

Managing air toxics under the new Clean Air Act Amendments

New CAA air toxics provisions have an impact on power plants. But help is available to manage substances, such as hydrochloric acid and mercury, if they are regulated

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The U.S. Environmental Protection Agency (EPA) has been regulating air toxics (hazardous air pollutants) under Section 112 of the 1970 Clean Air Act Amendments. To date, EPA has established emission standards for seven hazardous air pollutants. They include arsenic, asbestos, benzene, beryllium, mercury, vinyl chloride and radionuclides. EPA had determined that the low risks associated with electric utility fossil fuel power plant radionuclide emissions did not justify regulation under Section 112.

The Clean Air Act Amendments of

1990 greatly expand EPA's rulemaking authority over toxic or hazardous air pollutants. The law lists 189 chemicals that would be subject to control. Sources that emit 10 tons/yr or more of any one pollutant, or 25 tons/yr or more of any combination thereof, must apply maximum available control technology (MACT). By definition, MACT is at least as stringent as best available control technology (BACT) for similar sources. However, consideration of the cost and feasibility of control, energy impacts and environmental factors will be given in MACT.

Under the new amendments, the EPA will conduct a three-year study of the public health hazards from exposure to toxic emissions from utilities and report to Congress. EPA can regulate such emis-

sions only if the regulations are appropriate based on this study. Two additional studies addressing mercury are also required. The first directs the EPA to conduct a four-year study of mercury emissions from electric utility steam generating units, municipal waste combustion units, and other sources. Included are evaluations of the rate and mass of such emissions, of health and environmental effects, and of the available control technologies and their costs.

The second study directs the National Institute of Environmental Health Sciences to study the threshold level of mercury exposure to protect human health.

However, EPA is directed not to regulate these pollutants until the studies are completed and in no event will regulations be set sooner than three years nor later than five years after enacting the legislation.

There are good reasons why power plant emissions are not the primary focus of the new Clean Air Act Amendments' air toxics provisions. EPA studies show that those emissions of potential cancer-causing constituents pose small risks (less than one additional cancer incident per year in the United States) for the general population. EPA has stated, however, that this value is a rough estimate containing considerable uncertainty. Its studies included arsenic, selenium, hexavalent chromium, cadmium, formaldehyde, and radionuclides emitted from coal-and oil-fired boilers. An industry review of the study suggests that the estimate is conservative and that resolution of uncertainties may lead to a lower estimate.

Potential impacts on electric utilities

Regardless, the amendments potentially hold enormous financial implications for utilities. Coal-fired power plants could be subject to air toxics controls if acid gas emissions, such as hydrochloric acid, exceed 10 tons/yr. Of the 189 substances listed as air toxics, an EPRI literature search shows that 36 are found in utility flue gas emissions (Table 1).

The EPA has developed air toxic emissions factors for power plant boilers, but the values have many limitations. Quality assurance procedures were not performed, nor do the authors of the EPA report endorse the emission factors as representative. They note that "There is considerable uncertainty in these estimates due to the wide variability in trace element levels in coal, variations in the design and operating parameters of boilers and control devices, and uncertainty in sampling and analytical methodologies for detecting trace pollutants."

More recent analysis of these and later data supports lower emission factors, especially for chromium, manganese and nickel. Also, the study focused only on those chemicals classified as potential carcinogens. The list of 189 pollutants also

