted for quantification by this method included Sb, As, Pb, Hg, and Ni. The charcoal traps, though better than Method 29, also appeared to show low concentrations of trace metal species. In the other technique, selected vapor-phase metals were determined directly by AAS. A slipstream of product gas from the LGTI sour and sweet syngas locations was substituted for a portion of the instrument fuel gas. Species targeted for quantification by this method included As, Cd, Ni, Hg, Cr, Pb, and Se. This technique tended to yield the highest values of the three methods, although the detection limits also tended to be high. The on-line AAS technique may be promising, but first, additional elements need to be investigated and lower detection limits must be achieved. In a separate experiment, Radian attempted mercury speciation measurements in reducing gas streams using a gold amalgamation–cold-vapor AAS apparatus (CVAAS) in concert with various impinger solutions. It appears that this method captured the most mercury of all the sampling techniques. Details of the various techniques can be found in the site report.[2]

The results from these technique variations produced values differing by several orders of magnitude. Method 29 produced the lowest values and the on-line AAS yielded the highest values for selected trace metals. Table 2-1 gives some results of Radian's testing program for selected trace metals. None of the three methods has been validated for use in reducing gas environments. In general, if sampling in reducing environments is desired, a concentrated effort must be made to develop a technique for performing adequate sampling.

TABLE 2-1

Trace Metals Analysis Method Comparison

Element	Sour Syngas, $\mu g/m^3$			Sweet Syngas, $\mu g/m^3$		
	Charcoal	Method 29	On-line AAS	Charcoal	Method 29	On-line AAS
As	270	0.5	870	6.0	0.423	<2200
Cd	<0.85	0.27	<2.2	<0.03	0.44	9.5
Cr	93	1.6	142	3.6	1.4	<39
Ni	17	2.3	500	0.94	1.2	19
Se	2.8	0.18	560	0.18	0.26	200
Hg[1]	11	0.8	3.2–6.1	0.1	0.2	3.0–3.8

[1] Mercury was determined by modified Method 29 (increasing first two impinger concentrations) and the gold amalgamation–CVAAS method.

3.0 REVIEW OF ANALYTICAL TECHNIQUES

The analytes for which sampling and analysis were specifically requested by DOE includes trace metals, major elements, radionuclides, anions, inorganic compounds, and organic compounds. These elements and compounds are the 189 HAPs listed in the 1990 CAAA. The discussions in this report are limited to the 11 trace metals present in the CAAA list.

A variety of accepted analytical techniques were used to quantitatively determine the analytes. The sample preparation methods and analytical techniques used for the various collected samples were generally consistent among the reports. Deviations from overall analytical plans were minor. A description of the analysis methods applied to specific samples are in the individual contractor reports. The techniques included several atomic absorption spectroscopy methods (AAS, CVAAS, graphite furnace atomic absorption spectroscopy [GFAAS], hydride generation atomic absorption spectroscopy [HGAAS]), inductively coupled plasma methods (inductively coupled plasma–mass spectroscopy [ICP–MS], inductively coupled plasma–Auger electron spectroscopy [ICP–AES]), ion chromatography, and selective ion electrode analysis. Standard coal analysis procedures were applied to the fuel feedstock. In a few instances, contractors decided to use x-ray fluorescence (XRF) or instrumental neutron activation analysis (INAA or NAA) either as a screening tool or to expedite the analysis of major elements.

QA/QC information is related to measurement precision, accuracy, and blank effects. The types of samples used to determine data quality include replicate, duplicate, various analytical and sampling blanks, and various spiked samples. Site-specific QA/QC plans were developed at the individual plant sites, and details can be found in the plant reports. All sites generally followed the same reporting conventions. However, not all sites collected data from the same number of runs. Data from less than three runs would necessarily increase the data quality indicators.

Data quality indicators were present in all of the reports except Cool Water. The data presented in the Tidd report were the most complete of the data sets. The GE HGCU data were based on only two runs and additionally suffered from the sampling problems mentioned earlier. Although there is extensive data from the LGTI site, including QA/QC information, sampling problems made much of the internal stream data suspect. Both the Tidd and GE HGCU reports were reviewed for their use of data manipulation and statistical procedures. A statistical method similar to that used for the Tidd report was derived for use for these data. As a result of the uncertainty in estimating sampling and analytical bias without a large test matrix, and since the analytical reproducibility is assumed to be large compared to the sampling and analytical bias, the biases were ignored. Any values produced from "not detected" values were adjusted proportionately for the number of those values present. It is notable that duplicate analyses were performed only in the GE HGCU testing, and their reproducibility was very poor for many of the compounds quantified. The LGTI and Cool Water data did not undergo quantitative error estimates because of lack of information or the inability to truly estimate the analytical and sampling bias from the Method 29 technique. In the case of emission factors, error limits are not shown because for most of the systems they would be grossly inaccurate because of the inappropriate sampling and voluminous assumptions made.

4.0 ASSESSMENT OF THE IMPACTS OF ADVANCED POWER SYSTEMS ON THE ENVIRONMENT

This section of the report reviews the impact of the coal conversion technique on trace elements arriving at the gas cleanup system and the overall performance of the plants in controlling the emission of trace elements into the atmosphere. The systems included in this review are the LGTI facility, Cool Water system, and the Tidd plant. For completeness, total emission calculations, presented later in this section, were also performed on the GE HGCU data, assuming that the cleanup system was attached downstream of the Tidd PFBC.

4.1 Impact of Coal Conversion Technology

Coal conversion systems vary in their temperature, pressure, gas flows, and length of contact between solids and gases. Since each system is different, it is expected that each system will have a different impact on trace element emissions. Results from each of the three advanced power systems are outlined below. Detailed specifications for the plants can be found in the individual site reports.

4.1.1 Tidd Plant

The unit at the Tidd plant consists of a PFBC firing Pittsburgh No. 8 coal. The gases exiting the PFBC pass through a primary cyclone and are then divided into two streams. One stream carries six-sevenths of the flue gas, which then passes through a secondary cyclone, while the remaining flue gas passes through an APF. The gas streams are recombined prior to entering a gas turbine followed by an electrostatic precipitator (ESP) and then emitted to stack. The PFBC utilized a dolomite sorbent for this testing period. The data generated from the Tidd PFBC system are shown in Figures 4-1 through 4-3. In addition to the Tidd PFBC, the Cardinal station

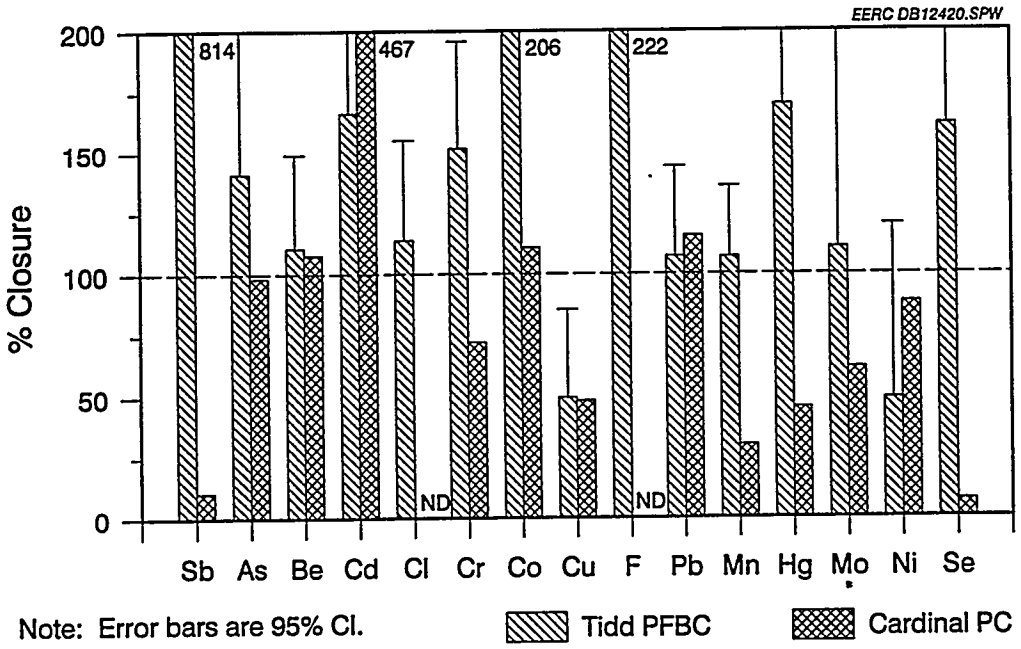


Figure 4-1. Mass balance of selected elements from the Tidd PFBC and Cardinal pc-fired "boilers." ND = not detected.

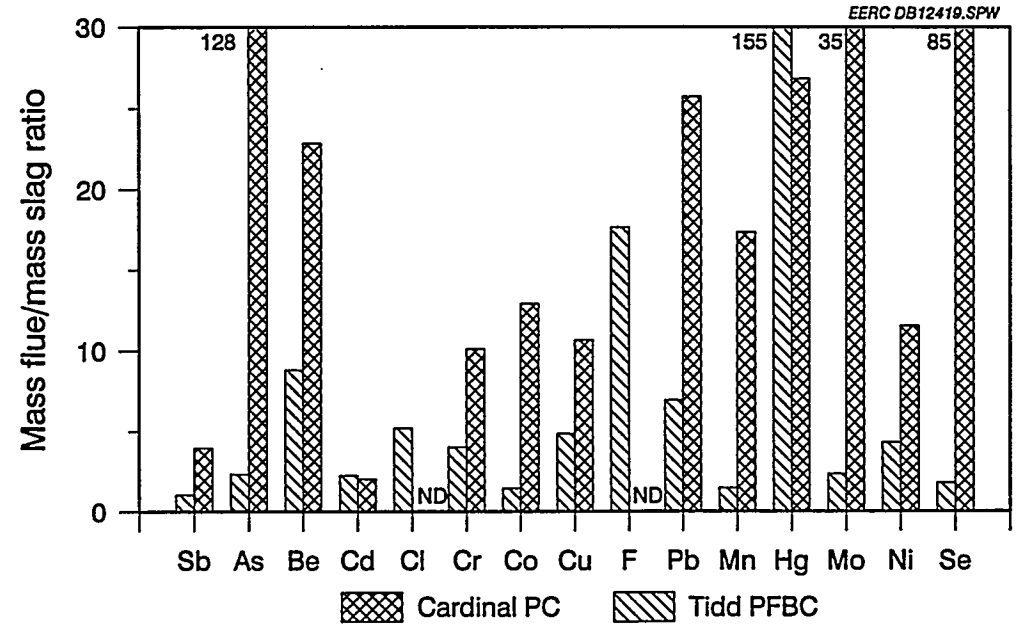


Figure 4-2. Partitioning of ash within the "boiler" for the Tidd PFBC and the Cardinal pc-fired units. The partitioning factor is equal to the ratio of the mass of element in the flue gas to the mass in the bottom ash. ND = not detected.

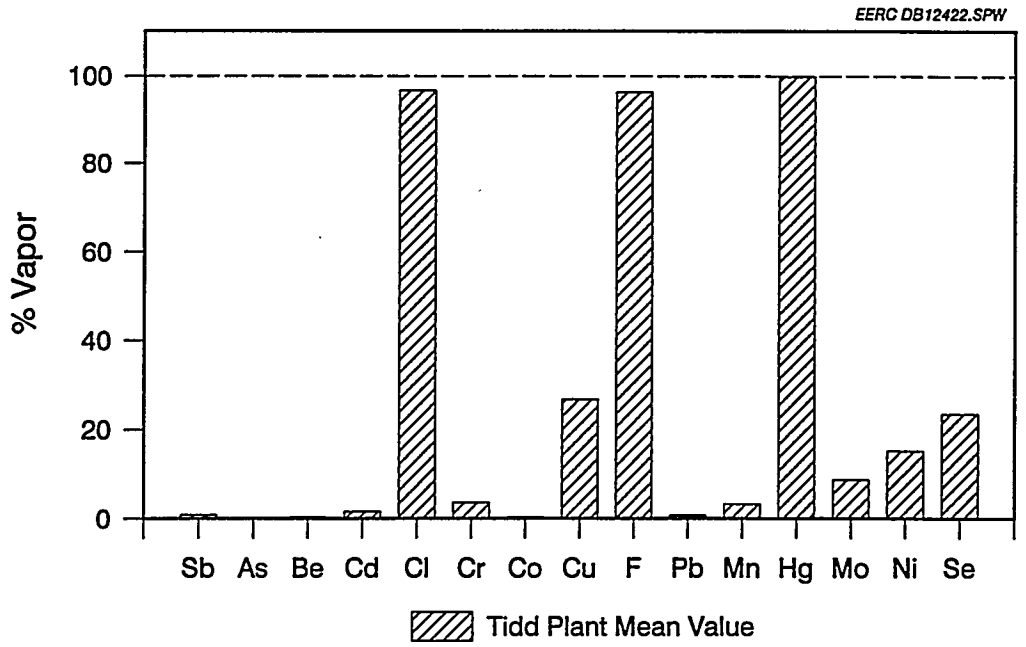


Figure 4-3. Percentage of a given element leaving the Tidd PFBC in the vapor state.

conventional pulverized coal (pc)-fired unit is also shown. The Cardinal station unit was sampled as part of a separate DOE project. The two systems burn the same coal, making comparisons meaningful. For the purpose of calculation, the PFBC "boiler" is assumed to include all input and output streams between the coal and sorbent feeds and the flue gas stream exiting the primary cyclone. (Note that the secondary cyclone is not considered part of the PFBC boiler in these calculations.) The error bars shown in the following figures represent a 95% confidence interval (upper end only) of the data as processed.

Figure 4-1 shows a wide range of mass balances for various elements, ranging from approximately 20% to 800%. The trace metals with mass balances within the range of 100 ±25% are Be, Cl, Pb, Mn, and Mo. Elements falling within the 50% to 200% range include the above as well as As, Cd, Cr, Cu, Hg, and Se. Ni, Sb, F, and Co show either less than 50% or greater than 200% closure. In general, the absolute validity of these measurements is questionable with such a large variability. However, mass balance closures of this sort are not uncommon in full-scale measurements. The mass balance of the major species (not shown here) from the PFBC ranged between 50% and 300%. Most of the major elements fell within the accepted range of 100 ±25%.

The ash partitioning of the various elements between the flue gas and the bottom ash, Figure 4-2, shows that many of the trace species are enriched in the flue gas stream compared to the bottom ash stream. The following elements show a partitioning factor of >3 (that is, >75% entered into the flue gas stream): Be, Cl, Cr, Cu, F, Pb, Hg, and Ni. All of the species shown have a partitioning factor greater than 1. Only calcium and magnesium (not shown here) had

partitioning factors of less than 1, and they are chiefly from the sorbent and would be easily captured by the primary cyclone.

"Vapor-phase partitioning" refers to the partitioning of the flue gas leaving the PFBC system (after the primary cyclone) as vapor or particulate species, shown in Figure 4-3. The Cl, F, Be, and Hg are all present primarily as vapor-phase species, while Cu, Mo, Ni, P, and Se are partially in the vapor phase. The remaining species are primarily present as particulate phases. The partitioning between vapor and particulate phases is important with respect to the ability of a control technology to capture a given trace element.

Comparison of PFBC and Cardinal Station

For comparison purposes, the data from the Cardinal station pc-fired boiler is shown with the Tidd PFBC system in Figures 4-1 and 4-2. Both of these systems use the same coal as a feedstock, making them easily comparable.

The mass balances around the Tidd PFBC and Cardinal station pc-fired boiler are both poor. Considerable amounts of deviation also existed among the major species at the Cardinal station, which provides evidence of problems with the sampling and analysis techniques.

The partitioning of ash between the bottom ash and the flue gas for both systems is shown in Figure 4-2. In all cases except mercury, lower quantities of trace elements are escaping into the flue gas of the PFBC than for the pc-fired unit. The mercury is very high in both cases. Although only two systems are being compared, and the mass balances showed poor-quality data, the overall implication is that a PFBC sends less ash and fewer trace elements to the cleanup systems than does a pc-fired system. The temperature at the outlet of a PFBC is about 1100°F, while it is about 1900°F at the nose of a pc-fired system where the partitioning occurs. In addition, the PFBC uses a primary cyclone for the partitioning, while the pc-fired system uses only separation by gravity within the box of the boiler.

4.1.2 LGTI Plant

The LGTI system comprises an oxygen-blown, entrained-flow gasifier with a venturi scrubber for ash removal (the ash from the scrubber is recycled into the gasifier so all ash leaves as slag). After the venturi scrubber, the gas is cooled and passed through the Selectamine® process to remove the sulfur, then to a gas turbine and out to the stack. The results pertaining to the LGTI gasifier system are shown in Figures 4-4 and 4-5. The "gasifier" in this case is assumed to include the gasification vessel as well as the venturi scrubber. Each of the graphs have been generated using both the modified Method 29 (a) and charcoal trap (b) data; thus there are two different graphs for each figure.

The overall mass balance around the gasifier, Figure 4-4a, shows that many of the elements of interest have low closures. The closure for As, Cd, Cl, F, Pb, Hg, and Se are all less than 50%, as calculated with the modified Method 29 data. Since Method 29 is assumed to be a poor collector of trace metals in reducing environments, the low mass balances are expected. The same mass balance calculations were performed using the charcoal trap data, Figure 4-4b, and the results are very similar.

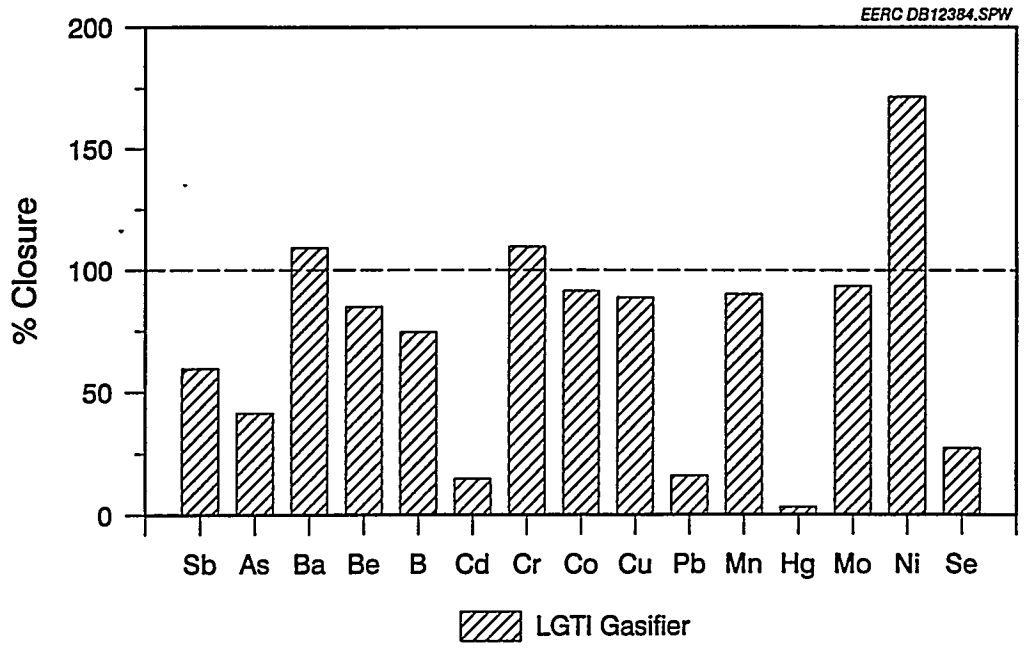


Figure 4-4a. Mass balance around the "gasifier" at the LGTI facility from data generated using Method 29 sampling results.

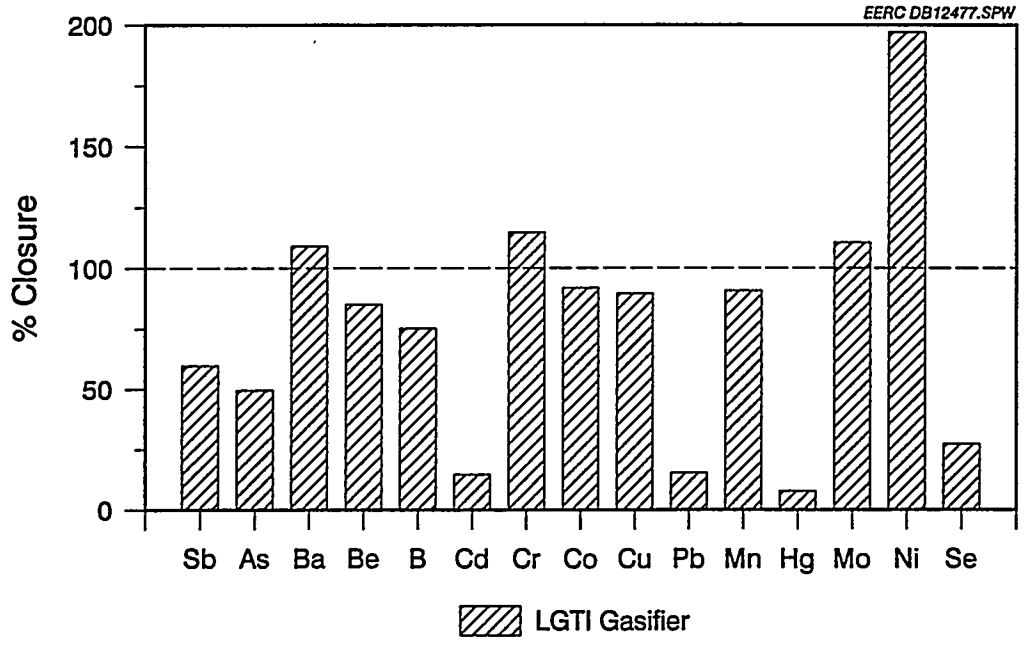


Figure 4-4b. Mass balance around the "gasifier" at the LGTI facility from data generated using charcoal trap sampling results.

The partitioning of the elements between the product gas and the slag are shown in Figures 4-5a and 4-5b for the modified Method 29 and charcoal trap data, respectively. Virtually all of the elements show partitioning to be less than 0.5, with the exception of Hg. This holds true for both the Method 29 and charcoal trap samples. According to the results, practically all of the elements are partitioning out into the slag and only very minor amounts are being released into the product gas stream. However, since the mass balance of many of the elements are low, the partitioning results may be erroneous. The inability to capture many of the vapor-phase elements in the reducing atmosphere following the gasifier may be the cause of this problem. Similarly, mass balances around the gas turbine show a very large increase of trace elements, which also appears to demonstrate the inability to capture trace elements in reducing atmospheres.

In general, it is believed that all of the data presented in this section may lead to an inaccurate assumption that all of the trace elements are being forced into the slag. Even without supporting data, however, it is more likely that a significant amount of trace elements are leaving in the product gas stream and are not being adequately analyzed. If the difference in the mass balance information were assumed to be due to missed vapor-phase species, then Hg, Pb, Se, F, Cl, Cd, and As would all have partitioning factors greater than 1. However, the resulting partitioning factors would still be generally lower than those for the Cardinal station presented earlier. The true partitioning is expected to lie between the measured and assumed values.

