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Assessment of HAPs Emissions from Advanced Power Systems

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Introduction

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 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 HAPs data currently available for presentation to the U.S. Department of Energy (DOE)[1].

TABLE 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	

The review of trace element emissions from advanced power systems and hot-gas cleanup systems included data from Tidd Station [2], General Electric hot-gas cleanup (GE HGCU)[3], Louisiana Gasification Technology Incorporated (LGTI)[4], and the Cool Water plant [5]. 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 2. In addition to the four demonstration and

full-scale systems reviewed, nine conventional systems were also reviewed for comparison with the advanced systems [6–14].

TABLE 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.

Methods

Sample Collection, Characterization, and Manipulation. The sample collection and characterization techniques used at Tidd and at the conventional sampling-sites can be found in the individual sampling reports [1–10]. In general, all sampling teams followed accepted EPA sampling and analysis techniques and most teams utilized American Society for Testing and Materials (ASTM) or American Society of Mechanical Engineers (ASME) data manipulation routines. Since significant differences in methodology among contractors was noted, the 95% confidence limit was calculated from raw data in the individual reports. The confidence limits include only the precision of the data and contain no information related to the bias of the measurements. Comments are offered to help qualify any potentially incorrect data.

Modeling. To aid in the interpretation of the advanced power systems emission data, a thermochemical equilibrium software package was used. FLUENT was used to generate predicted partitioning between vapors and solids at various locations within the system. The FLUENT code predicts this partitioning through the minimization of Gibbs free energy, over a given set of inouts and potential output phases.

Results

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 U.S. Department of Energy (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.

The primary methods used to obtain samples from flue gas streams were EPA Methods 5 and 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 to be 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 temperatures of the PFBC and the primary cyclone are the principal causes of this. Figure 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.

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 sufficient data were not available to support this assessment.

Total Plant Emissions. Figure 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, mercury and selenium. The CAAA trace element emissions for the GE HGCU and the Cool Water plant are significantly higher than for the other systems. The GE

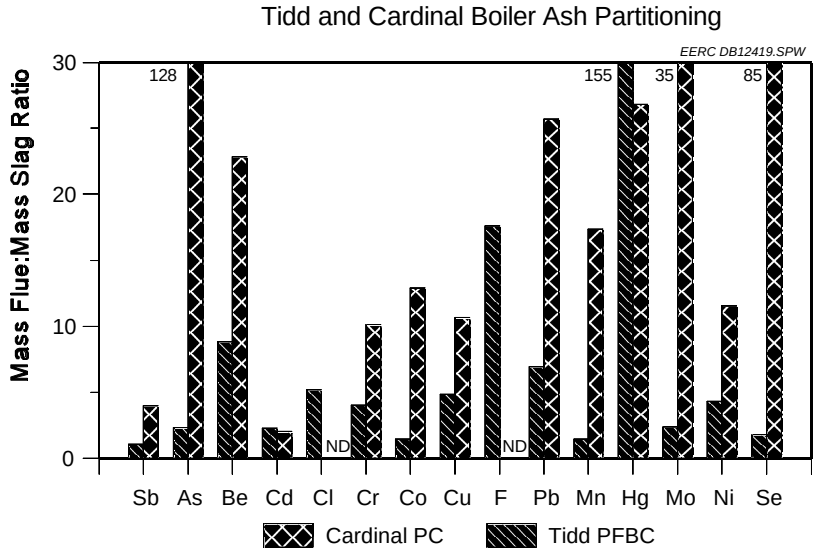

Figure 1. Partitioning of trace elements in ash within the "boiler" for the Tidd PFBC and the Cardinal pc-fired units. The partitioning factor is equal to the ratio of the mass of the element leaving the system in the flue gas to the mass in the slag/bottom ash. ND = Not detected.