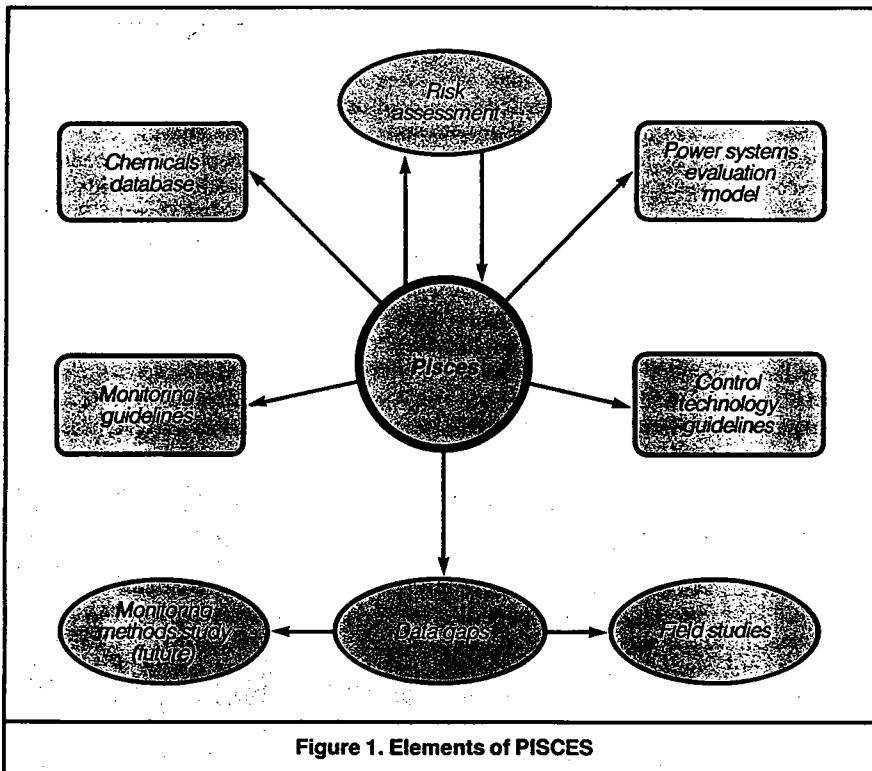


Figure 1. Elements of PISCES

includes chemicals such as hydrochloric acid (HCl), chlorine and phosphorous. They are not carcinogens. But based on chloride levels found in U.S. coals, if HCl emissions were counted, they would easily cause most coal-fired power plants to exceed the 10 ton/yr limit.

The worst-case scenario for a utility under the air toxics requirements involves retrofitting scrubbers to capture volatile species (such as HCl and mercury) and baghouses or high-efficiency ESPs for trace metals. An analysis by Temple, Barker and Sloane for the Senate version of the CAA (S. 1630) estimated that compliance with the air toxics provisions of that bill could cost an additional \$7.8 billion/yr beyond acid rain compliance. This assumes addition of scrubbers and baghouses to virtually all coal and oil units.

EPRI air toxics activities

To help utility staff members better understand power plant emissions of potentially toxic chemicals, EPRI initiated the PISCES (power plant integrated systems: chemical emissions study) project in mid-1988. This involves collection and review of data on the source, distribution and fate of chemicals in fossil-fired power plants.

PISCES includes a relational database on chemical species in power plant systems, a computerized power plant systems model to track the pathways of chemicals and quantify emissions. There also is a field monitoring program to measure emissions of 24 chemicals (Table 2) in flue gas at power plants that use different emission control technologies. In addition, the project provides emission control technology guidelines and an analytical methods guideline for measuring trace chemicals in utility process and discharge streams (Figure 1).

In parallel, EPRI's Environment Division currently is conducting risk assessment on 10 chemicals to define other research needs and priorities. Further, a study of atmospheric transformations for selected air toxics is underway to better understand their ultimate form and fate.

PISCES places multi-media in perspective wherein the study evaluates the presence and fate of chemicals in air, water and solid waste discharges (Figure 2). This holistic approach allows controls to be applied with full knowledge of impacts on other plant process streams.

The database

The project to date has focused on information collection for conventional coal-, oil-, and gas-fired power plants. More than 500 chemicals have been identified in power plant process streams. Of these, about 80 were selected for additional data search on regulatory limits and health effects. In general, more and better data were available for inorganic species in liquid and solid process streams than for

air toxics. Fewer data are available for inorganic species in gaseous process streams and for organic species in general.