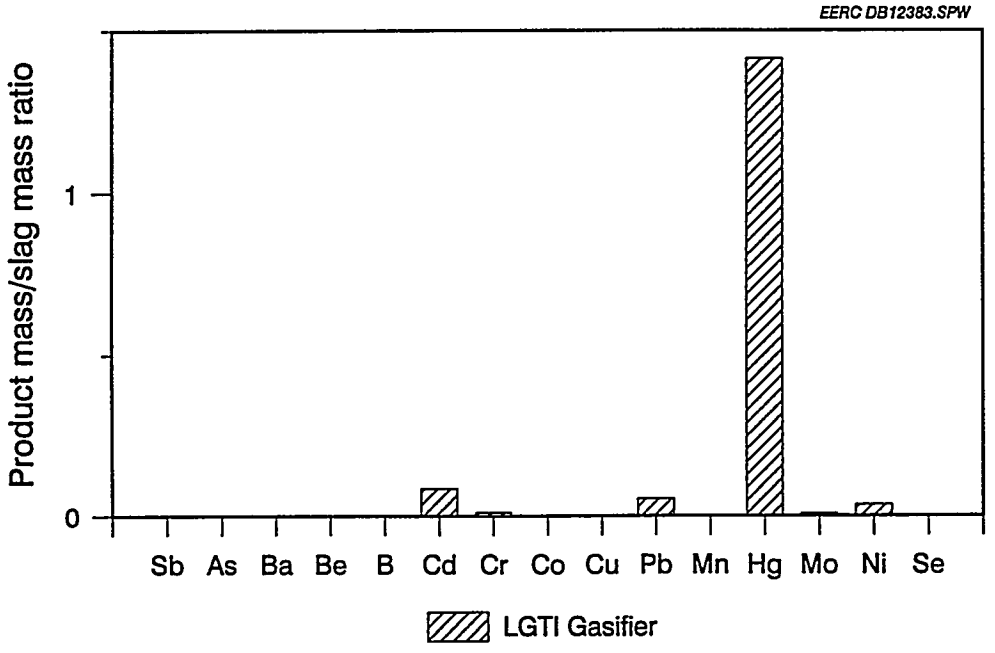


Figure 4-5a. Partitioning of ash within the "gasifier" at the LGTI facility data generated using Method 29 sampling results.

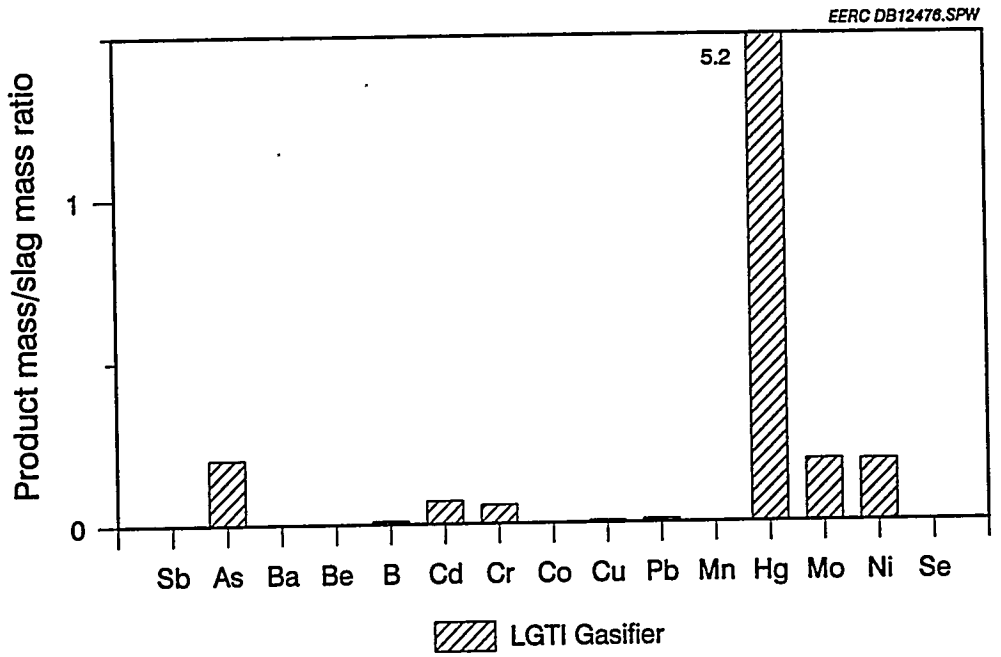
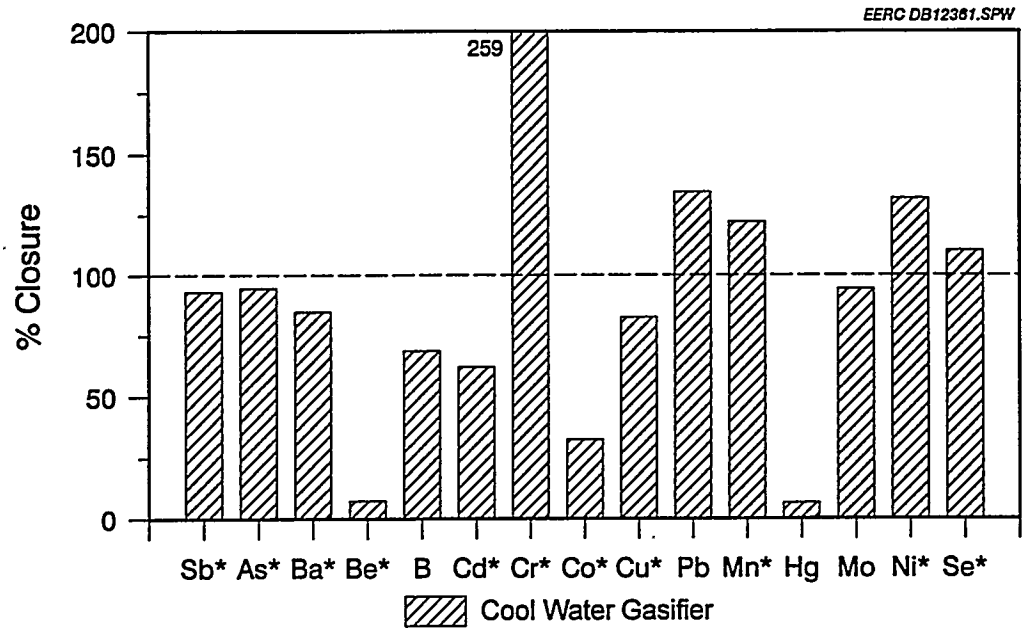


Figure 4-5b. Partitioning of ash within the "gasifier" at the LGTI facility from data generated using charcoal trap sampling results.

4.1.3 Cool Water Plant

The Cool Water plant uses the Texaco coal gasification process. In this system, coal and oxygen are fed into the gasifier. The product gas and ash flow into the waste heat boilers where much of the ash is removed. The gas stream is then scrubbed to remove remaining particulates. The clean product gas is then cooled and run through a sulfur removal process. The resulting gas is directed through a turbine, a heat-exchange system, and then to stack. In addition, an incinerator is used to burn tail gas from the sulfur removal process.

The only calculation performed around the Cool Water "gasifier" is a mass balance, shown in Figure 4-6. Because of insufficient data, no other calculations were performed around the gasifier. Note that for many of the elements of interest, no data were present in the reports for the concentration in the product gas stream exiting the gasifier, resulting in a mass balance biased low. The overall mass balances vary greatly, but are mainly less than 100%, which is probably due to the missing product gas data. The mass balance for Hg is only about 6%. No conclusions can be drawn on the impact of the Cool Water gasifier on the partitioning of the elements. Data quality problems extend to other calculations attempted for this system. Total particulate collection efficiency is good at 99.8%, but the collection efficiency for total CAAA trace metals is only 61% and for Hg alone is a negative 160% (impossible). All results from the Cool Water plant are highly suspect. These results are shown in Section 5.2.



Note: Elements with * flag are missing flue gas values in the calculations.

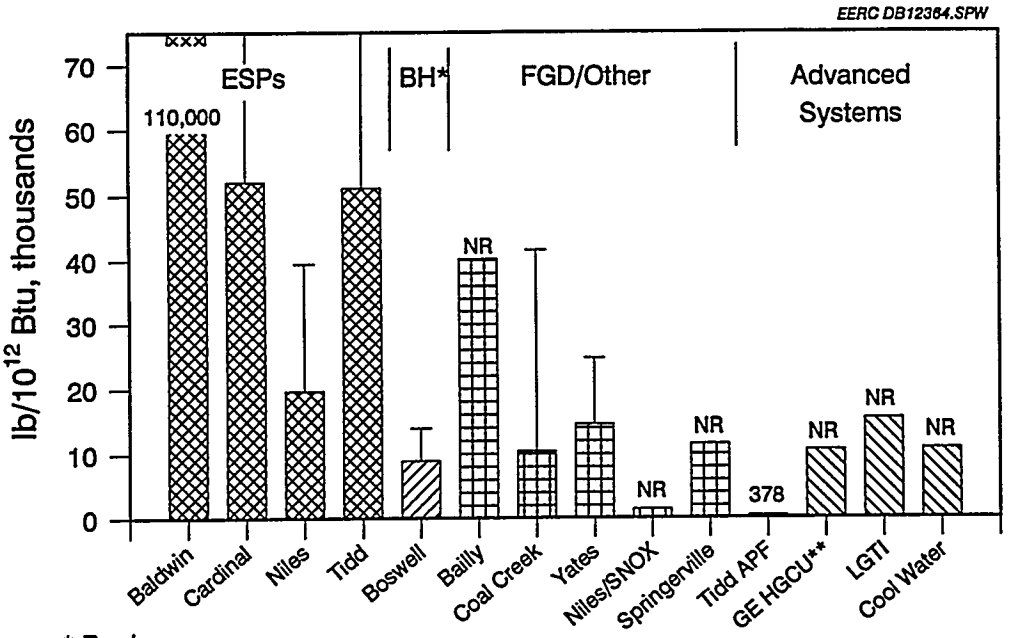
Figure 4-6. Mass balance of elements around the Cool Water gasifier. Note: Elements with * flags are missing flue gas values in the calculations.

4.2 Plant Stack Emissions

4.2.1 Emission Levels for Both Advanced and Conventional Systems

Figures 4–7 through 4–23 display the measured emission levels of total particulate and selected elements for 10 conventional systems and 5 advanced systems. Estimates are included for both the Tidd plant configured with the ESP (the ESP here considered as a conventional system) and as if the Tidd had only the APF configuration. For purposes of comparison, the GE HGCU system is included assuming it was attached to the Tidd PFBC in the place of the APF. Table 4-1 lists the trace elements present in the Clean Air Act Amendments (CAAA) that were measured from the advanced power systems at 'relatively' higher levels than in the conventional systems. Because of the range of variability between the conventional systems, 'relatively' is defined as being greater than 80% (8 of 10) of the conventional systems.

It is noted that the Tidd APF and the LGTI systems are very effective at controlling emissions in relation to conventional systems. The GE HGCU system appears to be very poor, but much of that result is due to the poor quality of the data. The data from the Cool Water system is also significantly flawed and thus highly suspect. As mentioned in Section 4.1.3, the total particulate control for the Cool Water plant was 99.8% while the trace element control was only 61%. The overall trace element sampling and analysis are believed to be in error. The four elements that show higher emission factors in the Tidd system configured with the APF are Ni, Cr, As, and Hg. The Ni and Cr are believed to be from contamination during sampling at the outlet of

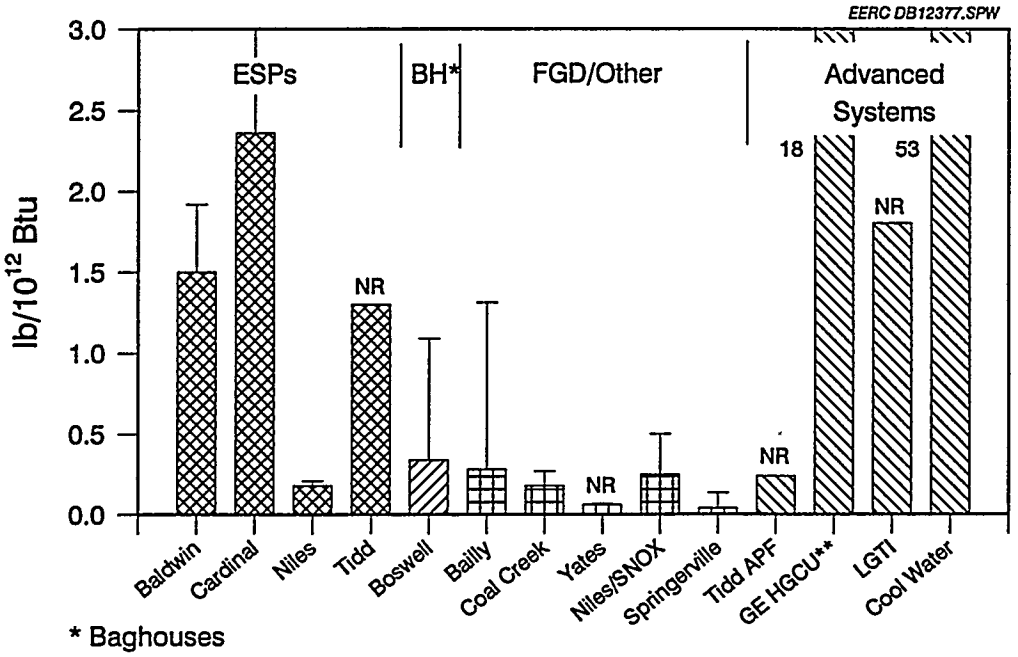


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-7. Total particulate emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

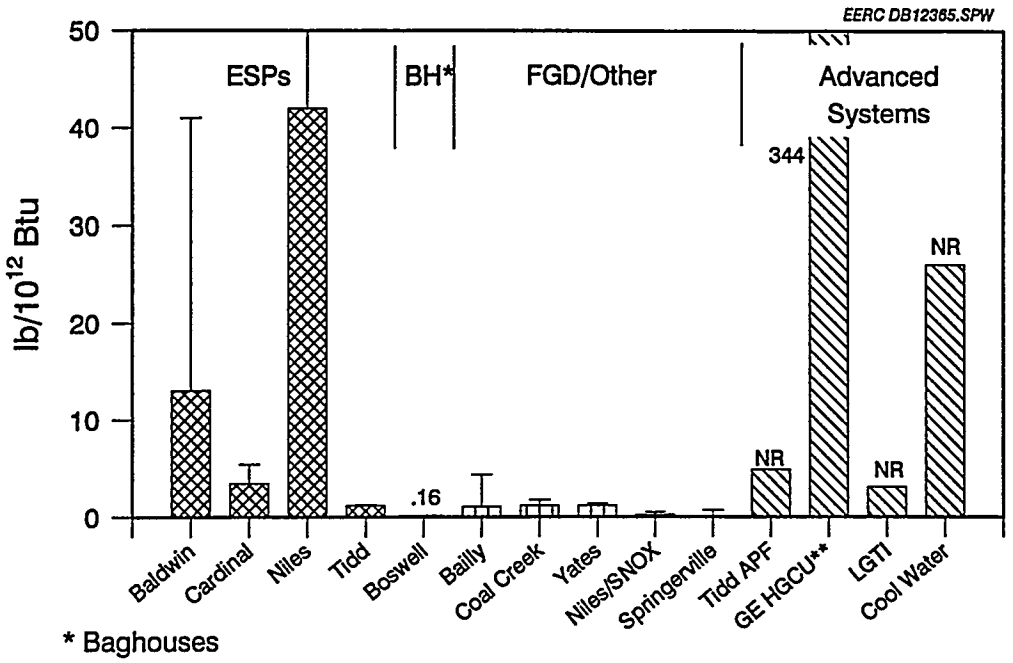


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-8. Antimony emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

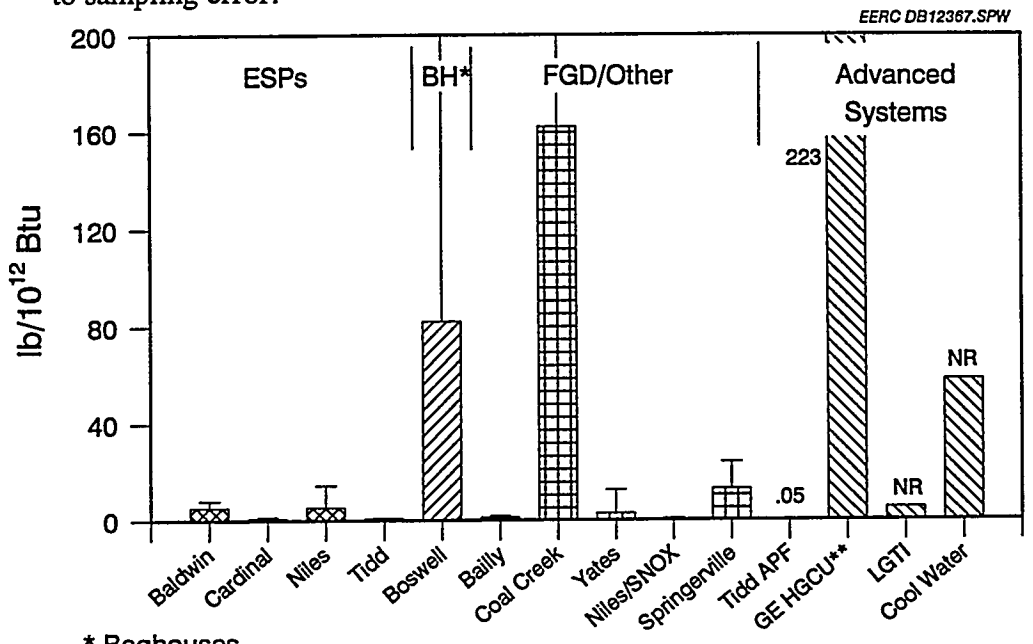


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-9. Arsenic emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

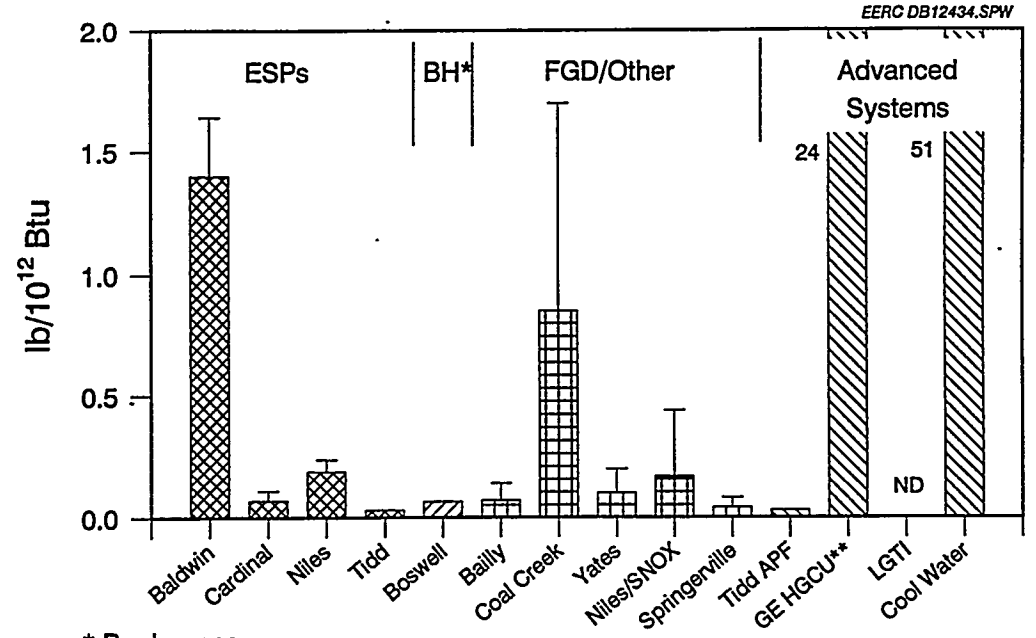


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-10. Barium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

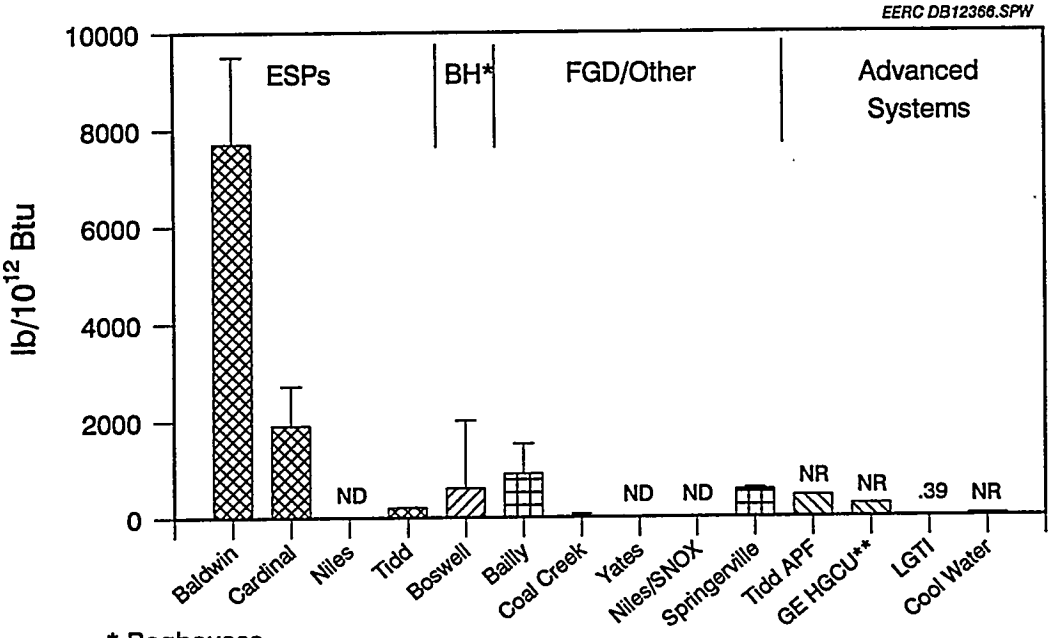


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-11. Beryllium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

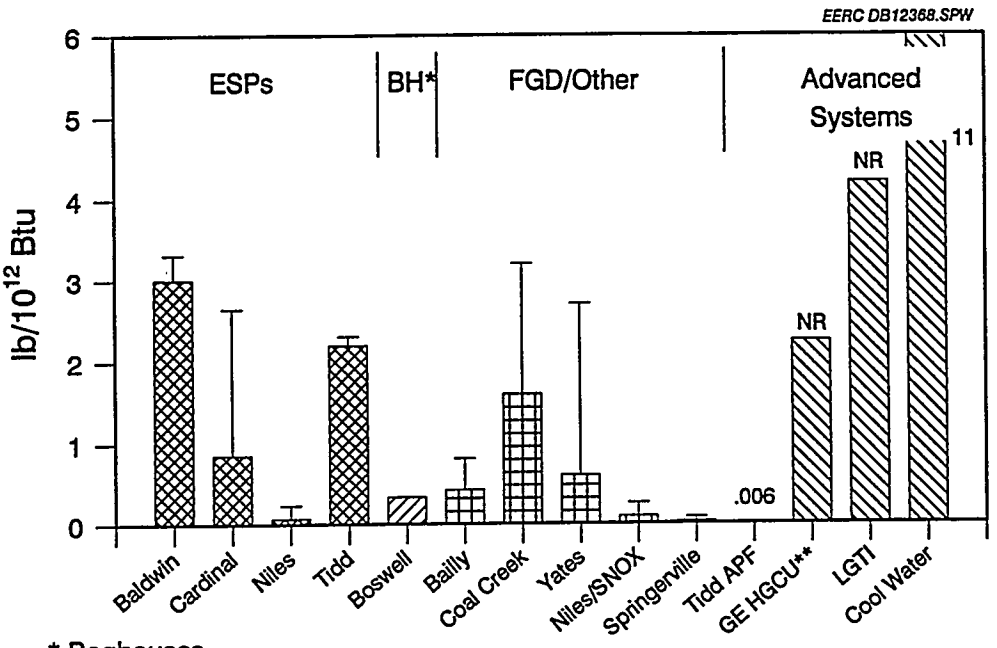


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-12. Boron emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