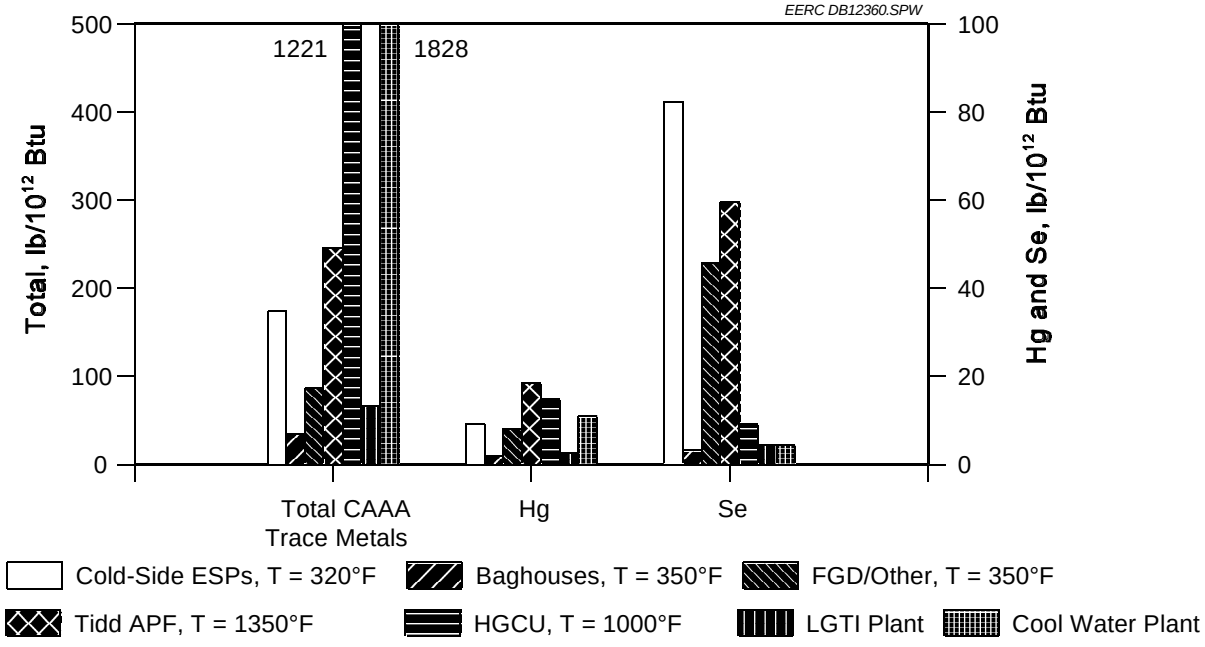

Figure 2a. Summarized emission factors of total CAAA trace elements, Hg, and Se. Note that contamination of Cr and Ni in the Tidd APF outlet samples is suspected. Results from both GE HGCU and Cool Water were subject to sampling error.

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 that it is the third highest emitter. However, most of these emissions are chromium and nickel, which are believed to be contamination from the sampling probe. Thermochemical equilibrium calculations also suggest that this is contamination. By assuming that the chromium and nickel 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 2b. Considering this assumption, both the Tidd APF and the LGTI systems show emission as low or lower than conventional systems.

The emissions of mercury and selenium appear to be elevated in the Tidd APF, likely because of the high operation temperature of the system. Since the mercury 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.