At this writing, the interim database contained more than 150 megabytes of information, including 80,000 records of reported quantity data. The database allows users to assemble data on chemicals in power plant process streams. Then, they can organize it to explore relationships between chemicals, process streams and plant systems or components.

An example of information derived from the database is shown in Figure 3. It depicts the concentration of nickel in various power plant fuels. These curves represent the probability of finding nickel at less than a specific concentration for each fuel. Thus, while there is a 95% chance that the nickel concentration in lignite is less than 10 ppm, the probability diminishes to 75% for subbituminous coal, 30% for bituminous coal and 5% for fuel oil.

Alternatively, the further a curve proceeds to the right for a given probability, the higher the nickel content in the fuels. A similar chart for mercury (Figure 3)

illustrates less dramatic differences between coal types.

Monitoring chemical species

Reliable evaluation of potentially toxic emissions depends on the industry's ability to accurately sample and measure chemical species. This is especially critical because most of those listed in the Amendments appear only in trace amounts in power plant process streams.

To furnish utilities with interim guidance, PISCES has produced a compendium of available methods for measuring trace substances in process streams, including flue gases. This information should help in power plant sampling programs and assist the staff to assess air toxics emissions and understand the limitations of measurement methods. Future project efforts will involve field evaluation studies of specific areas such as sampling techniques that yield poor trace species recoveries (e.g., mercury).

Control technology capabilities

Control technology guidelines also are being prepared. They will help to determine performances of various emission control devices in removing trace chemicals, a capability needed if a risk assessment supports the need for controls at a given power plant. These documents will provide emission factor estimates and insights into the mechanisms of chemical removal. For example, the role of temperature, ESP size and performance, and the concentration and form of trace elements in the coal will be discussed (if known) in terms of their impact on emissions and removal. Interim guidelines will begin to appear as a series of documents in published form by the summer of 1991.

Figure 4 shows preliminary PISCES data on the performance of conventional air quality control devices. The plots represent an aggregate of power plants, including those that burn bituminous, subbituminous and lignite fuels. Mercury, nickel and hydrochloric acid are illustrated because of their interest to utilities.

These figures identify two important issues that are related to the database and our grasp of the ability of conventional air pollution control devices to remove trace pollutants from flue gases. First, quality data are not available; second, available data exhibit wide variabilities.

Although there are a large number of data points for plant emissions of various chemical species, the number of paired data sets—inlet and outlet—on any given control device is sparse. For example, the database furnished no performance data for nickel or chloride removal by fabric filters. The numbers shown with each range bar indicate the number of data pairs from the PISCES database. Without much information about a device, partitioning of chemicals into gaseous, solid or

Table 1. Listed chemicals in combustion flue gas.

Acetaldehyde
Antimony compounds
Arsenic compounds
Benzene
Beryllium compounds
Biphenyl
Bis(2-ethylhexyl) phthalate (DEHP)
Cadmium compounds
Carbon disulfide
Carbon tetrachloride
Carbonyl sulfide
Chlorine
Chlorobenzene
Chloroform
Chromium compounds
Cobalt compounds
Dibenzofurans
1,4-Dichlorobenzene(p)
Formaldehyde
Hexachlorobenzene
Hydrochloric acid
Hydrofluoric acid (Hydrogen fluoride)
Lead compounds
Manganese compounds
Mercury compounds
Naphthalene
Nickel compounds
Pentachlorophenol
Phenol
Phosphorous
Selenium compounds
2,3,7,8-Tetrachlorodibenzo-p-dioxin
Tetrachloroethylene (Perchloroethane)
Toluene
Trichloroethylene
2,4,5-Trichlorophenol

liquid phases is difficult to estimate.

In addition, large variabilities in the performance of control technologies raise questions over their capability for effective, dependable removal of the myriad chemicals perceived as toxic. A number of factors, such as the performance of sampling and analytical methods or size and operating conditions of the device, may contribute to these reported variables. Although the 28 clustered data-points show the effectiveness of cold-side ESPs at removing nickel (by 90-99%), firm conclusions cannot be drawn on other conventional air quality control devices because of a lack of data.