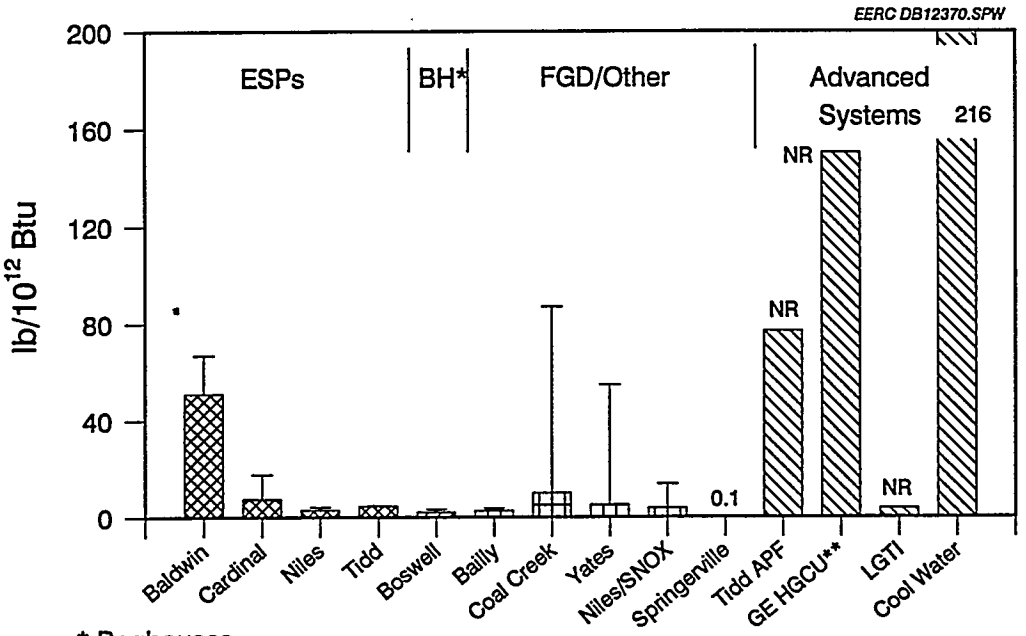


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-13. Cadmium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

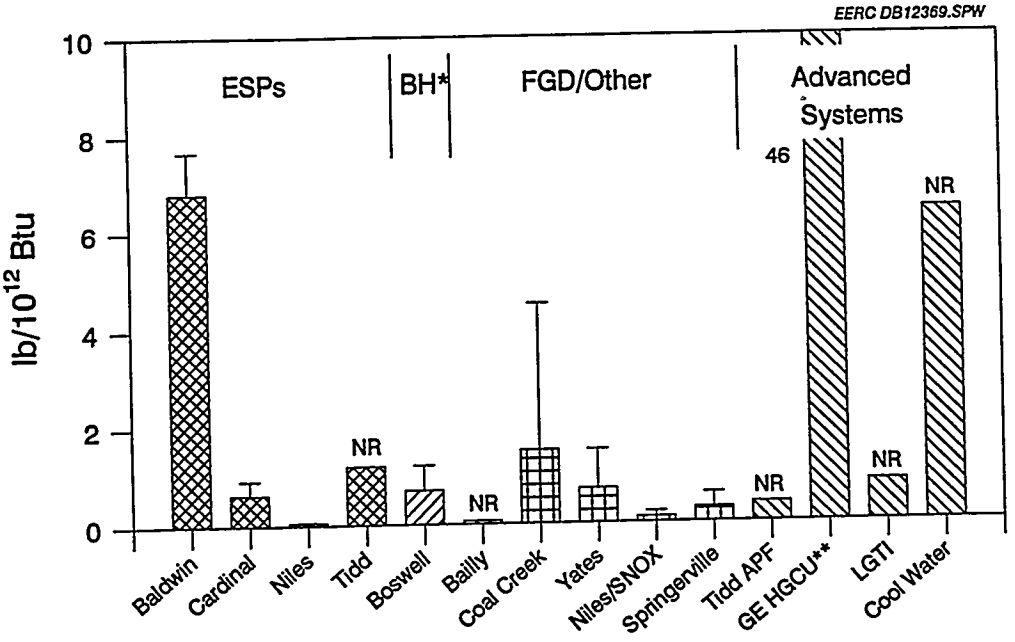


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-14. Chromium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

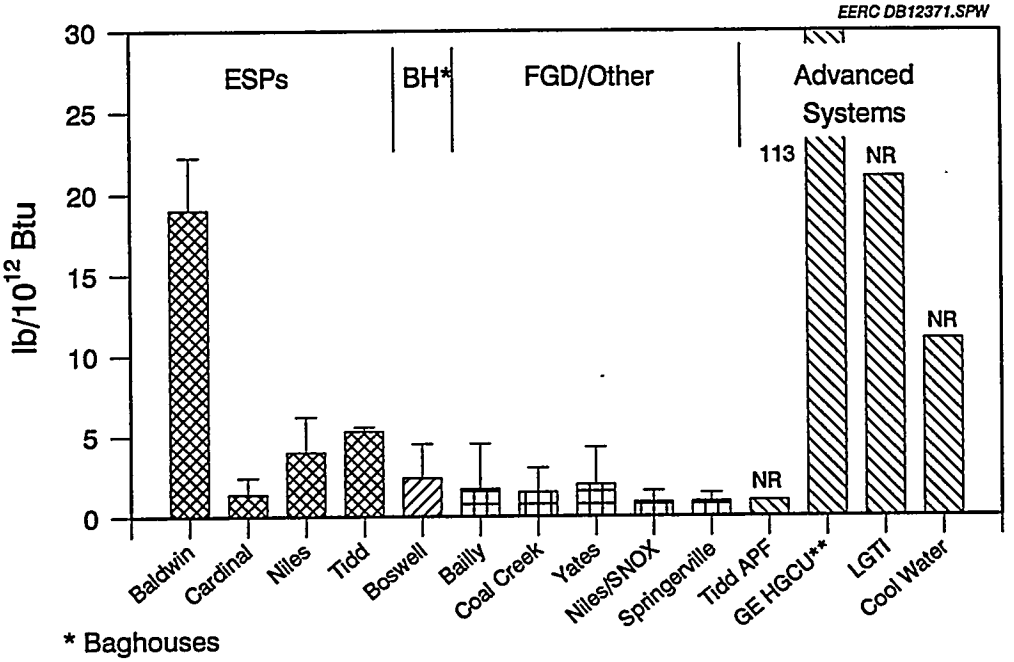


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-15. Cobalt emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

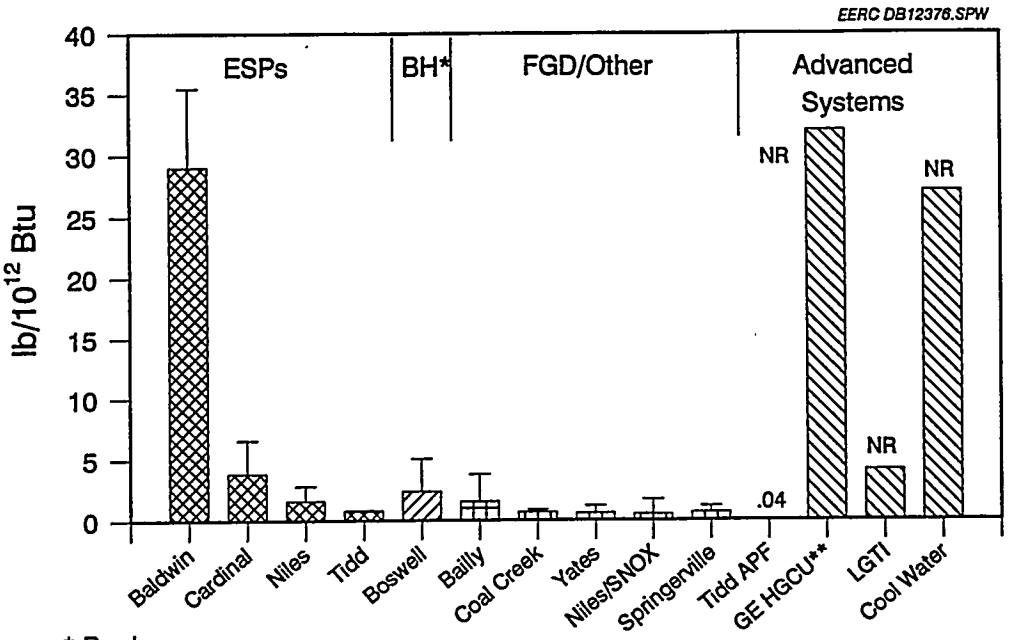


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-16. Copper emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

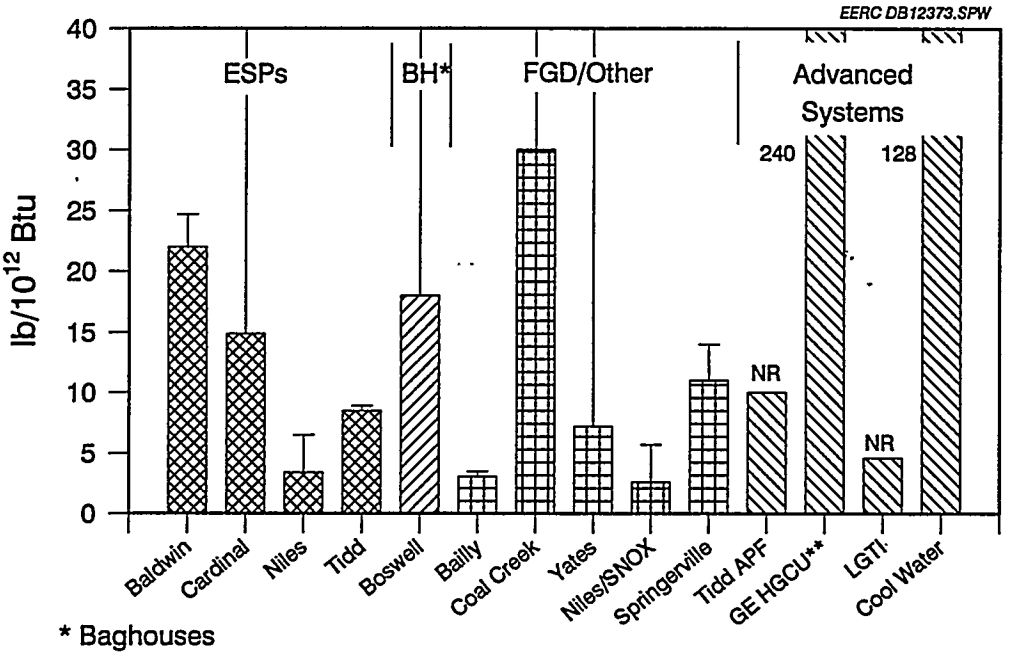


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-17. Lead emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

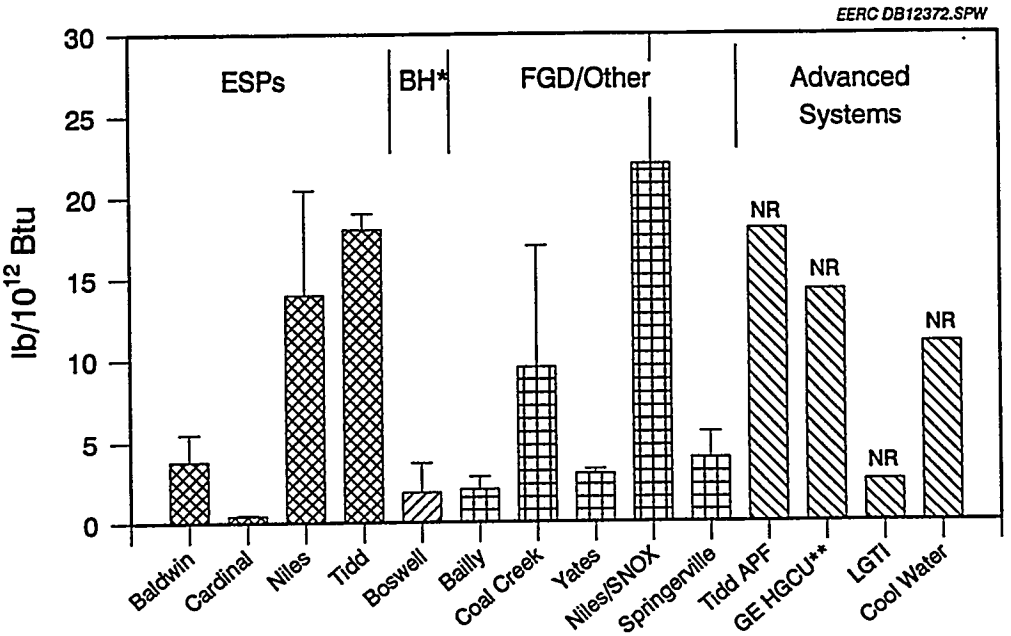


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-18. Manganese emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

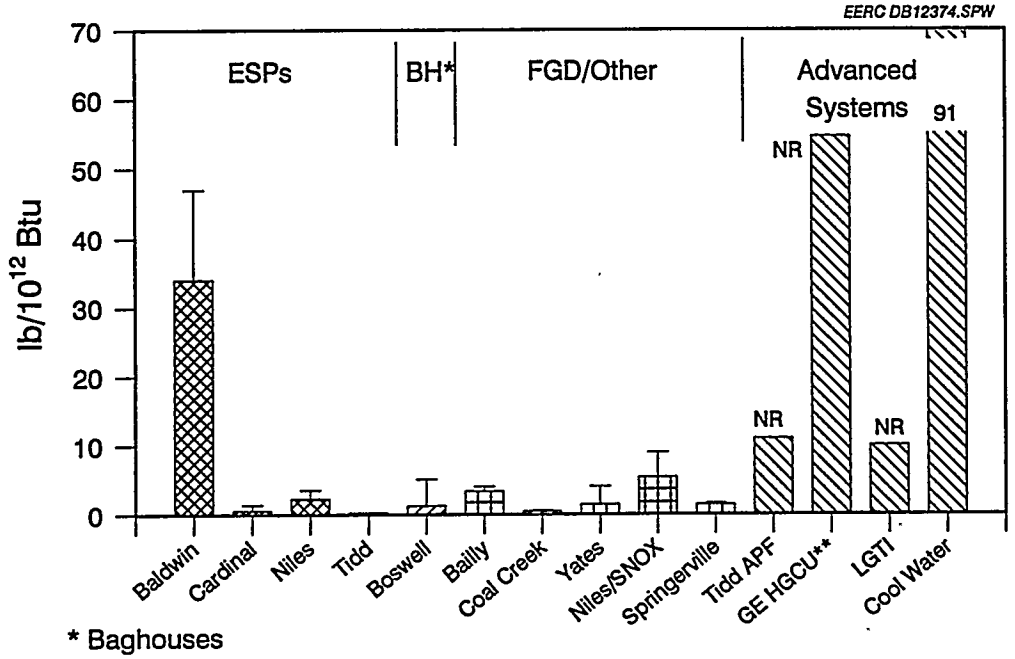


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-19. Mercury emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

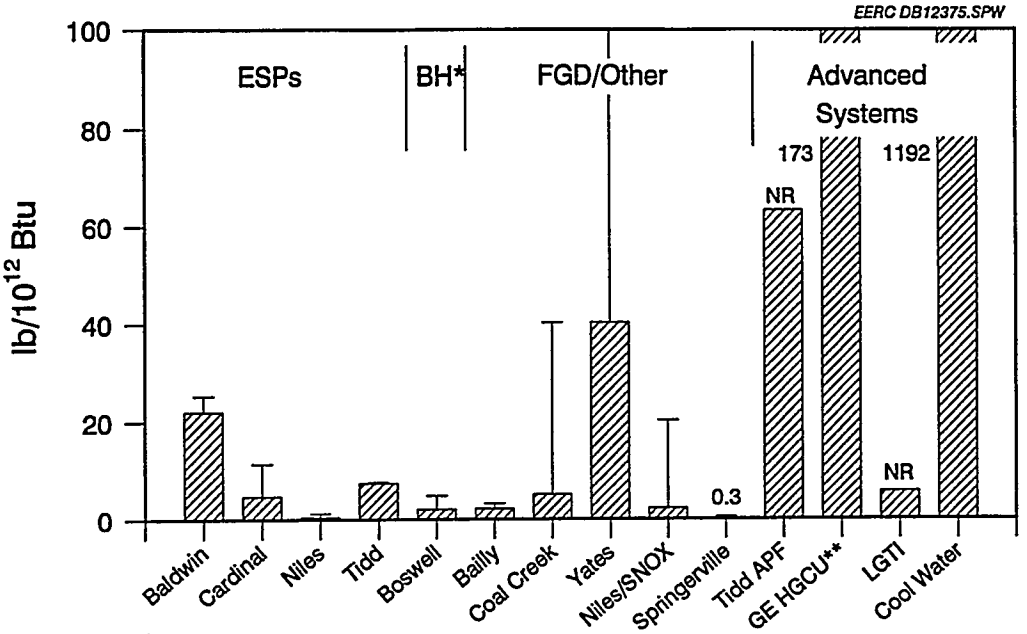


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-20. Molybdenum emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

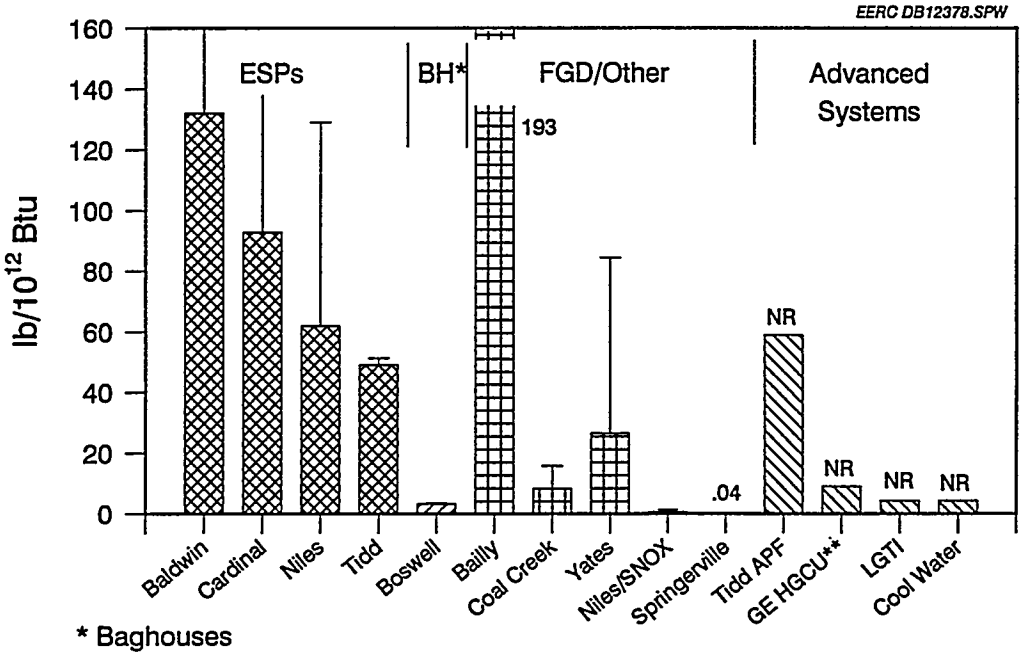


* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-21. Nickel emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.



* Baghouses

** Calculated assuming flow rates from Tidd plant.

Note: Error bars are 95% CI. NR = Confidence interval not reported.

Figure 4-22. Selenium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

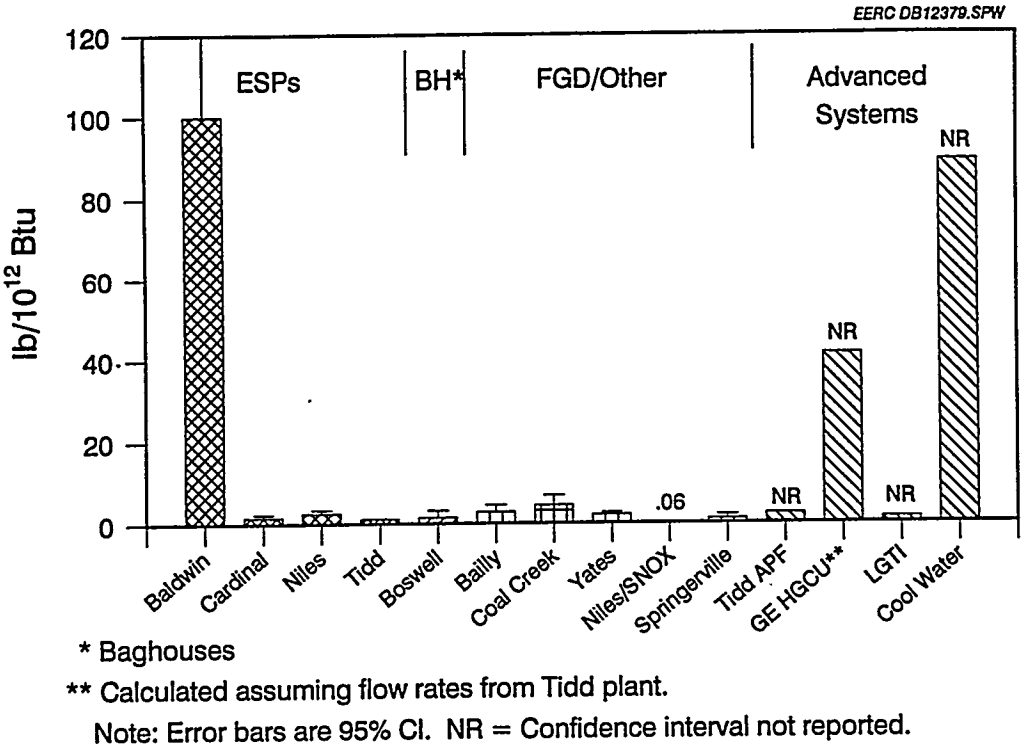


Figure 4-23. Vanadium emission factors from conventional and advanced power systems grouped by control technology. Note that contamination of Cr and Ni in Tidd APF outlet samples is suspected, and results from both GE HGCU and Cool Water were subject to sampling error.

the APF. Assuming that the Ni and Cr emissions from the Tidd system are from contamination, then only the Hg and As emissions are higher in the Tidd system with APF. This makes sense because of the higher temperatures in the APF than in conventional technologies.

TABLE 4-1

Emission Factors for CAAA Trace Elements from Advanced Power Systems with a Relatively Higher Emission Factor Than Conventional Systems[1]

Tidd with APF[2]	As, Cr, Hg, Ni
GE HGCU[3]	Sb, As, Be, Cr, Cd, Hg, Pb, Ni
LGTI	Sb, Cd, Pb
Cool Water[3]	Sb, As, Be, Cd, Co, Cr, Hg, Mn, Pb, Ni,

[1] "Relatively" refers to greater than 80% (8 of 10) of the conventional systems used in the comparison.
[2] Contamination of Cr and Ni in Tidd APF outlet samples is suspected.
[3] Results from both GE HGCU and Cool Water were subject to sampling error.

4.2.2 Total CAA Emissions

Figure 4-24a summarizes the emissions data for the 11 trace elements listed in the CAAA. In addition, the two most commonly volatile elements, Hg and Se, are also shown. The CAAA trace element emissions for the GE HGCU and the Cool Water plant are significantly higher than for the other systems. The GE HGCU and Cool Water data are highly suspect and should not be considered valid for these comparisons, as discussed previously. The Tidd APF data indicate the third highest emitter. However, most of these emissions are from Cr and Ni, which are believed to be contamination from the sampling probe. By assuming the Cr and Ni values are from contamination and that they are present primarily as particulate (discussed in Section 5.3), a new estimate for the CAAA emissions can be calculated. The new results after removal of 99% of their values (which allows 1% for breakthrough, a high estimate) are shown in Figure 4-24b. With this assumption, both the Tidd APF and the LGTI system show emissions as low or lower than conventional systems. Thermochemical equilibrium calculations, Section 5.3, also suggest that the Cr and Ni should be in the particulate form, which should have been captured by the filter.