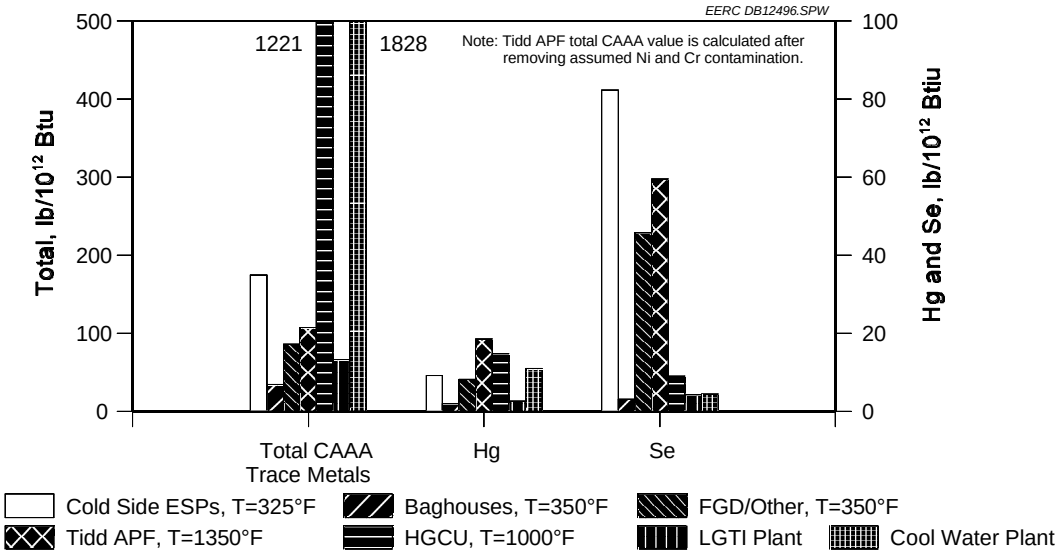

Figure 2b. Summarized emission factors for all 11 CAAA trace elements, Hg, and Se with the Tidd APF total CAAA value corrected for contamination of Cr and Ni.

Evaluation of Control Technologies. The average control efficiency for total particulate, total CAAA trace elements, and mercury and selenium are shown in Figure 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 chromium and nickel 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 in 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 4 and 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.

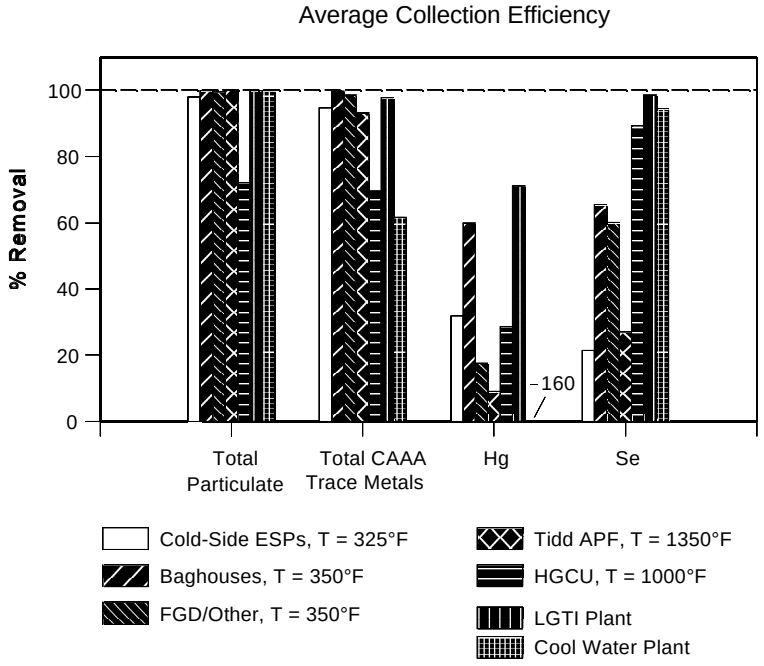

Figure 3. Average collection efficiency for all 11 CAAA trace elements, Hg, and Se for both conventional and advanced control systems.

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, 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 1 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.