Field monitoring

To fill the critical need for more data, a PISCES multi-media field monitoring program was begun in May 1990 with the collection of data on 24 chemicals. Emissions and discharges will be measured from several control technologies, including cold-side ESPs, fabric filters (conventional and pulse-jet), low- NO_x burners, post-combustion NO_x systems, spray dry FGD and wet lime/limestone FGD systems. Plant mass balances for each of the 24 chemicals will be performed to define their sources, pathways and the way they partition in the plant system. Therefore, all appropriate liquid and solid waste streams also will be sampled.

A variety of coal types will be sought to test in different types of combustion systems. Combustion sources include wall-, tangential-, and cyclone-fired boilers and fluidized bed systems. Also, oil- and gas-fired power plant emissions will be examined for a smaller subset of air toxics. Improved sampling and analytical procedures will be used to acquire new, high-quality data from current utility operations. This will upgrade the database and the interim Control Technology Guidelines.

Systems model

The power systems model, being developed by Carnegie-Mellon University, provides either deterministic or probabilistic estimates of the gaseous, liquid, and solid emissions from a specified power plant configuration. Stream conditions for coal-fired plants are characterized for 15 plant subsections that are used to configure a plant for analysis. These systems range from coal, ash and sludge handling/disposal through steam, makeup and cooling water to particulate collection/disposal and miscellaneous equipment.

Major plant flow rates are quantified based on internal mass and energy balance calculations for a specified plant size, equipment design, and fuel choice. To operate the model, users must specify inputs, such as power system design parameters, performance characteristics, emission constraints, fuel properties and pollution control performance measures.

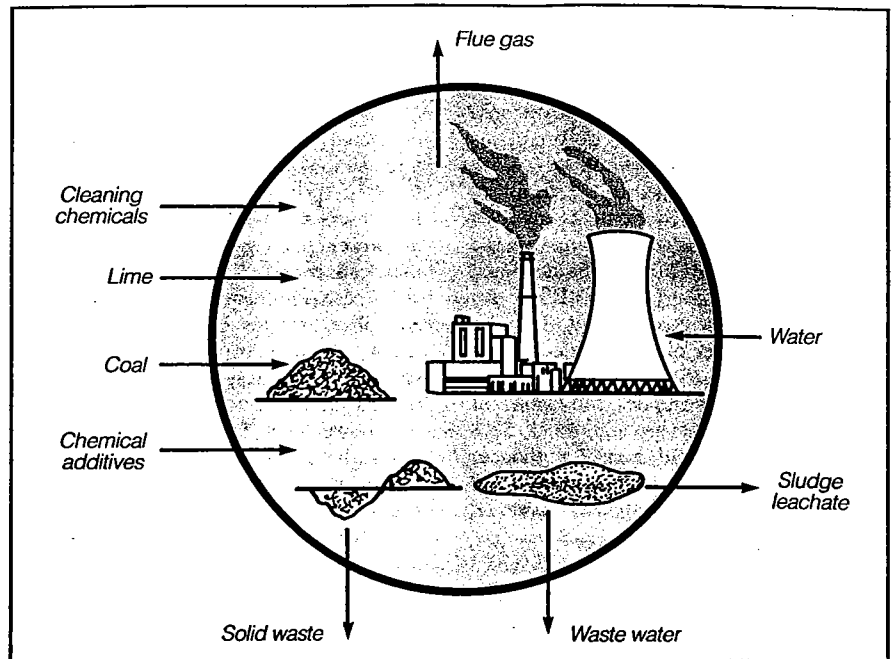


Figure 2. A holistic concept.

The pollution control performance measures can be acquired in one of two ways. Based on operating experience, utilities may have site specific performance data on environmental control devices. Or, partitioning factors for various chemical species between solid, liquid and gaseous streams can be derived for a device if sufficient data exist in the PISCES database.