The emissions of Hg and Se appear to be higher in the Tidd APF, likely due to the higher operation temperature of the system. Since the Hg mass balance around the APF, shown in

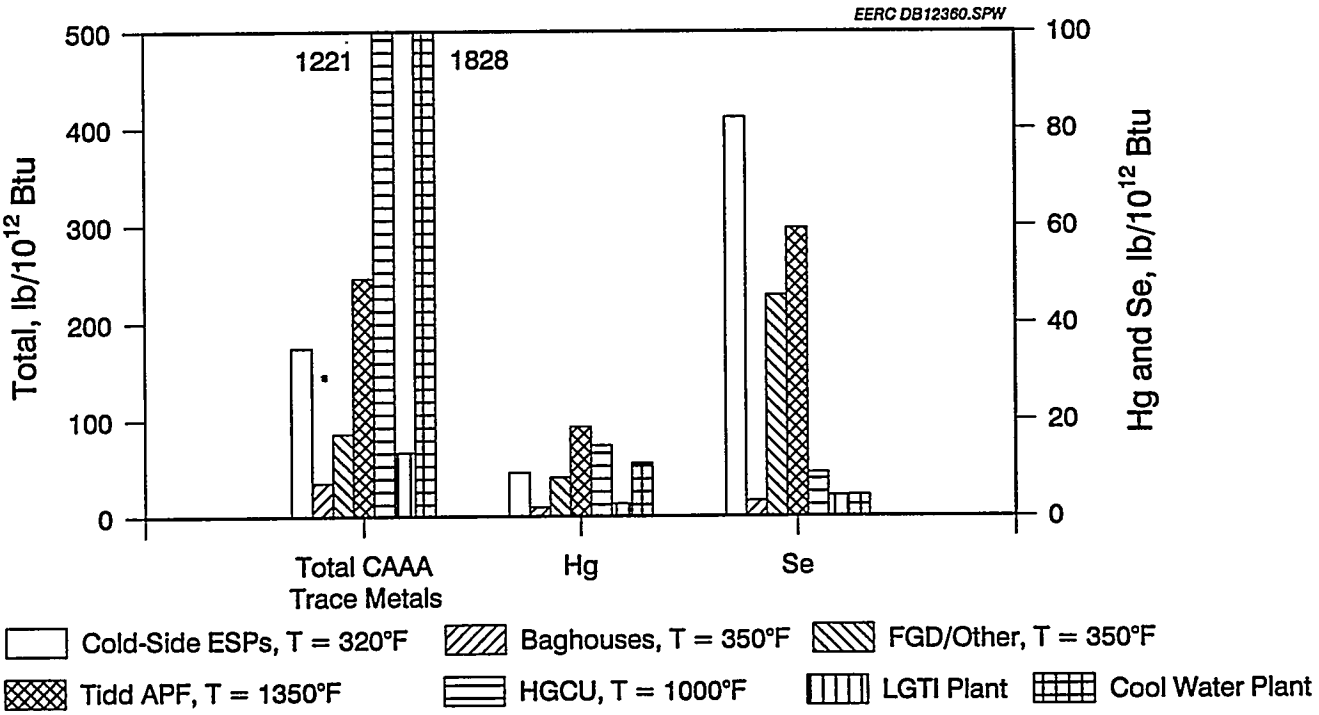


Figure 4-24a. Summarized emission factors of total CAAA trace elements, Hg, and Se. Note that contamination of Cr and Ni in the Tidd APF outlet samples is suspected. Results from both GE HGCU and Cool Water were subject to sampling error.

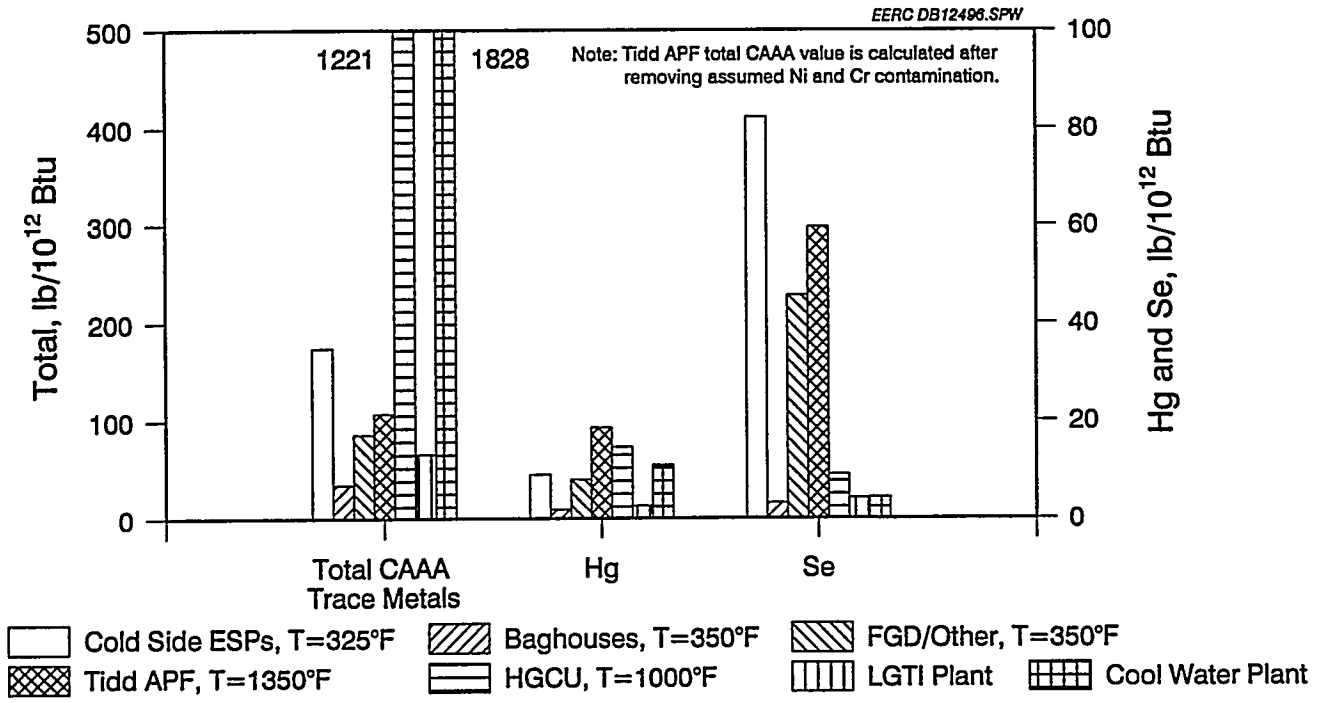


Figure 4-24b. Summarized emission factors of total CAAA trace elements, Hg, and Se, with the Tidd APF total CAAA value corrected for contamination of Cr and Ni.

Section 5.1, is very close to 100% with only a small deviation, it is assumed that the elevated mercury emissions are real and warrant future attention. The GE HGCU and Cool Water systems also show slightly elevated mercury emission values. However, since sampling errors occurred, the true extent of the emissions is not clear.

4.2.3 Potential Regulatory Impact

The potential for the regulation of advanced power systems is currently being driven by the 1990 CAAA. The CAAA list 189 compounds considered HAPs that must be minimized. The current form of the regulations would allow only 10 tons/year of any single HAP and 25 tons/year of all HAPs combined. Any major source exceeding these limits will be required to apply the maximum achievable control technology to their system to meet the regulations. It is assumed that advanced systems will be governed under regulations derived from the results of conventional system testing.

Assuming that only the Tidd APF and LGTI data sets are valid, with the Ni and Cr in the Tidd samples due to contamination, the overall emission of trace elements from advanced power systems appears to be equal to or lower than that of conventional systems, on average. If one considers a 250-MW plant burning a 12,000-Btu fuel with 80% operability throughout a year, the total CAAA emissions for a single year for any of the systems can be calculated by multiplying the emission factors by approximately 16. Both the Tidd with APF and the LGTI systems would be

below 1 ton per year for all trace elements emitted. The only area of concern is likely the emission of mercury from the advanced power systems. Regulation of mercury is expected because of its environmental and health risks. Informal reports indicate that the EPA believes there is significant mercury contamination of lakes from air deposition and that coal-burning power plants are one of the major sources. Since the Tidd APF and other future advanced technologies will operate at temperatures exceeding conventional technologies, it is anticipated that mercury emissions will be an issue.

5.0 ASSESSMENT OF THE IMPACTS OF HOT-GAS CLEANUP SYSTEMS ON HAPS EMISSIONS

5.1 Advanced Technology Control Efficiencies

This section evaluates the effectiveness of both conventional and advanced control systems in removing trace elements from flue and product gases. The cleanup systems used in the LGTI and Cool Water systems are not included as advanced systems because of their lqw operation temperatures.

5.1.1 APF and ESP Data from Tidd

The APF unit located at the Tidd plant operates from a slipstream. Approximately one-seventh of the gas stream exiting the primary cyclone of the PFBC enters the APF. The APF operates at 1350°F and at approximately 150 psi. The remaining six-sevenths of the gas flows through a secondary cyclone. The gases exiting the APF and the secondary cyclones are recombined and fed into a ruggedized turbine. All gases exiting the turbine are passed through an ESP for final cleaning before being vented to stack. The ESP is a cold-side unit operating at 400°F.

The mass balance for the APF, Figure 5-1, shows that most of the elements fall within the 100 ±25% range. Only Cr, Cu, F, and Mo show mass balances below 75%, and none was above 125%. The ESP showed slightly higher variability, with Sb, As, Be, Cd, Co, F, Pb, Mo, and Ni placing outside of the 100 ±25% range. The confidence limits shown represent a 95% confidence interval as calculated without analytical or sampling bias.

The trace metals control efficiency of the APF, Figure 5-2, looks very good for most species. Only Cl, Cr, F, Hg, Mo, Ni, and Se show collection efficiencies of under 90%, with most of the others >99%. As discussed previously, the APF outlet samples are suspected to have been contaminated with Cr, Mo, and Ni, from a probe nozzle, resulting in a lower collection efficiency than expected for those three elements. The Cl, F, Hg, and Se are all expected to have low collection efficiencies because of their presence as vapor species at the APF operating temperature. The overall particulate collection efficiency of the APF was calculated to be >99.5%.

The collection efficiency of the ESP, Figure 5-2, was lower than that of the APF, with the exception of Cr, Mo, Ni, and Se. Overall, the APF performed much better than the ESP at Tidd. The overall particulate control efficiency for the ESP was calculated at 97.2%.

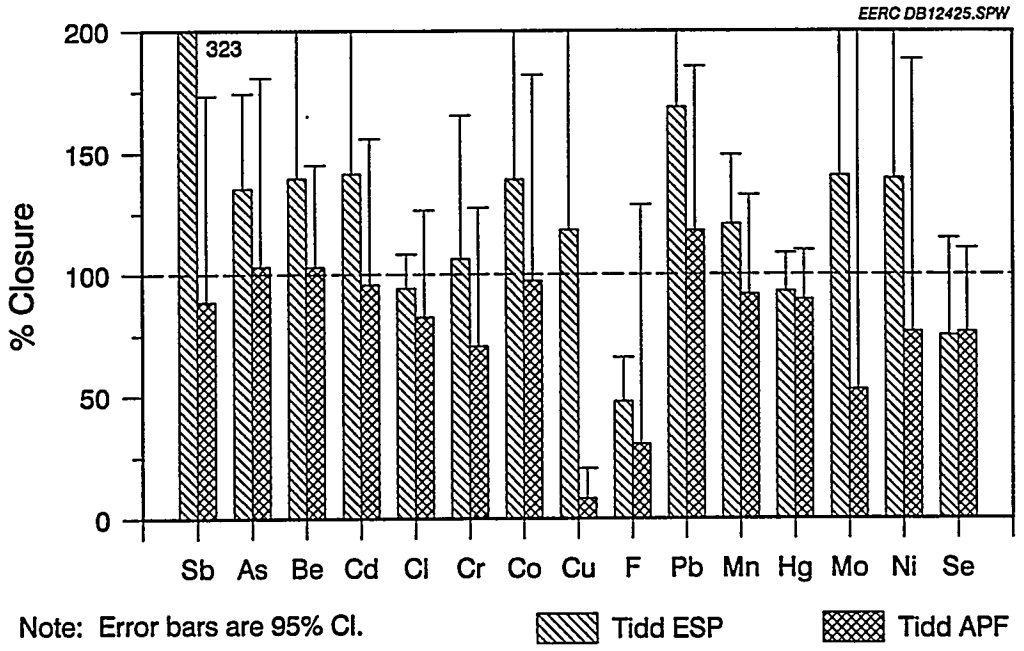


Figure 5-1. Mass balances around Tidd APF and Tidd ESP.

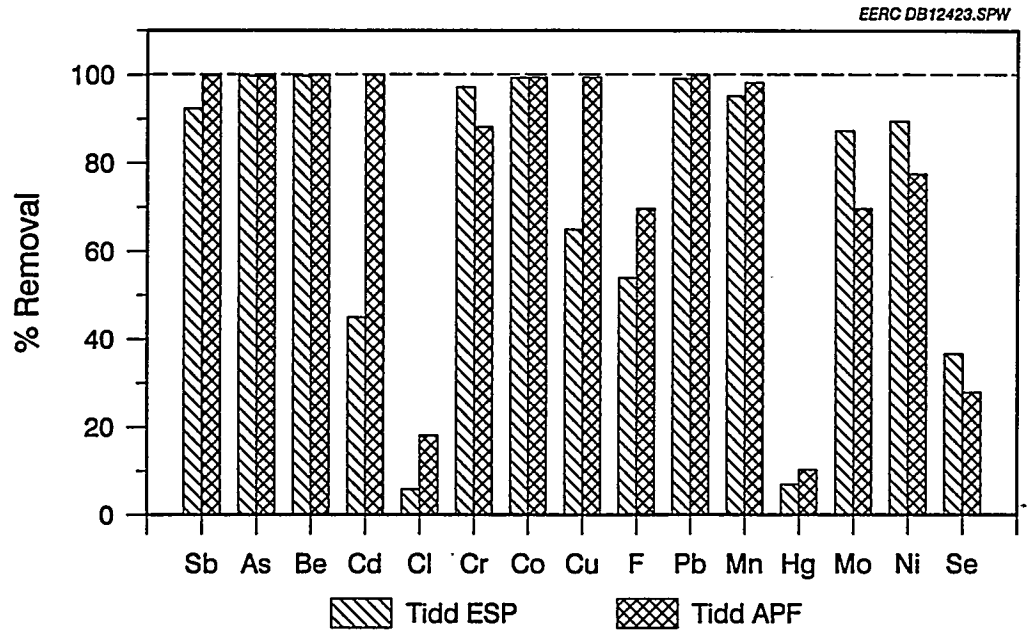


Figure 5-2. Control efficiencies around the Tidd APF and Tidd ESP, reported as percent of element removed.

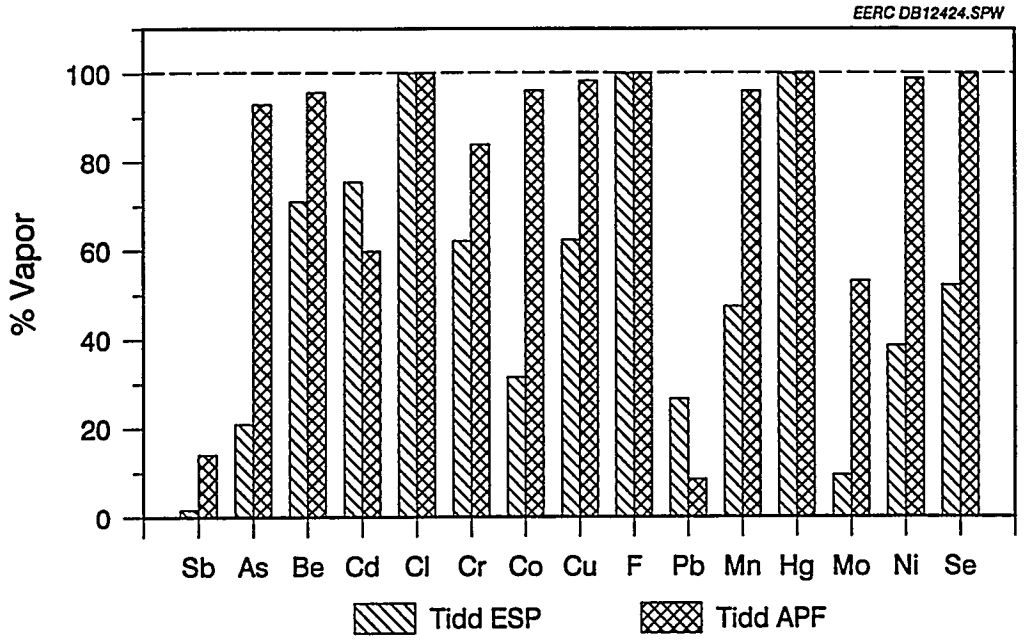


Figure 5-3. Percentage of element leaving the Tidd APF and Tidd ESP in the vapor state.

The flue gas partitioning values, Figure 5-3, show that most of the elements leaving the APF were in the vapor state, as expected. Only Sb, Ba, Cd, Cr, Pb, Mo, Ag, and V showed less than 80% of the exiting mass in the vapor state. Since little evidence of particle breakthrough in the filter exists for major species, it is assumed that either the emissions exiting the APF have high amounts of very small (0.05-micron) particulates, the metals were in the vapor phase prior to exiting the APF, or the amounts detected within the samples is very small (and the analytical uncertainty is large). The difficulty is probably a combination of these factors. The Tidd ESP showed a much higher concentration of particulate species escaping the unit than did the APF.

5.1.2 Reduction of GE HGCU Data

Product gas from a fixed-bed gasifier was first cleaned by a primary cyclone and then sent to the HGCU system. The GE HGCU system comprises a zinc titanate sorbent unit followed by a secondary cyclone. The data from the GE HGCU was not manipulated in the same manner as that from the Tidd APF, because not all of the appropriate streams of the unit were sampled (data are missing from the sorbent stream). The mass loadings show that approximately 73% of the particulate entering the HGCU and secondary cyclone unit were removed, indicating the very poor efficiency of the system for particulate removal. As shown in Figures 5-4 and 5-5, respectively, the collection efficiency of the system and also the percent vapor for both the inlet and outlet of the HGCU were calculated. It is noted that only two samples were taken for each sampling point, and the differences between the results were very large in many cases. The site report also notes a problem with particle breakthrough during particulate and vapor sampling, which is evident in the

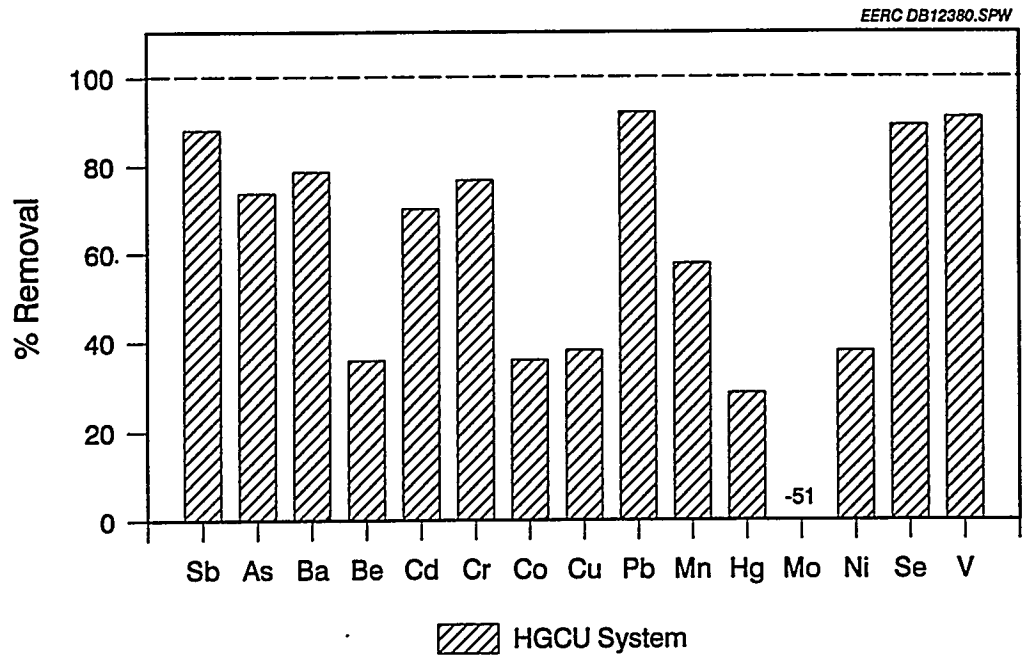


Figure 5-4. Control efficiency of GE HGCU for selected elements, reported as percent removed.

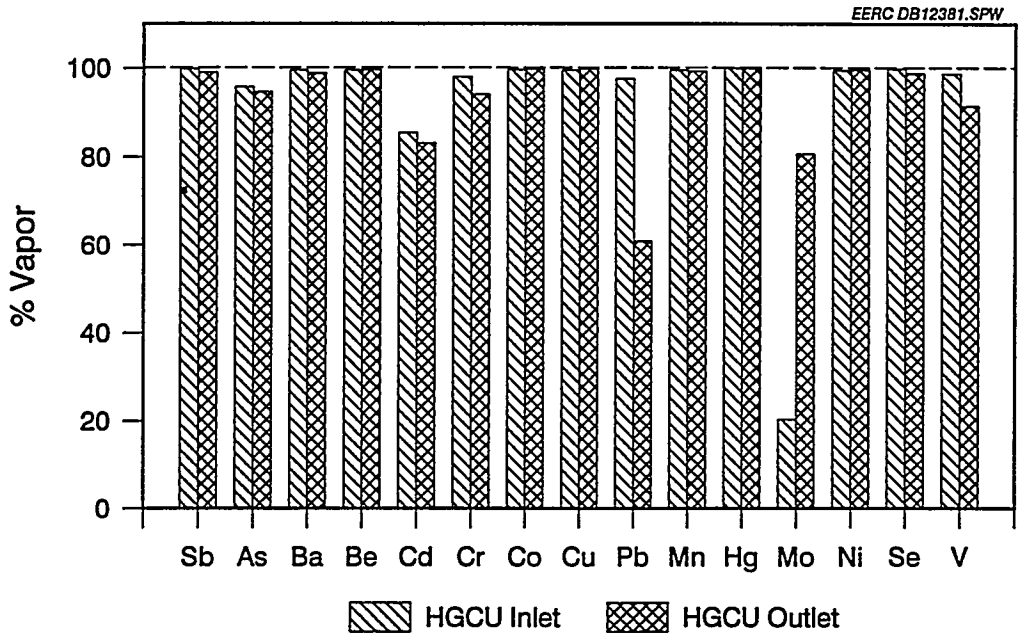


Figure 5-5. Partitioning of selected elements entering and exiting the GE HGCU expressed as percent in the vapor form.

data. Refer to Appendix A for comments from Dr. Alan Feitelberg of General Electric on the sampling activities.

Although numerous problems were associated with the sampling, the data were used for comparisons since they are the only pilot-scale data available for this sorbent material. The control efficiency of the HGCU system in removing most of the trace elements was below 80%. Only Sb, Pb, Se, and V showed control efficiencies above 80%. As a particulate control system, the HGCU (including the secondary cyclone) is not very effective, but that is not the initial purpose of the system. It is noted that the 95% confidence intervals shown on the graph are in the 100% to 200% range, making the data very unreliable.

Sufficient data were available to calculate the particulate–vapor splits entering and leaving the HGCU system (shown in Figure 5-5). Unexpectedly, the outlet stream shows a higher percentage of elements present as particulate than does the inlet stream. This is most likely due to the extensive sampling problems experienced, including particulate breakthrough within the filtration system and sample nozzle contamination.

5.2 Comparison with Conventional Cleanup Systems

Figures 5-6 through 5-22 display control efficiencies of the various conventional control systems compared to the advanced systems discussed within this section. Each of the figures contains two graphs showing different scales of the same data to allow the reader to interpret the information more readily, i.e., the reduced scale allows better visualization of differences at the higher values. As mentioned earlier, much of the GE HGCU data has significant error limits, resulting in questionable data. Table 5-1 lists the elements that show a relatively lower collection efficiency for the Tidd APF and GE HGCU systems compared to conventional systems.

TABLE 5-1

CAAA Trace Elements Showing a Relatively Lower[1] Collection Efficiency in Advanced Systems Than in Conventional Systems

Tidd APF	Sb, Hg, Cr, Ni
GE HGCU	Sb, As, Be, Cd, Co, Cr, Mn, Ni, Pb

[1] Lower than the average of all given technologies.

The table shows that the GE HGCU does not do a very good job controlling particulate emissions (keeping in mind the poor quality of the data). However, the Tidd APF does a very good job in comparison to conventional systems, the only exceptions being Hg and Sb (assuming the low efficiencies on Cr and Ni are due to contamination).