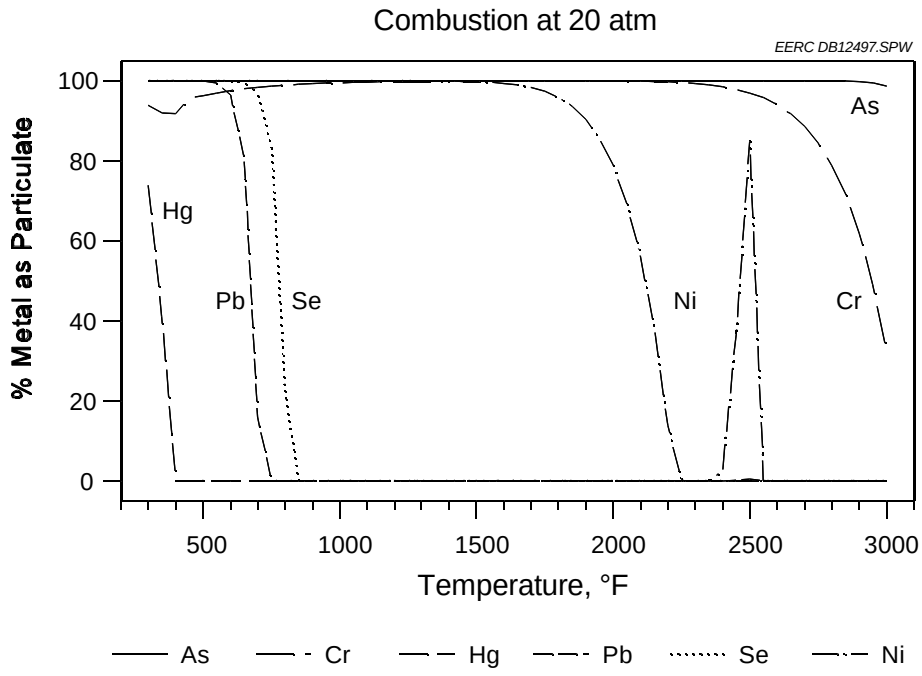

Figure 4. Amount of each element present as particulate as a function of temperature under typical combustion conditions as simulated for the Tidd PFBC system at 20 atm.

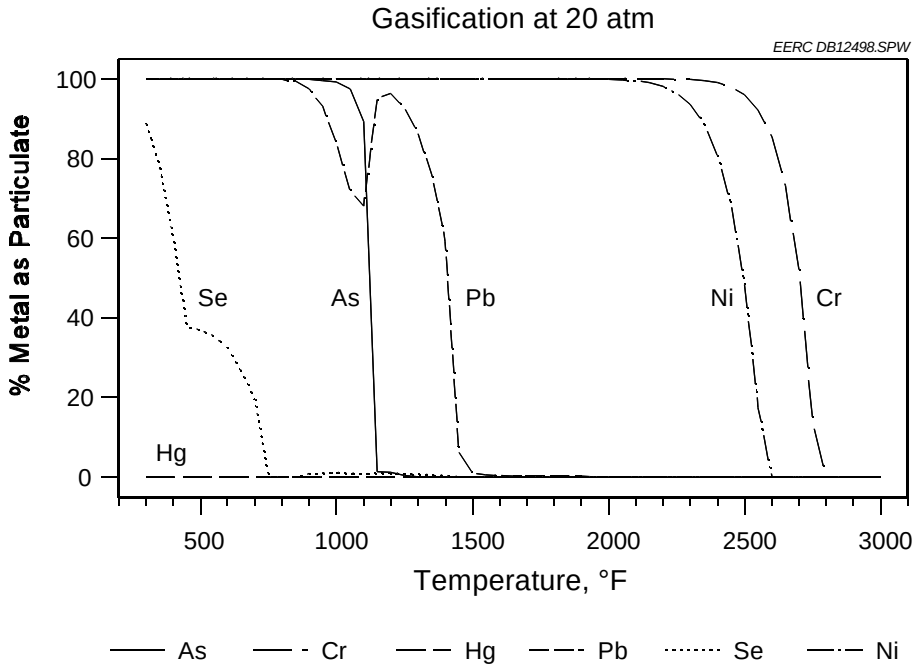

Figure 5. Amount of each element present as particulate as a function of temperature under typical combustion conditions as simulated for an entrained-flow gasifier at 20 atm.

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, starting with the most important.

- **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 highly 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.

Contract Information

The work reported here was performed under U.S. Department of Energy Contract No. DE-AC21-92MC28016.

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