An important application of the PISCES model will be to characterize the chemical composition of various power plant emission streams, such as collected flyash, bottom ash, FGD by-product, ash pond effluents, and stack gases.

The probabilistic feature of the model allows an uncertainty factor to be incorporated into calculating emissions of various chemicals. This uncertainty can stem from the variability of specific chemicals in coal, plant operations, and sampling and analytical variability. This feature allows utilities to assess the likelihood of emitting a substance at a specific rate with a given confidence level.

Such estimates may be used to evaluate overall emissions of a specific plant. It is anticipated that interim versions of the model for conventional coal-, oil- and gas-fired power plants will be available for utility testing in early 1991.

Managing HCl and mercury

Two chemicals—hydrochloric acid and mercury—received significant attention in the air toxics provisions of the amendments. Because of the inorganic chlorides in coal, hydrochloric acid emissions still generally exceed 10 tons/yr.

Mercury, on the other hand, is emit-

ted in relatively small quantities. Uncontrolled emissions from a typical 500-MW plant would be about 500 lb/yr. Actual emissions probably are much less because of the performance of current environmental control technology. The annual contribution from U.S. fossil fuel-fired utility boilers represents roughly 2% of the six million kilograms global mercury budget and less than 4% of global anthropogenic emissions.

Hydrochloric acid

Chloride concentrations vary widely in U.S. coals, from virtually unmeasurable quantities to more than 0.5%. Generally, eastern high-sulfur coals have higher chloride concentrations than western subbituminous and lignite coals. More than 95% of the chloride is released from the coal during initial phases of furnace combustion and 90% of that is in the form of gaseous HCl.

There is little interaction between the gaseous HCl and the ash. HCl will deposit only on flyash that is below 60 C (140 F), the acid dewpoint for HCl. This is true regardless of the flyash's pH. Data indicate extremely low to nondetectable levels of chloride in flyash from lignite, bituminous and subbituminous coals.

Relative to SO_2 , HCl is a small contributor to acidic deposition. HCl reacts quickly with ammonia and calcium in the atmosphere and generally is not detected beyond 10 kilometers (8.3 miles) of the stack. SO_2 is engaged in much different and more complex atmospheric chemical processes than HCl.

HCl emissions are not a major health concern. For a power plant emitting 100 tons of HCl per year and with a stack