The average control efficiency for total particulate, total CAAA trace elements, Hg, and Se is shown in Figure 5-22. The LGTI and Cool Water plants are included for comparison of entire plant efficiency, not of control technology efficiency. The poor performance of the GE HGCU system was expected, and the poor performance of the APF is due to the Cr and Ni contamination in the APF data.

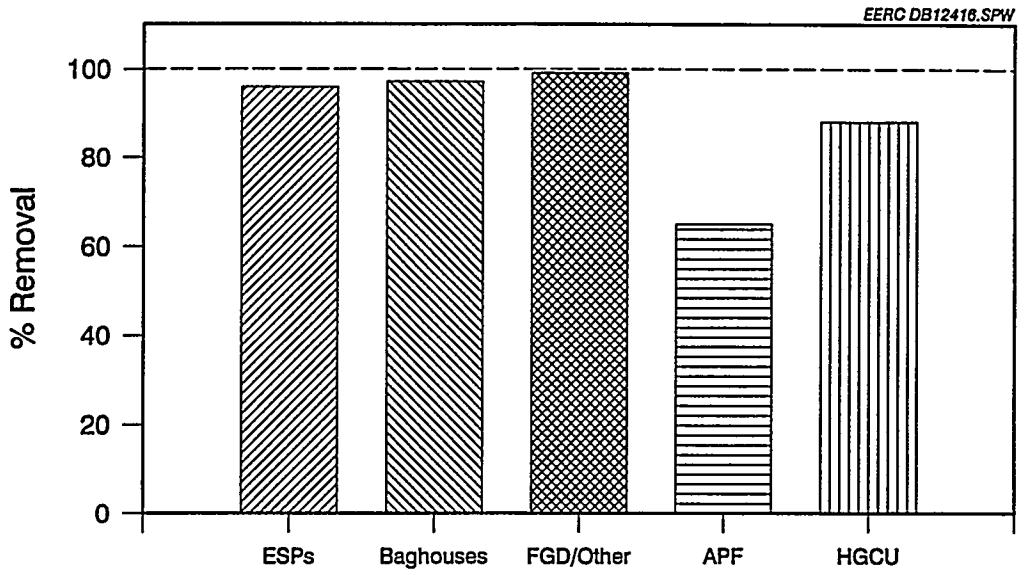


Figure 5-6a. Calculated Sb control efficiency averages for conventional systems as compared to advanced systems, full scale.

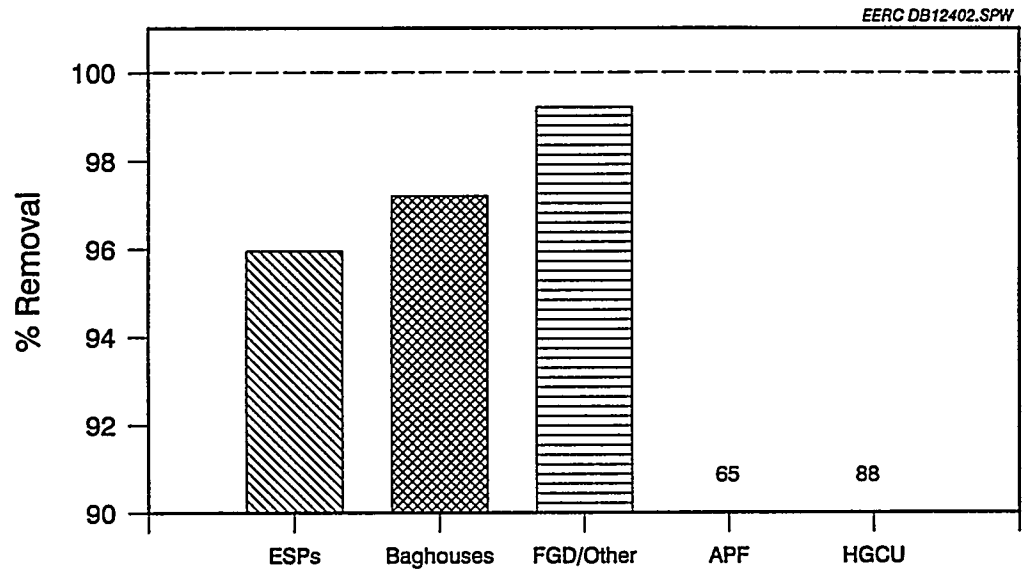


Figure 5-6b. Calculated Sb control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

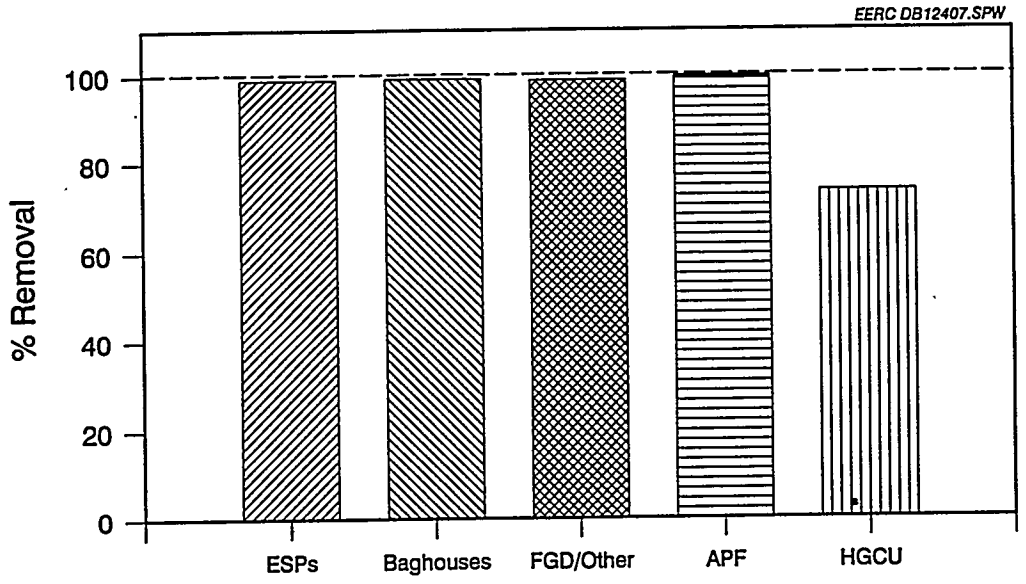


Figure 5-7a. Calculated As control efficiency averages for conventional systems as compared to advanced systems, full scale.

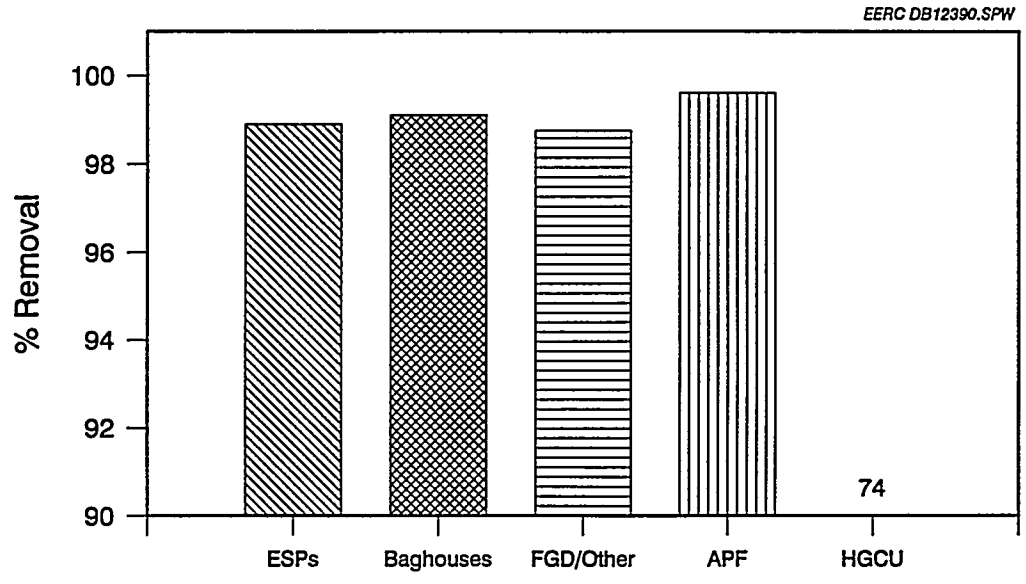


Figure 5-7b. Calculated As control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

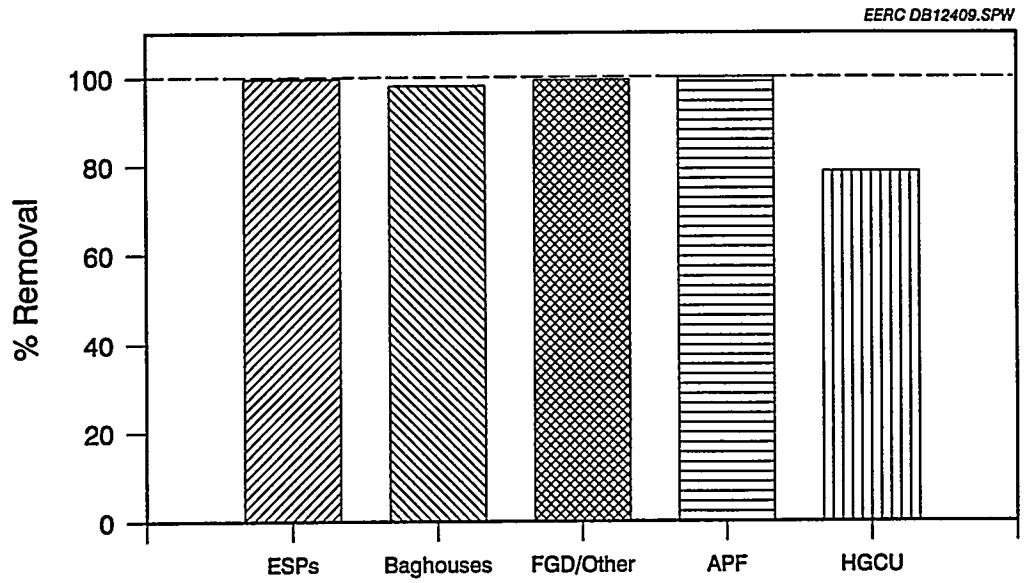


Figure 5-8a. Calculated Ba control efficiency averages for conventional systems as compared to advanced systems, full scale.

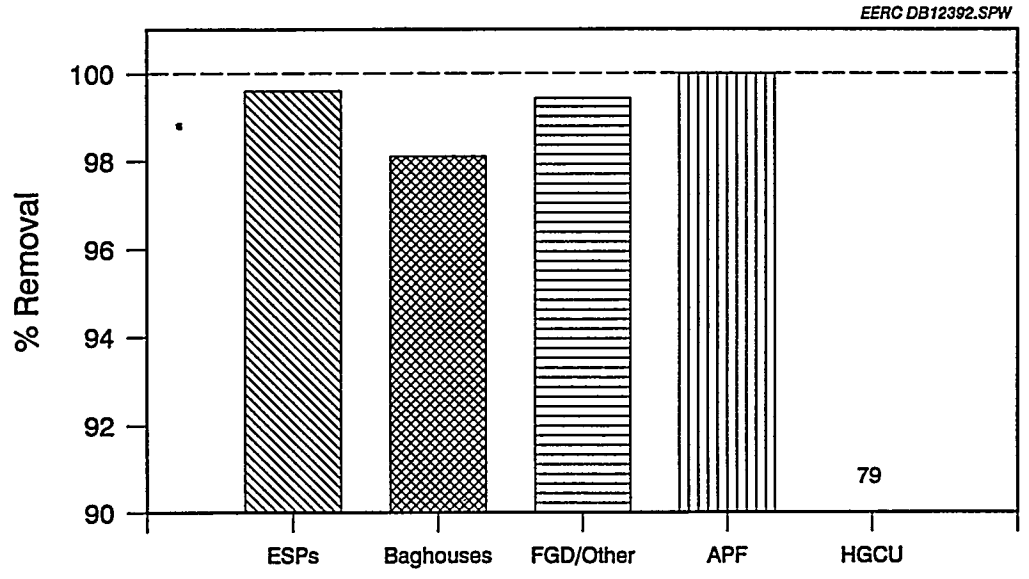


Figure 5-8b. Calculated Ba control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

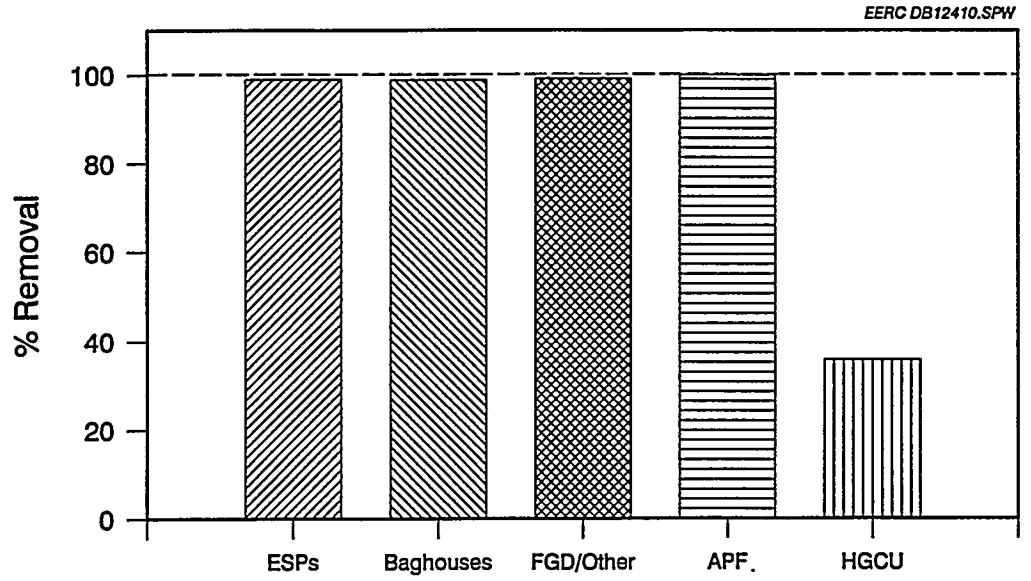


Figure 5-9a. Calculated Be control efficiency averages for conventional systems as compared to advanced systems, full scale.

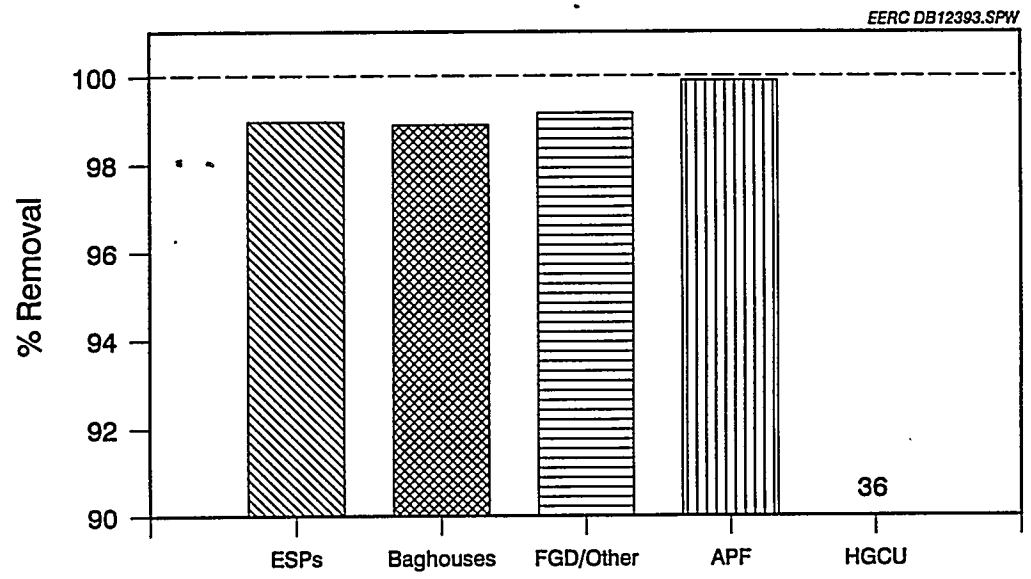


Figure 5-9b. Calculated Be control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

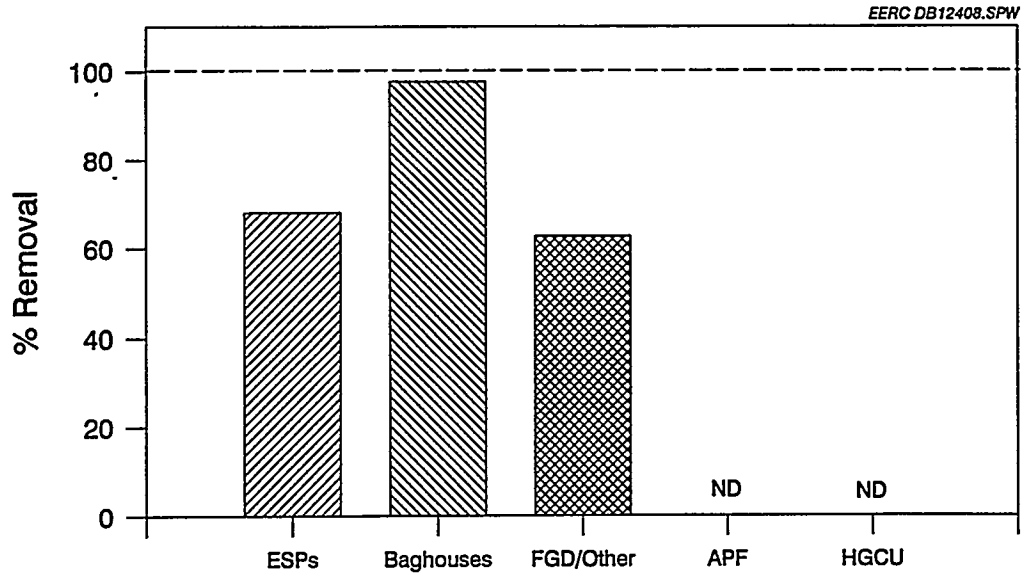


Figure 5-10a. Calculated B control efficiency averages for conventional systems as compared to advanced systems, full scale.

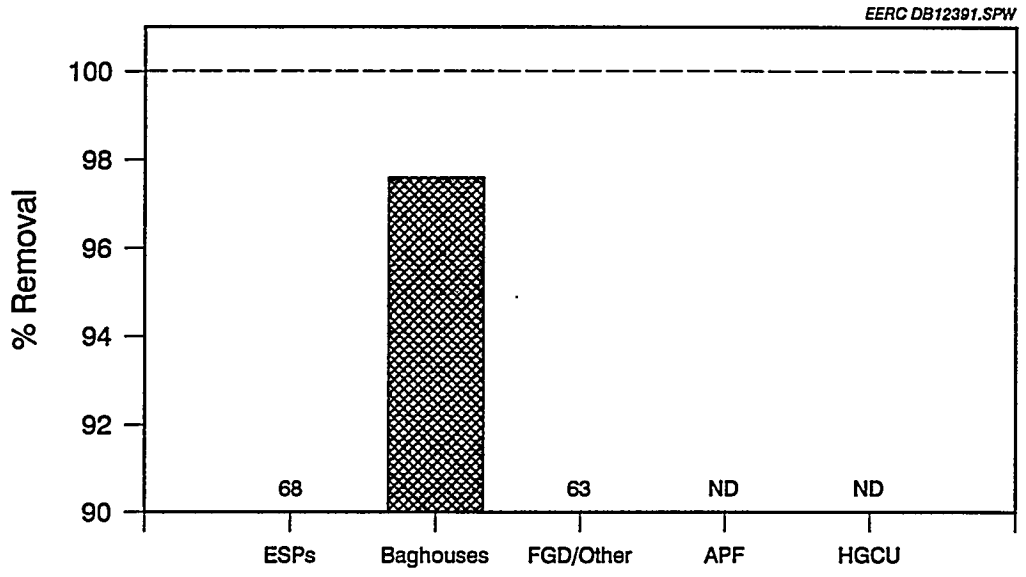


Figure 5-10b. Calculated B control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

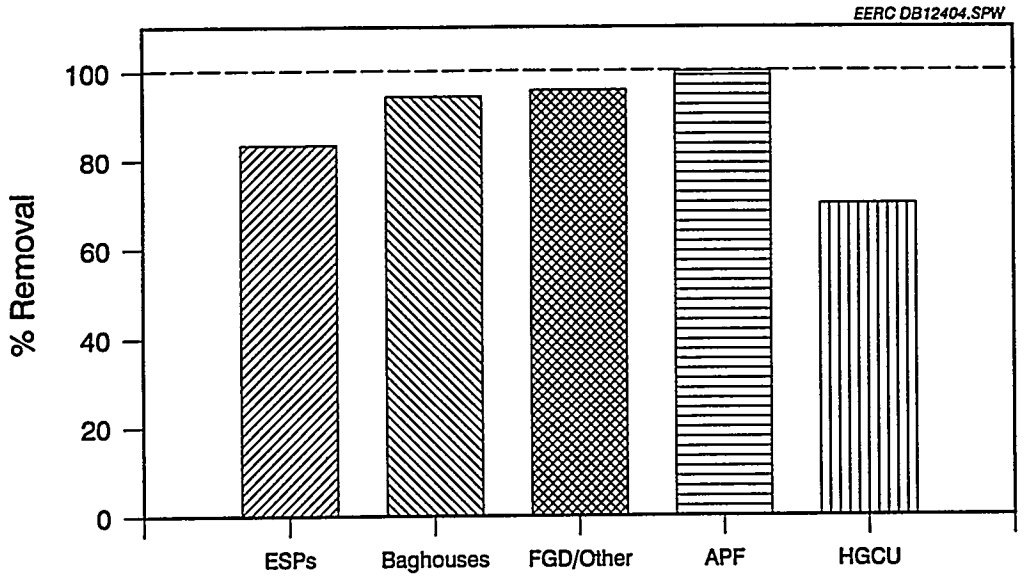


Figure 5-11a. Calculated Cd control efficiency averages for conventional systems as compared to advanced systems, full scale.