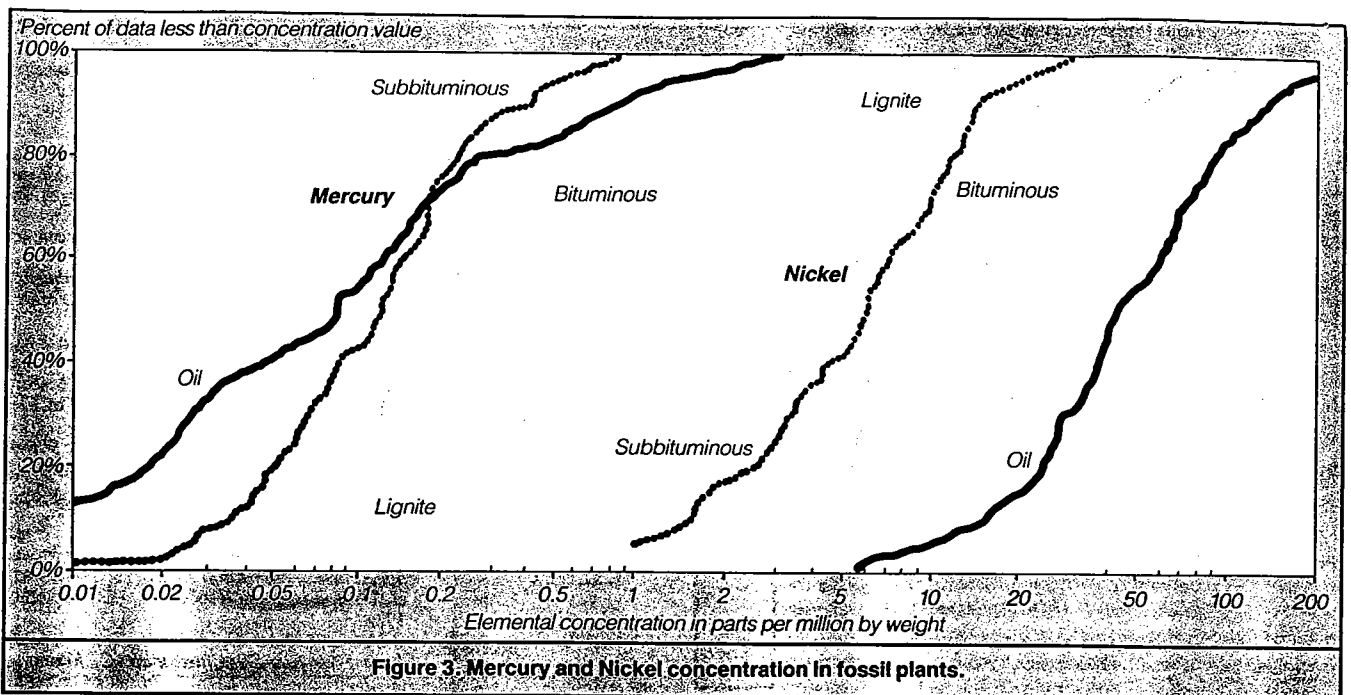


Figure 3. Mercury and Nickel concentration in fossil plants.

height at GEP (good engineering practice), average ground level concentrations in one hour would be less than one microgram/cubic meter during adverse weather conditions. This is negligible compared to the threshold limit value for occupational health effects of 7000 micrograms/cubic meter.

HCl can be controlled by conventional scrubbers. In fact, a number of existing flue gas desulfurization systems have prescrubbers for chloride removal. Municipal waste incinerators employ scrubbers primarily for HCl removal.

Mercury

Mercury levels in U.S. coals vary from about 0.01 to 8 ppm. Typical values, however, are about 0.24 ppm for Appalachian coals, 0.14 for Interior Eastern coals and 0.21 ppm for Illinois Basic coals. Mercury probably is emitted primarily in its elemental form, but it also could be in one of its many combined forms in much lower concentrations.

The literature on mercury emissions from coal-fired power plants is not always clear on whether the measured mercury was total, vapor phase, or condensed on particulates. Also, the sampling and analytical methods used may have been unreliable.

A literature review by I. Smith of IEA Coal Research showed mercury removals ranging from 10% to 50% through fabric filters or ESPs. This reference also reported that FGD system removal spans a range of 20% to 95%. In contrast, the current PISCES database indicates 20%-90% removal for cold-side ESPs (five data points) and 85%-90% for fabric filters (three data points). The database agrees with the Smith report, however, on the wet FGD system re-

moval range. The only distinction pertains to the use of combined particulate and SO₂ reduction systems (e.g., venturi scrubbers where there are five data points). In this case, 50%-95% mercury control was indicated.

A recent study of a coal-fired power plant in Japan showed approximately 33% mercury removal in the particulate control system (cold-side ESP) and 36%

by the FGD system (wet lime). The remainder was vented up the stack. The same study cited another coal-fired plant, using a hot-side ESP and an FGD system, with 25% flue gas bypass around the scrubber. This data showed virtually no removal in the ESP, 26% removal in the FGD system, and the remainder went up the stack.

It appears from these data that temperature plays an important role in mercury emissions. The likely explanation is that mercury is condensing on coal ash particles at the lower temperatures and remaining volatile at the higher temperatures found in a hot-side ESP.

The Japanese data are corroborated by a recent test in Florida. Here a 450-MW coal-fired power plant showed approximately 40% mercury removal in the FGD system, 40% in the cold-side ESP, and 10% in the bottom slag (a wet bottom boiler). The remainder was vented. Thus, total mercury removal was more than 90%.