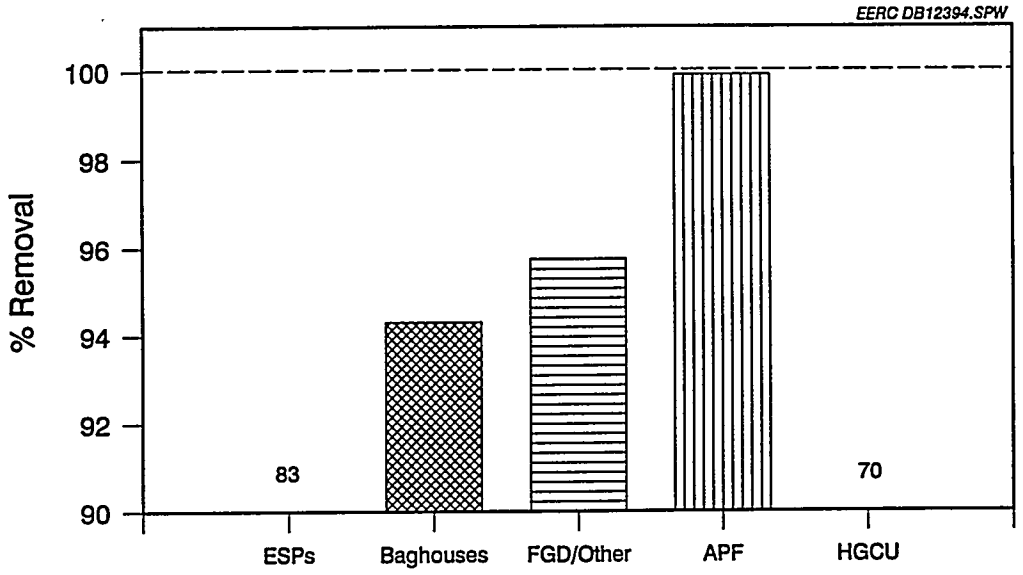


Figure 5-11b. Calculated Cd control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

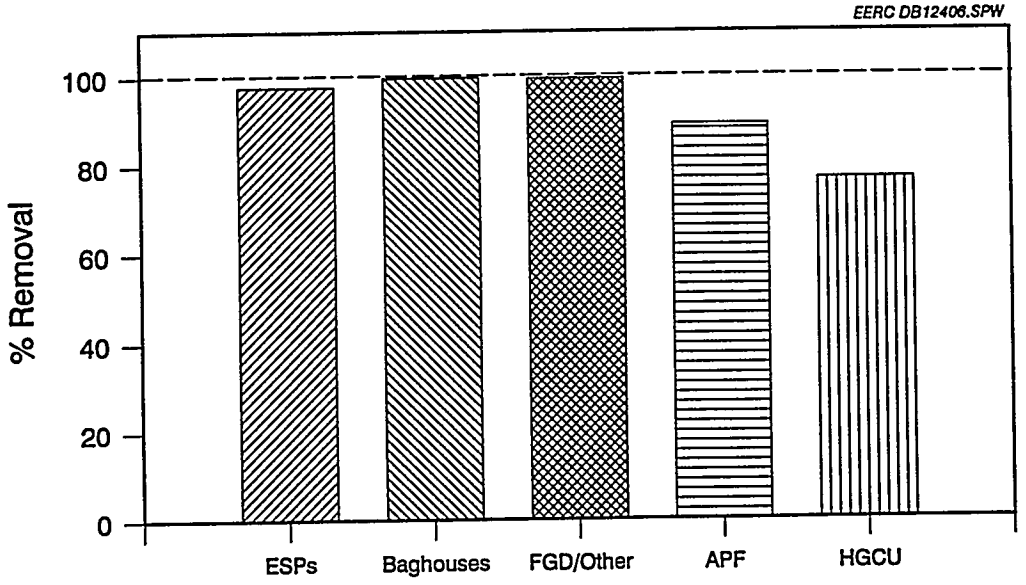


Figure 5-12a. Calculated Cr control efficiency averages for conventional systems as compared to advanced systems, full scale.

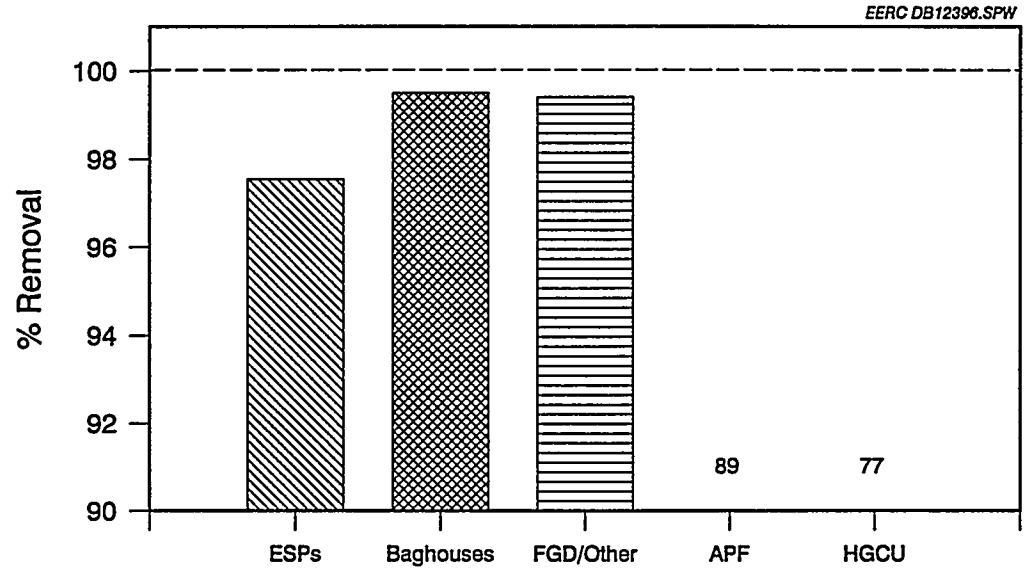


Figure 5-12b. Calculated Cr control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

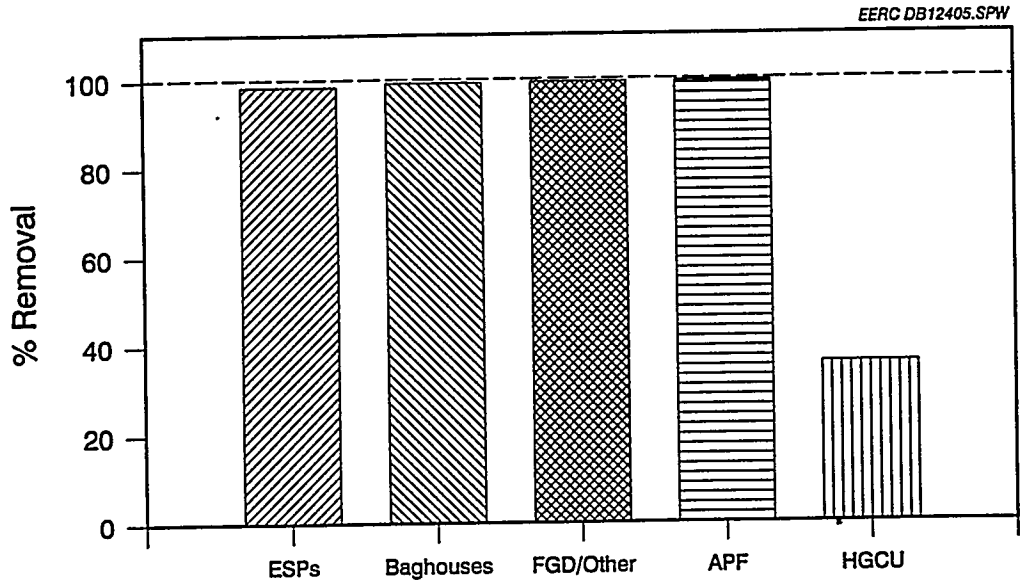


Figure 5-13a. Calculated Co control efficiency averages for conventional systems as compared to advanced systems, full scale.

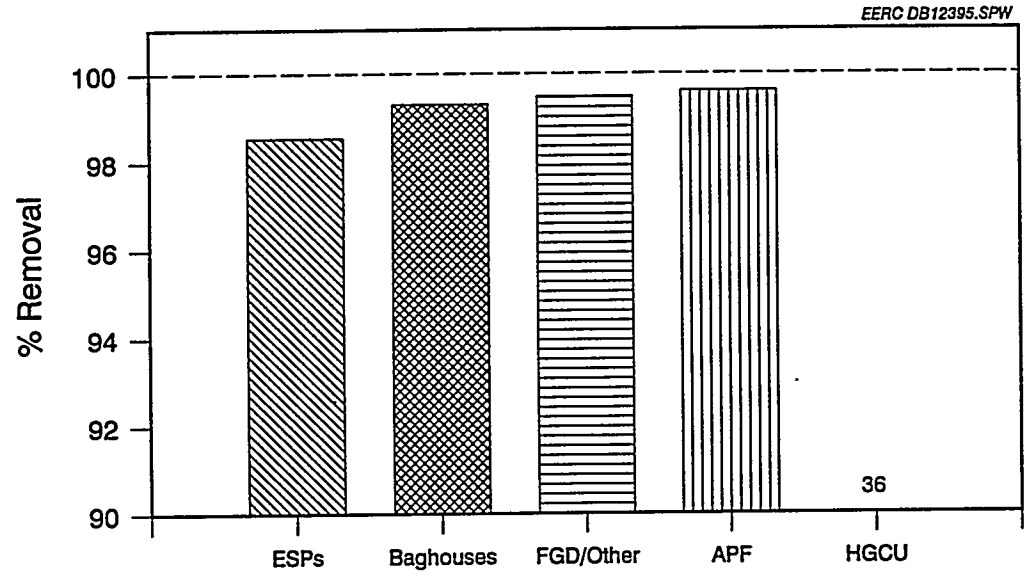


Figure 5-13b. Calculated Co control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

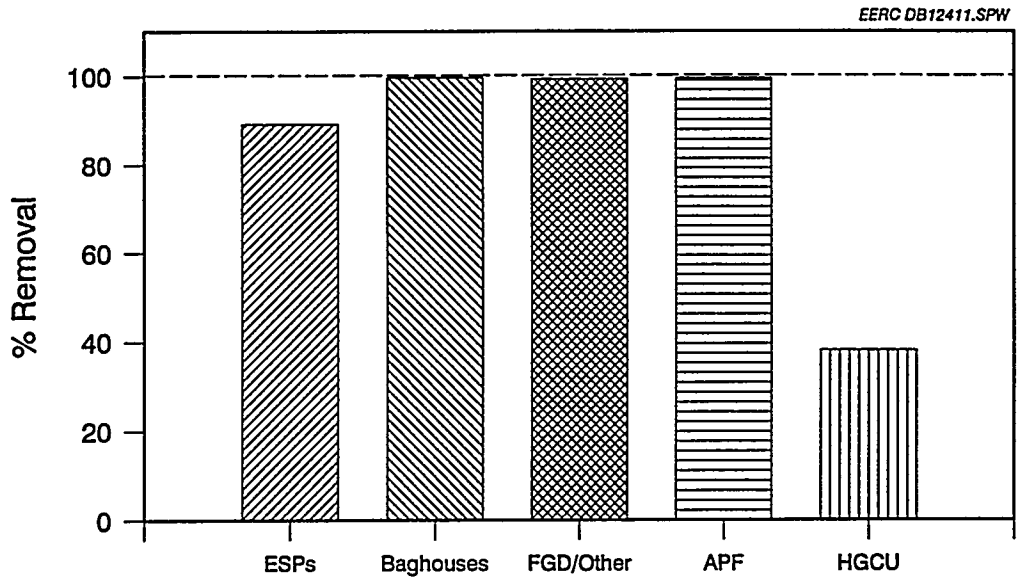


Figure 5-14a. Calculated Cu control efficiency averages for conventional systems as compared to advanced systems, full scale.

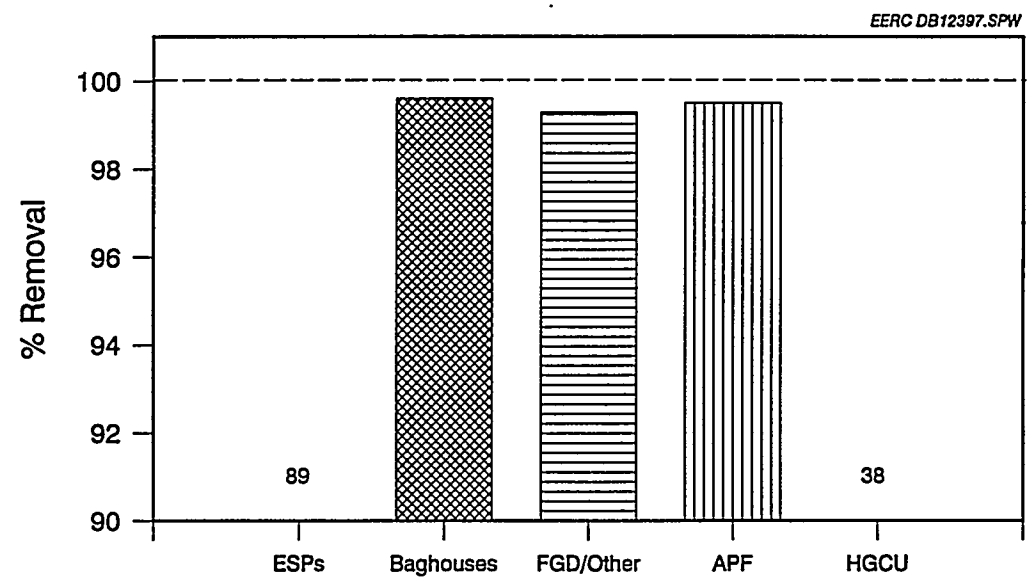


Figure 5-14b. Calculated Cu control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

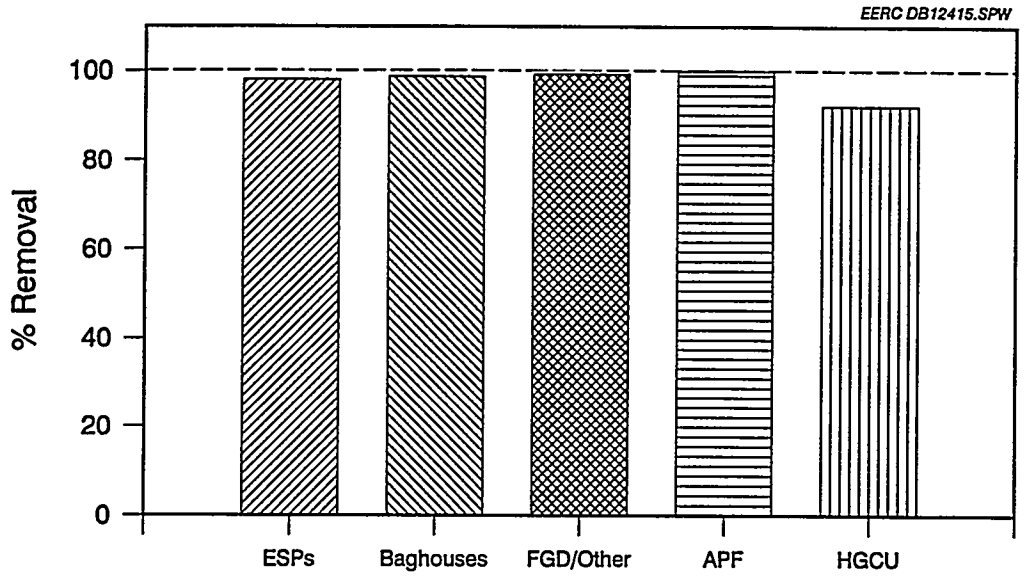


Figure 5-15a. Calculated Pb control efficiency averages for conventional systems as compared to advanced systems, full scale.

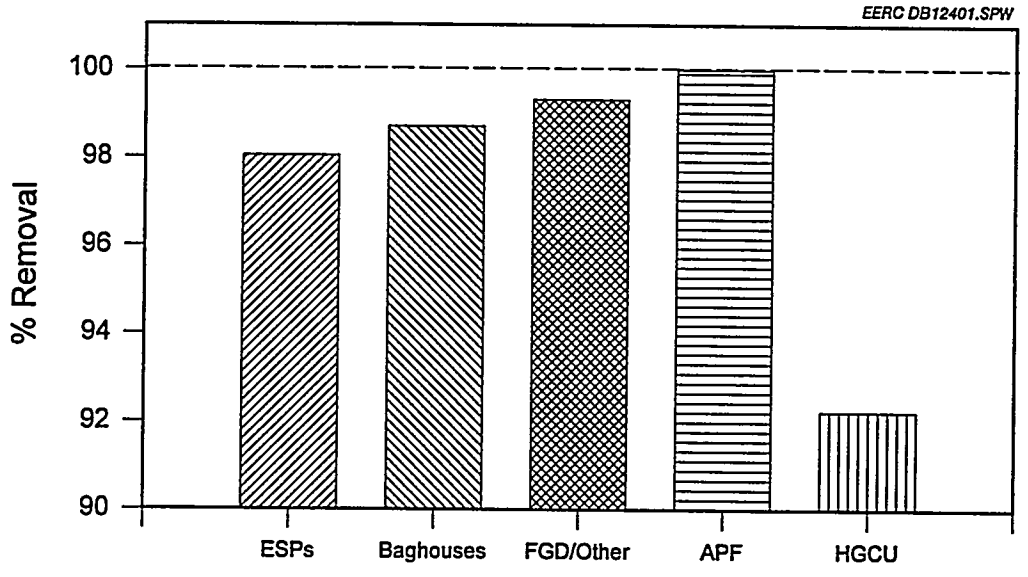


Figure 5-15b. Calculated Pb control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

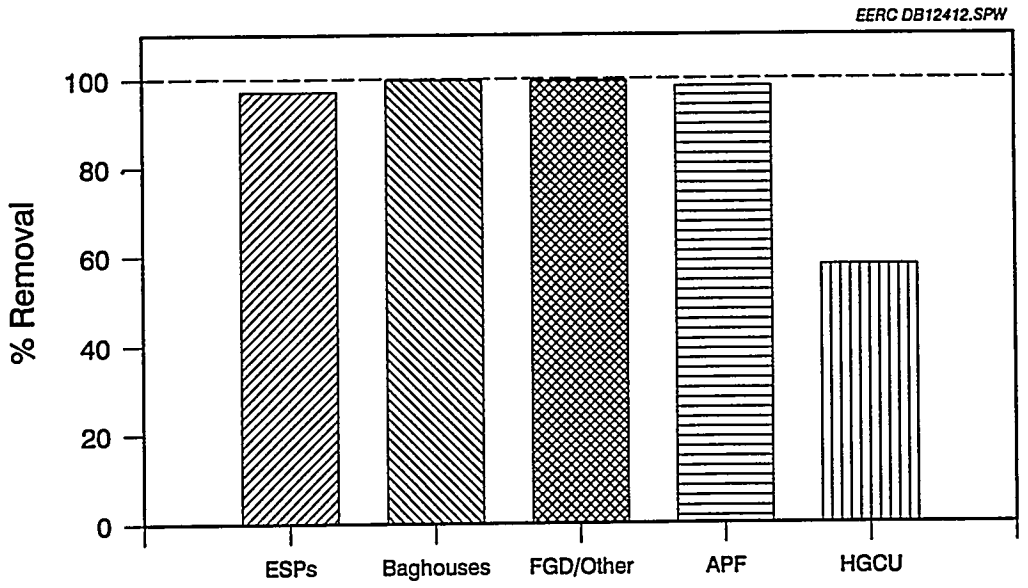


Figure 5-16a. Calculated Mn control efficiency averages for conventional systems as compared to advanced systems, full scale.

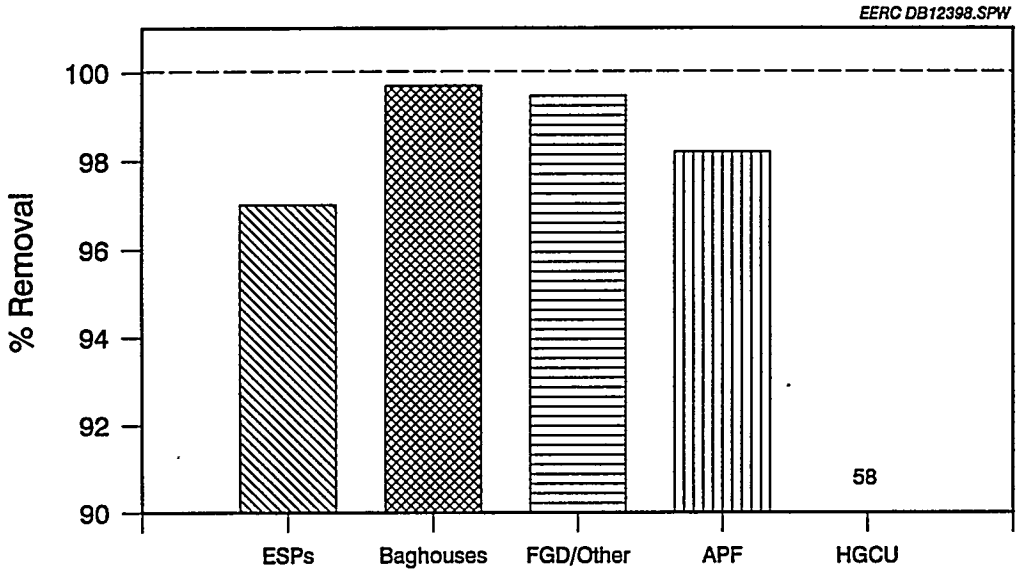


Figure 5-16b. Calculated Mn control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

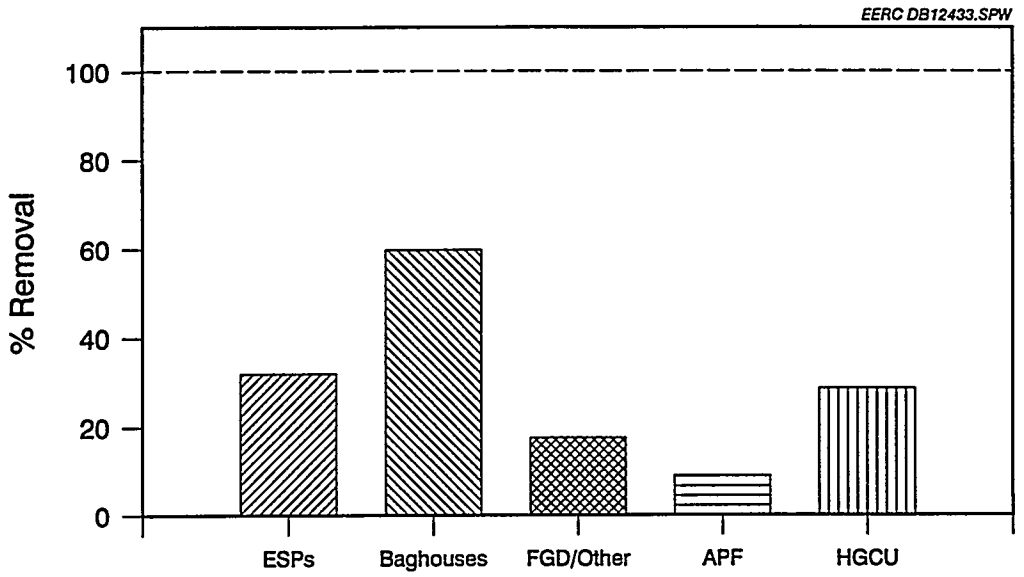


Figure 5-17a. Calculated Hg control efficiency averages for conventional systems as compared to advanced systems, full scale.

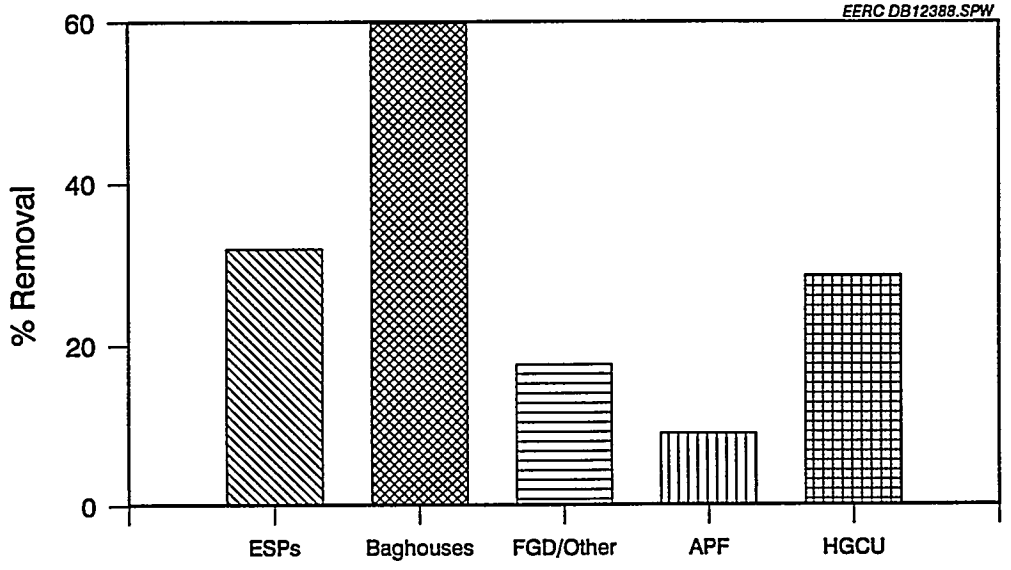


Figure 5-17b. Calculated Hg control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

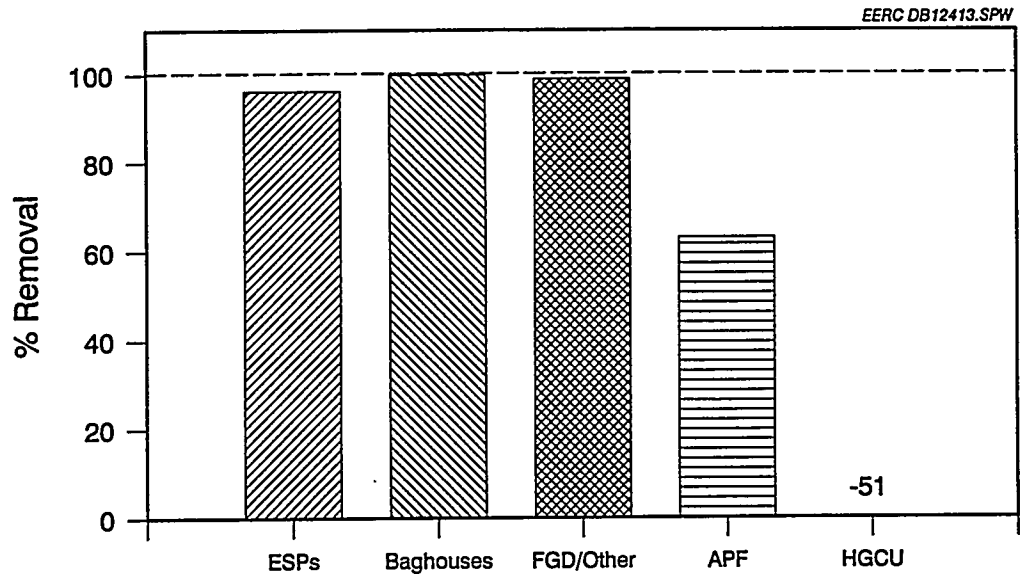


Figure 5-18a. Calculated Mo control efficiency averages for conventional systems as compared to advanced systems, full scale.

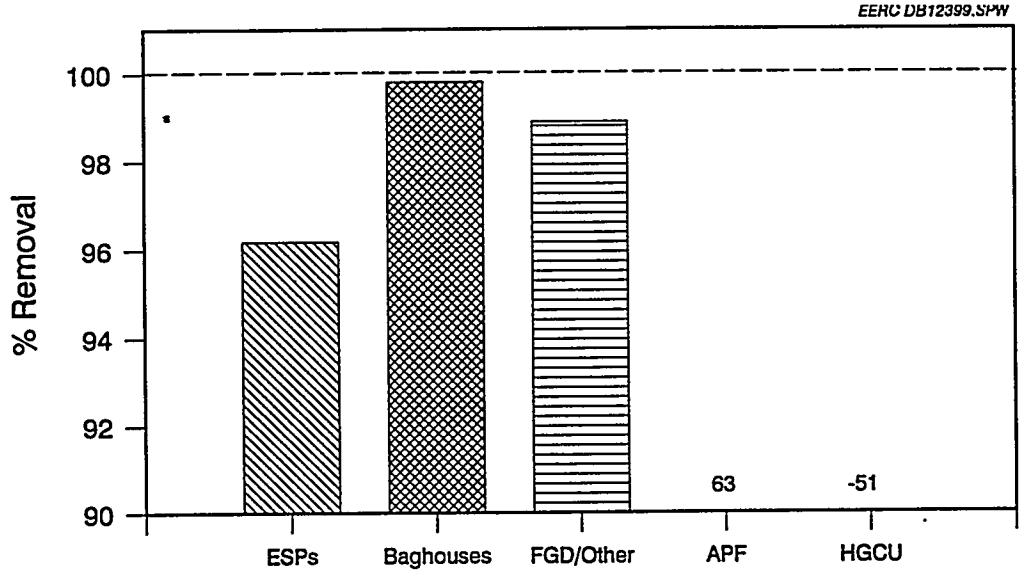


Figure 5-18b. Calculated Mo control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

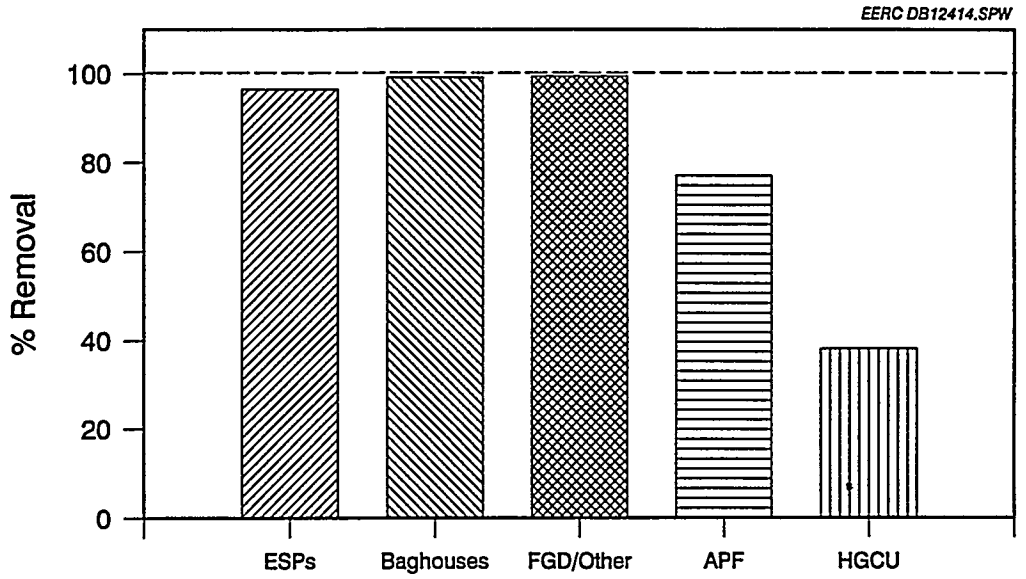


Figure 5-19a. Calculated Ni control efficiency averages for conventional systems as compared to advanced systems, full scale.

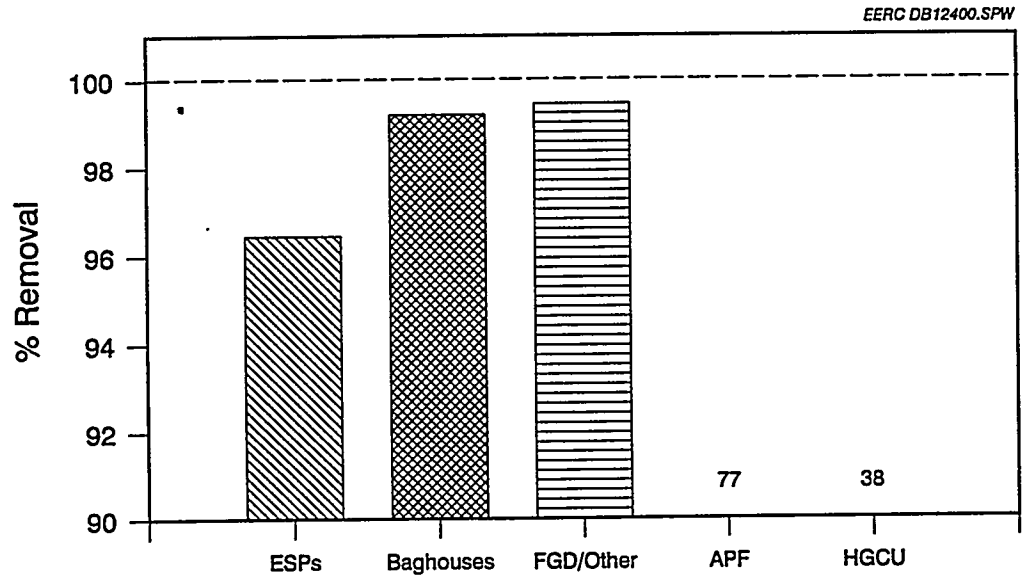


Figure 5-19b. Calculated Ni control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

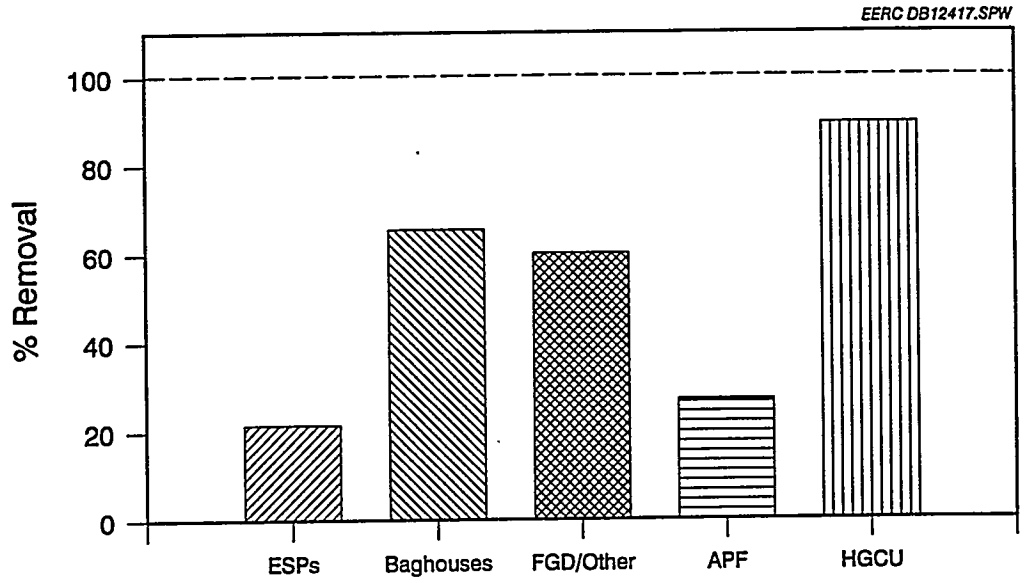


Figure 5-20a. Calculated Se control efficiency averages for conventional systems as compared to advanced systems, full scale.

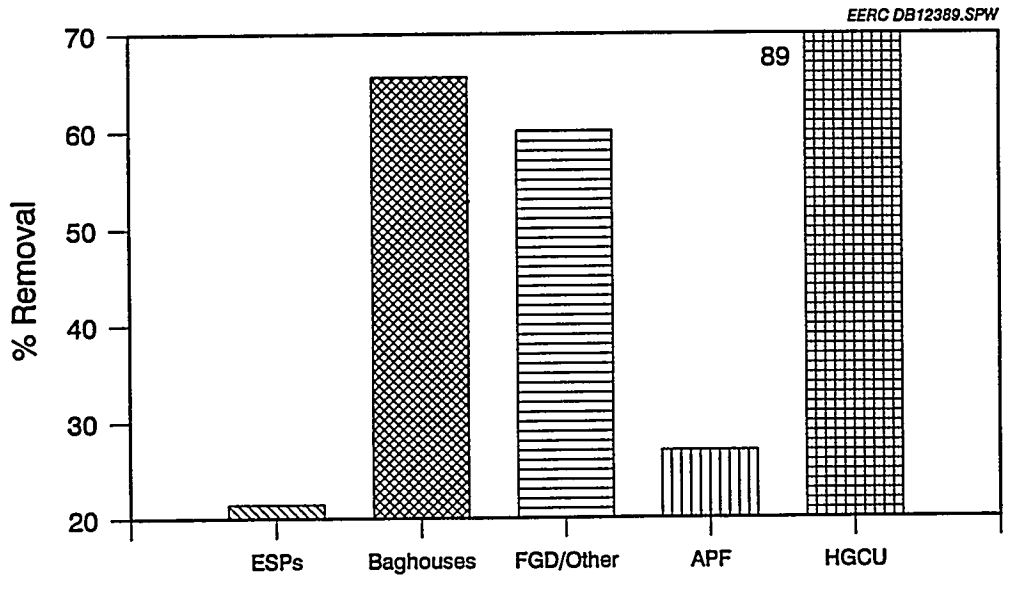


Figure 5-20b. Calculated Se control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

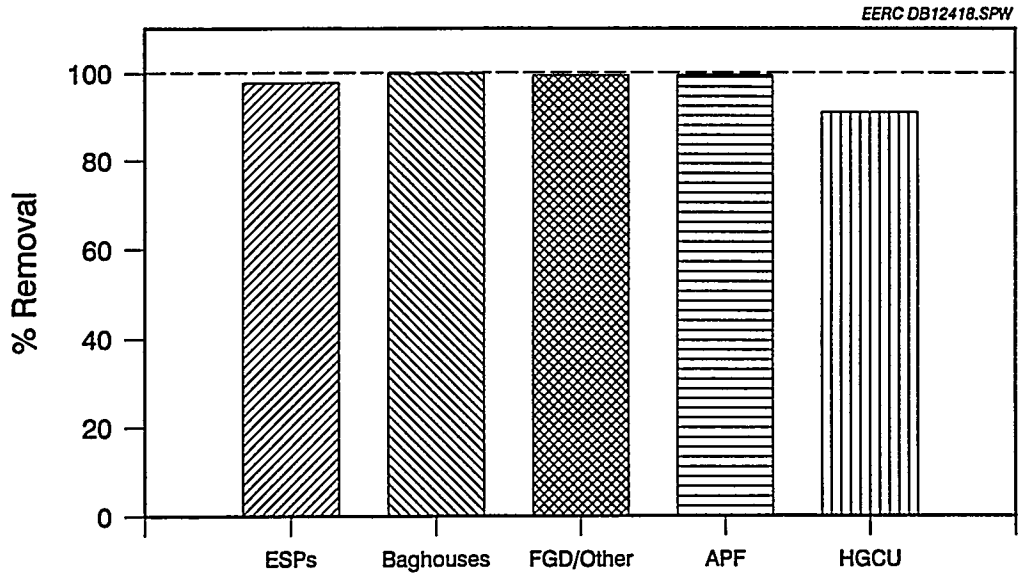


Figure 5-21a. Calculated V control efficiency averages for conventional systems as compared to advanced systems, full scale.

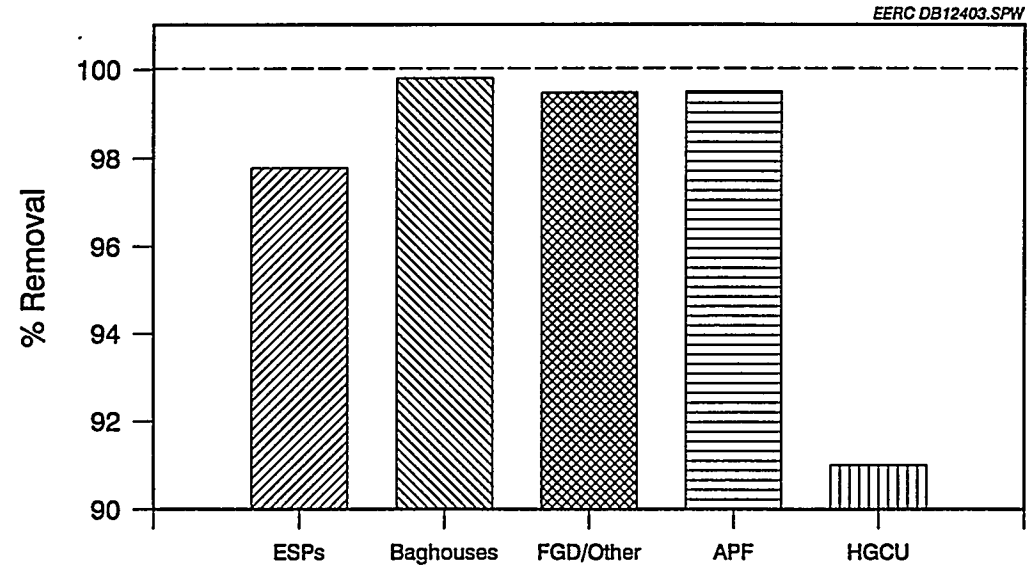


Figure 5-21b. Calculated V control efficiency averages for conventional systems as compared to advanced systems, reduced scale.

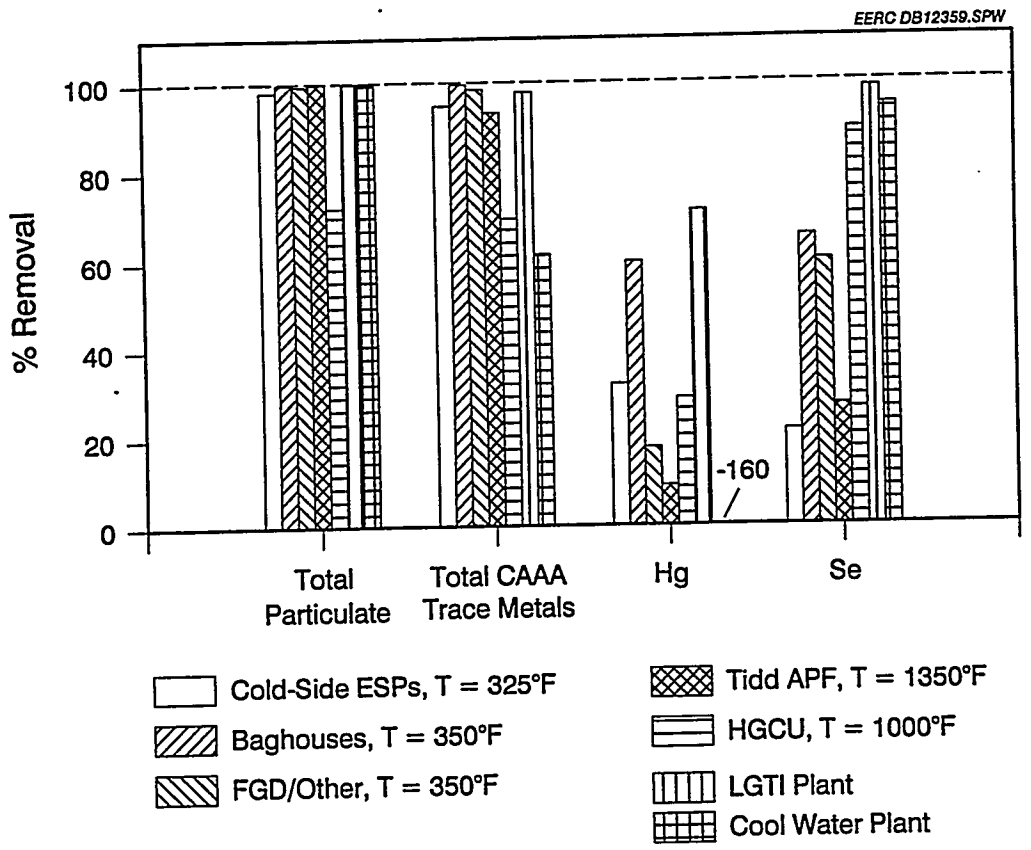


Figure 5-22. Average collection efficiency for all 11 CAAA trace elements, Hg, and Se for both conventional and advanced control systems.

5.3 Effects of Temperature on Cleanup Efficiencies – A Thermochemical Equilibrium Approach

The efficiency and environmental friendliness of emerging advanced power systems largely depends upon the effective removal of particulates from the gas stream at temperatures higher than those in conventional systems. These higher temperatures result in a change between the equilibrium abundances of inorganics present in the solid and vapor state, as compared to conventional systems. The ability to physically collect inorganic species depends largely upon their existence as particulate. Thermochemical equilibrium programs are an effective tool to aid in the determination of trace metal partitioning between vapor and solid species.

Vapor- and solid-phase information was researched for the 11 trace metals on the CAAA list shown in Table 1-1. Flemming Frandsen et al.[18] and the EERC, using its internal thermochemical equilibrium predictive capabilities, attempted to determine the partitioning of the elements of interest into vapor and particulate species. Frandsen looked at the effects of temperature for both gasification and combustion systems at atmospheric temperature on 10 of the 11 elements under generically defined conditions. The EERC performed calculations for six of the trace elements at 20 atm as a function of temperature under conditions to simulate a PFBC and an entrained-flow gasifier.

Figure 5-23 and 5-24 present partitioning of the trace elements under combustion and gasification conditions, respectively, at 1 atm. For the combustion system at 1 atm, over the

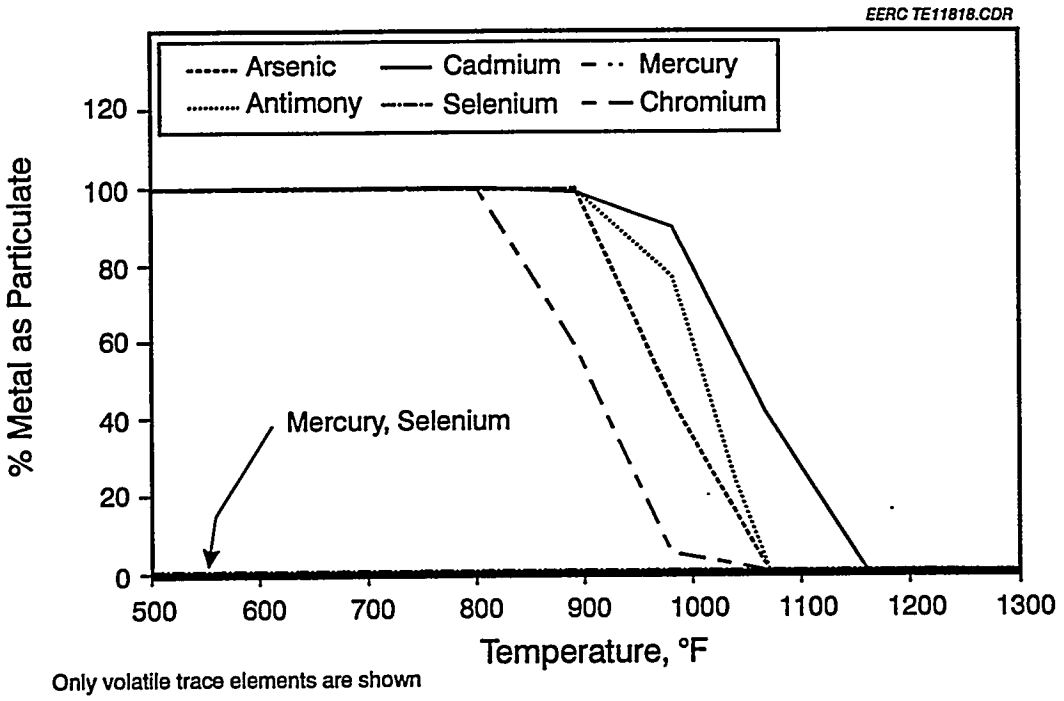


Figure 5-23. Amount of each element present as particulate as a function of temperature under typical combustion conditions for a subbituminous coal at 1 atm. The elements included in the predictions were As, Cd, Cr, Se, Hg, Sb, Ni, Pb, Co, and Be. Be, Ni, Pb, and Co were present primarily as particulate at all temperatures.

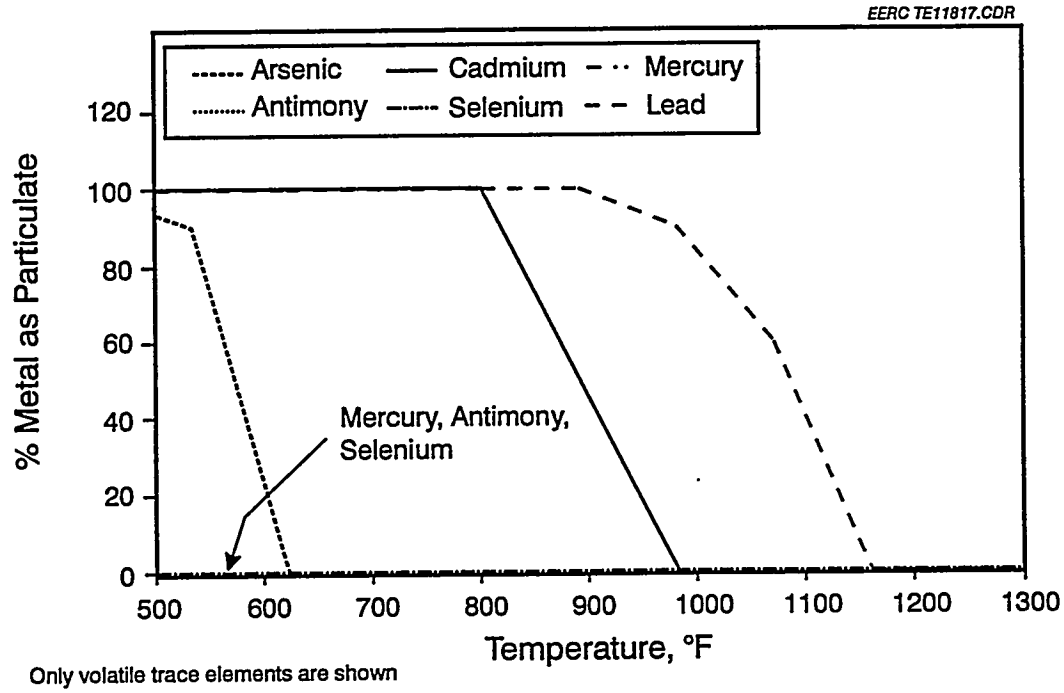


Figure 5-24. Amount of each element present as particulate as a function of temperature under typical gasification conditions for a subbituminous coal at 1 atm. The elements included in the predictions were As, Cd, Cr, Se, Hg, Sb, Ni, Pb, Co, and Be. Be, Ni, Cr, and Co were primarily present as particulate at all temperatures.

temperature range from 900° to 1100°F , there is a significant drop in the amounts of As, Cd, Sb, and Cr present in the vapor state. Similarly, for the gasification system at 1 atm, over the 850° to 1100°F temperature range, there is a decrease in the amounts of cadmium and lead present in the vapor state.

Figures 5-25 and 5-26 show similar results for combustion and gasification systems at higher pressures where the temperature ranges are shifted higher. In both cases, the vapor-phase species are shifted to higher temperatures as compared to the 1-atm predictions. Figure 5–25 also shows no vapor-phase Ni or Cr at 1050°F, which supports the idea that the high Ni and Cr values in the Tidd APF outlet samples are indeed due to contamination. The presence of lead as a vapor below 700°F at combustion conditions is due to the formation of various lead chlorides that are typically not present in real systems. Research at the EERC is ongoing to solve this predictive problem.

In using the thermochemical equilibrium programs to aid in the design and operation of higher-temperature cleanup systems, predictions must be made using exact parameters. However, to generalize from Figures 5-23 through 5-26, the lower the pressure, the lower the temperature needed for effective collection. At atmospheric pressure, systems should be run below approximately 900°F, while under higher pressures, temperatures can be extended to 1100°F (at 20 atm).

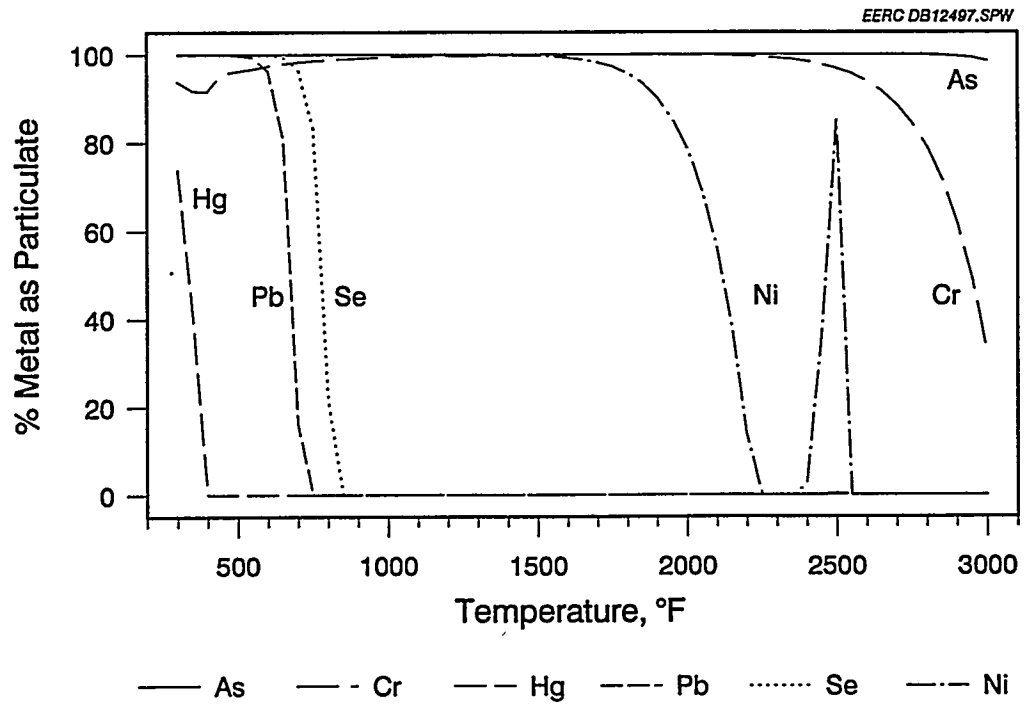


Figure 5-25. Amount of each element present as particulate as a function of temperature under typical combustion conditions as simulated for the Tidd PFBC system at 20 atm. The elements included in the predictions were As, Cr, Pb, Se, Hg, and Ni.

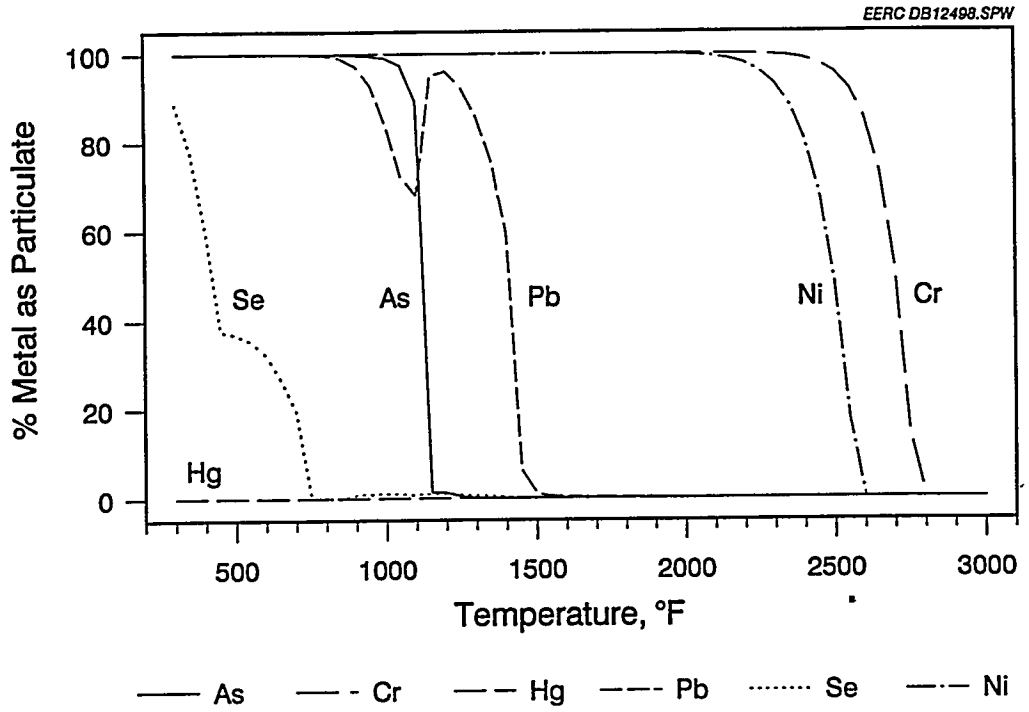


Figure 5-26. Amount of each element present as particulate as a function of temperature under typical gasification conditions as simulated for an entrained-flow gasifier at 20 atm. The elements included in the predictions were As, Cr, Se, Hg, Ni, and Pb.

6.0 SUMMARY AND CONCLUSIONS

The following conclusions can be drawn from the work reviewed in this report. Because of the limitations of some of the data, caution should be used in interpreting them. Whenever possible, the original reports should be reviewed to ensure data integrity and to gain an understanding of the problems associated with the sampling programs.

6.1 Available Data

- The overall review of HAPS from advanced power systems included four demonstration/full-scale systems and an equilibrium modeling exercise.

The review of trace element emissions from advanced power systems and hot-gas cleanup systems was limited to the data from Tidd, GE HGCU, LGTI, and Cool Water. Very few other sources of information were located and those that were investigated contained significantly flawed information that was not of value to this project. To offset the shortage of information, thermochemical equilibrium predictions were used in evaluating advanced control systems.

- Much of the data reviewed are poor quality and should be used with caution. The entire GE HGCU and Cool Water data sets are very questionable and should not be used.

High-quality data available for review in this report was scarce. The four primary reports reviewed all contained data limitations (as can be expected from full-scale sampling activities), and three of the four reports contained significant data limitations. In general, only the Tidd plant data and the external stream data from the LGTI are of sufficient quality to make any comparisons with conventional systems.

6.2 Sampling and Analysis

- Sampling and analysis of samples from oxidizing conditions were performed according to accepted methods.

- Sampling of reduced atmosphere streams was significantly flawed.

The sampling and analysis of vapor and particulate species within an oxidized gas stream is a fairly routine process that is carried out using standardized (EPA, American Society for Testing and Materials [ASTM]) techniques and procedures. For trace elements, these techniques have been shown to be reliable and accurate and to meet EPA guidelines. Some of these techniques are undergoing modifications to improve performance; however, as yet the general techniques are currently being used. When applied to reducing atmosphere conditions, these techniques are no longer appropriate to sampling trace elements, especially Method 29. The impinger solutions used in Method 29 are not effective in treating the reducing and caustic environment of a gasification product gas. To use Method 29 effectively, both the caustic gas (H_2S) and the reduced species (CO, H_2) need to be removed from the sample stream or compensated for by revising the solutions.

Radian Corporation attempted to address the reducing gas problem in the LGTI report. A comparison was made between the modified Method 29, packed charcoal tube traps, and on-line atomic absorption spectroscopy. The results are inconclusive, as the analytical data varied among the three techniques by 1 or 2 orders of magnitude.

6.3 Effect of Conversion Technology

- The Tidd plant PFBC "boiler" released fewer trace elements into the flue gas that would need to be controlled downstream than the Cardinal station pc-fired system.

Coal conversion technology can affect total emissions by reducing the amount of emissions that the hot-gas cleanup system must encounter. The Tidd PFBC showed a lower release of trace elements to the cleanup device than did the neighboring Cardinal station, a pc-fired system. This was apparent for most trace elements. The lower temperature of the PFBC and the primary cyclone unit are the principal reasons for this. Mercury emission was about the same for both systems, as expected.

- Partitioning of trace elements between the slag and product gas within the LGTI gasifier is not known because of insufficient information on internal streams.

The emission of trace elements from gasification systems was not adequately measured in the studies reviewed. The commonly held view that everything is forced into the slag within a gasification system is readily apparent upon inspection of the gasification data. However, samples

taken exiting the gasifier were subject to very low closure because of an inappropriate sampling technique. It is more likely that a significant amount of trace elements do indeed exit the gasifier, but that these elements are removed during the cooling and sulfur removal stages, processes that were not studied in the project. Since these particular sulfur removal processes will not be used in the newer technologies, this may present an emission problem, although sufficient data were not available for this review to support this assessment.

6.4 Total Plant Emissions

- The total CAAA trace elements released from the Tidd PFBC with APF and the LGTI system are approximately equal to or lower than that in conventional power systems.

The total CAAA trace element emissions from the advanced power systems are not properly reflected in the data reviewed in this report. The GE HGCU and Cool Water data sets contain flawed data that are poor of quality, and the emission values are believed to be highly inaccurate. The Tidd APF system data were also compromised by suspected contamination of Ni, Cr, and Mo during sampling of the APF exit stream. This would lead to an overestimate by more than 100 pounds of CAAA trace elements. It is believed that the APF system would be equivalent to baghouse systems if this error could be corrected (see Figure 4-24b). The LGTI system shows a very low emission of CAAA trace elements into the atmosphere. It is believed that the total CAAA trace element emissions from advanced power systems is comparable to or lower than that of conventional power systems, though it is not substantiated by the data reviewed.

- Mercury emissions from the Tidd APF are significantly higher than those from conventional combustion systems.

- Mercury emissions from the LGTI system are very low compared to conventional combustion systems.

Compared to conventional systems, the LGTI gasification system shows a very low emission of mercury, while the Tidd APF shows a higher emission. Since the APF operates at a high temperature, the emission of mercury is significantly higher than that for the combustion systems. The mercury data in the GE HGCU and Cool Water reports are considered unreliable.

6.5 Technology Control Efficiencies

- The overall efficiency of the Tidd APF is very good with respect to all particulate matter.

- The control efficiency of the GE HGCU system appears to be very low, but the data are unreliable.

The overall control efficiency of the Tidd APF is better than that for most of the conventional control technologies except for Cr, Ni, and Mo, and Hg. Mercury is the only element that appears to pose a potential control problem in the APF. The Ni, Cr, and Mo results are believed to be artifacts of sampling and are not considered accurate. The control efficiencies of the GE HGCU system are poor as a result of severely flawed data.

6.6 Potential Regulatory Impact

- Although EPA has yet to release its recommendations for the control of trace elements, it is believed that only mercury will be regulated in a manner affecting the operation of advanced power systems.

The potential for the regulation of advanced power systems is currently being driven by the 1990 CAAA. The CAAA list 189 compounds considered as HAPs that must be minimized. The current form of the regulations would allow only 10 tons/year of any single HAP and 25 tons/year of all HAPs combined. Any major source exceeding these limits will be required to apply the maximum achievable control technology to their system to meet the regulations. It is assumed that advanced systems will be governed under regulations derived from the results of conventional system testing.

Assuming that only the Tidd APF and LGTI data sets are valid, the overall emission of trace elements from advanced power systems appears to be equal to or lower than that of conventional systems, on average. Both systems fall below 1 ton of emission per year (assuming a 250-MW plant as previously discussed in Section 4.2.3). The only area of concern is likely the emission of mercury from the advanced power systems. Regulation of mercury is to be expected because of its environmental and health risks. Informal reports have shown that the EPA believes that there is significant mercury contamination of lakes from air deposition and that coal-burning power plants are one of the major sources. Since the Tidd APF and other future advanced technologies will operate at temperatures exceeding conventional technologies, it is anticipated that mercury emissions will be an issue.

7.0 RECOMMENDATIONS FOR FUTURE WORK

The following is a list of recommendations for future work involving the evolution of advanced power systems into proven, environmentally safe coal conversion systems. These recommendations are shown in order of importance as determined by the authors of this report.

- **Control of Mercury in Advanced Combustion Systems.** Since mercury is likely to be regulated, notwithstanding its low concentration, a suitable method of control must be identified for advanced power systems. For the current gasification systems using low-temperature cleanup devices, this does not appear to be a problem. As systems switch to high-temperature cleanup technologies, this will become a problem. In PFBC systems, this problem is evident from the sampling around the APF. Research should focus on the use of high-temperature mercury sorbents (possibly scrap metals) in both oxidizing and reducing environments and on the economics of placing low-temperature mercury cleaning systems prior to stack emission (now being developed for conventional combustion systems).

- **Development of Sampling Techniques for Use in Reducing Environments.** To fully research the impacts of cleanup technologies on trace elements, an effective technique to quantitatively sample trace elements is needed. The technique may be either a modification to the existing EPA Method 29 technique or a completely new one. Until

such a technique is found, all gasification system sampling for trace metals should be limited to the fully oxidized gas streams (flue gas exiting turbines and incinerators). The most near-term solution to this sampling problem may be to oxidize the gas stream after particulate removal and prior to impinger sampling. A second filter should be located just prior to the impingers to capture any metals that condense during the oxidation. The overall gas-phase concentration can then be calculated from the second filter and the impingers. Optional methods of oxidizing the gas stream include installing a burner or passing the gas over/through an oxidizing catalyst (platinum) with excess oxygen.

- **Need for More Data.** Much of the information presented within this report is based on a very limited amount of data, of which a large part is significantly flawed. Considering the imminent arrival of clean coal technologies, it is recommended that an initiative be undertaken to sample emissions from numerous advanced power systems. Internal process measurements should also be mandated, but only if the appropriate sampling techniques exist. The use of ceramic filters should be monitored closely for mercury control as noted in the first recommendation. All sampling projects should be very structured including validation of sampling and analysis prior to initiation.

- **Use of Modeling to Aid in Research.** In cases where data do not exist or sampling methods are not yet appropriate, thermochemical equilibrium modeling can be performed to aid in research. Thermochemical equilibrium predictions can support the development of sampling techniques by identifying species present and can assist in the design of hot-gas cleanup systems where it can be used to predict points of condensation and particulate capture. Models do not replace advanced research, but rather help focus the research to provide answers at a lower cost.

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3. Electric Power Research Institute. "Cool Water Coal Gasification Program: Final Report," Report No. GS-6806; December 1990.

4. Radian Corporation. "Trace Element Determinations During Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System, and Gas Turbine Simulator," final report DCN 94-643-011-01 for General Electric Company; July 1994.

5. Radian Corporation. "A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP While Demonstrating the ICCT CT-121 FGD Project," final report DCN DE-AC22-93PC93252 for U.S. Department of Energy; June 16, 1994.

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APPENDIX A

CORRESPONDENCE BETWEEN DR. ALAN FEITELBERG AND THE EERC

Energy & Environmental Research Center

UNIVERSITY OF NORTH DAKOTA

15 North 23rd Street — PO Box 9018 / Grand Forks, ND 58202-9018 / Phone: (701) 777-5000 Fax: 777-5181

January 10, 1995

Dr. Alan Feitelberg
GE Company
Corporate Research and Development
Building K-1, Room ES103
PO Box 8
Schenectady, NY 12301

Dear Alan:

I am currently working on a project entitled "Assessment of HAPs Studies from Advanced Power and Hot-Gas Cleanup Systems" for the Morgantown Energy Technology Center (METC). This project is designed to assess the current knowledge of HAPs behavior in advanced power systems and hot-gas cleanup systems in terms of potential legislation and economics.

As part of that project, I am reviewing data from hot-gas cleanup systems. I received a report entitled "Trace Element Determination During Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System, and Gas Turbine Simulator" from Dr. Peter Botros at METC. He has requested that I include this study in my project. I am trying to calculate the total amount of trace metals removed across the system, but I am missing some of the critical numbers. I need to be able to compare the inlet and outlet streams for both the particulate and vapor, as well as combine the particulate and vapor streams into a total amount. Specifically, the two sets of numbers I need are 1) the mass of particulate entering and leaving the HGCU/time and 2) the Nm^3 of gas entering and exiting the HGCU/time. I assume these numbers have been measured or calculated during the testing. Our definition of the HGCU is the same as used in the report which includes both the absorber/Zn titanate and the secondary cyclone (i.e., the input stream is after the primary cyclone and the output stream is after the secondary cyclone). Though it is not shown in the diagram in that report, I assume there is also a gas stream out of the Zn titanate absorber that carries the sulfur-rich gas. Would it be possible to get the concentrations and mass flow rates of this steam also (if you have them)?

In addition, if available, I would appreciate getting a copy of the analytical characterization of the sorbent including trace elements, before and after operation of the system, and the mass flow rate and composition of the secondary solids.

I will hold all information given to me in the strictest confidence and will consider it proprietary. I would be happy to send you a copy of our resultant mass balance, control efficiency, and partitioning calculations. The Department of Energy and I would appreciate your quick response on this matter because of impending time lines.

Sincerely,

Thomas A. Erickson
Senior Research Manager

TAE/pjr

c: Peter Botros, METC
Steve Benson, EERC
Dave Brekke, EERC

GE Corporate Research
& Development

Dr. Alan S. Feitelberg
Building K-1, Room ES 103

General Electric Company
P.O. Box 8, Schenectady, NY 12301
518 387-
5737
FAX: (518) 387-7258
E-mail: feitelberg@crd.ge.com

January 19, 1995

Thomas A. Erickson
Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street
Grand Forks, ND 58202

I have prepared the following information in response to your letter of January 10.

The report you sited, "Trace Element Determination During Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System, and Gas Turbine Simulator," was prepared from data collected at the GE-CRD pilot plant during the week of 11/1 through 11/5/93. We refer to this time period as Long Duration Test 5. During this test the coal gas flow rate entering the absorber averaged 2.1 lb/s, ± 10%. The mean molecular weight of the coal gas was about 22 g/mol, yielding a coal gas volumetric flow rate of approximately 1.1 Nm^3/s (normal conditions = 1 atm, 298 K).

The total particulate loading in the coal gas entering the absorber was found to be about 90 ppm by weight. The coal gas leaving the secondary cyclone contained about 25 ppm by weight of particulate. These concentrations translate into about 1.9×10^{-4} lb/s of particulate matter entering the absorber with the coal gas, and about 5.3×10^{-5} lb/s of particulate matter leaving the secondary cyclone with the coal gas.

As we discussed on 1/18, there is no sulfur-rich gas stream leaving the absorber. Sulfur leaves the absorber in the solid phase, as part of the zinc titanate sorbent pellets. Sorbent pellets flow into a second vessel, the regenerator, where oxygen is added. The oxygen regenerates the pellets to their original state, after which they are returned to the absorber. Sulfur leaves the regenerator in an SO_2 rich gas stream which, in a full-scale plant, would be used to make sulfuric acid. We have not sampled this SO_2-rich gas stream for trace elements in either the vapor phase or the particulate phase.

If you are using the Radian report to perform trace element balances around the process, then you should be aware that the vapor phase coal gas samples were severely contaminated with particulate matter. Even a casual examination of the vapor phase samples shows that the vapor phase concentrations of some elements are extraordinarily high, many times above expectations at the nominal hot gas cleanup temperature of 1000°F. After the test, we discovered that operator error had caused most of the particulate filters in the sample train to break, allowing

particulate matter to enter the vapor phase sample traps. I should add that the Radian test personnel who collected the trace element samples were in no way responsible for this blunder. I should further add that this test was our first (and, to date, our only) attempt to sample the hot coal gas for vapor phase trace elements, and it was very much a learning experience for all involved.

Although the filter elements broke, and allowed particulate matter to enter the vapor phase samples, the particulate loading measurements themselves are fairly accurate. Only a small amount of particulate matter leakage is needed to result in a large error in the vapor phase samples. In addition, we have particulate loading measurements from previous and subsequent tests which agree with the results from Test 5, within the accuracy of the measurements.

We believe the vapor phase turbine simulator exhaust samples were also contaminated with some particulate matter, although the source of the contamination is not completely clear, and the degree of contamination appears to be less severe than the coal gas vapor phase samples. One possible source of contamination is the metal tubing in the sample train, downstream of the particulate filter but upstream of the vapor phase sample traps. This tubing was not cleaned before collecting the vapor phase samples. Metal filings and other debris left inside the tubing during assembly may have been transported to the vapor phase sample traps.

To the best of my knowledge, we have not performed a complete trace element analysis on the Test 5 secondary cyclone catch or the zinc titanate sorbent. However, I have attached a mineral analysis of the Test 5 secondary cyclone catch which includes some trace elements (see Table 1). The secondary cyclone removed approximately 7.1 lb/hr of solids from the coal gas during Test 5.

Please contact me if you have any questions or require any additional information. None of the information provided here should be considered proprietary. We look forward to receiving a copy of your mass balance, control efficiency, and partitioning calculations.

Regards,

Alán S. Feitelberg

cc: D. J. Najewicz
A. H. Furman
R. E. Ayala
S. Bevan, GEESI

Mineral	Concentration (% by weight)
Silica, SiO_2	12.25
Alumina, Al_2O_3	6.62
Titania, TiO_2	17.6
Iron oxide, Fe_2O_3	5.1
Calcium oxide, CaO	0.47
Magnesium oxide, MgO	0.28
Potassium oxide, K_2O	0.83
Sodium oxide, Na_2O	6.08
Sulfur trioxide, SO_3	8.13
Phosphorous pentoxide, P_2O_5	0.19
Strontium oxide, SrO	0.05
Barium oxide, BaO	0.06
Manganese oxide, Mn_3O_4	0.06
Zinc oxide, ZnO	40.9

Table 1: Mineral analysis of the secondary cyclone catch from Test 5. The high concentrations of zinc and titania suggest the bulk of the secondary cyclone catch is sorbent fines carried over from the absorber.