From this study and the Japanese data, it appears that conventional wet FGD, combined with conventional particulate removal (a cold-side ESP operating near NSPS levels), can remove approximately 60% to 80% of the mercury present in flue gas. Although less data are available for mercury removals by fabric filters, the indications are that their performance is at least as good as an ESP.

Two other recent papers show that mercury can be removed from flue gases by chemical additives. Joy Technologies reported that use of an additive in a spray dryer system and operation of that system at lower exit gas temperatures both improved mercury removal. Joy's data show that a spray dry/baghouse

Table 2. Chemicals for PISCES field emissions monitoring.

Inorganics

Ammonia
 Arsenic
 Barium
 Beryllium
 Cadmium
 Chlorine/Hydrochloric acid
 Chromium
 Cobalt
 Copper
 Cyanide
 Lead
 Manganese
 Mercury
 Molybdenum
 Nickel
 Phosphorus/Phosphate
 Radionuclides (U-238)
 Selenium
 Vanadium
 Fluorine/Hydrofluoric acid

Organics

Benzene
 Formaldehyde
 Polynuclear Aromatics
 Toluene

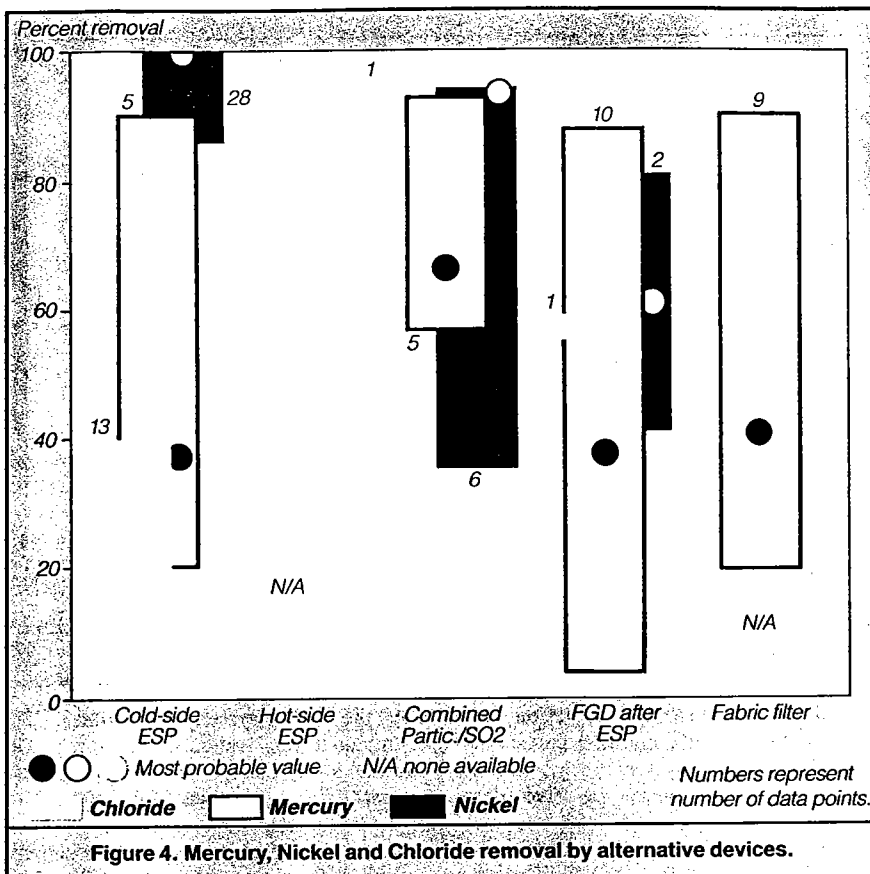


Figure 4. Mercury, Nickel and Chloride removal by alternative devices.

combination operating on a municipal water incinerator removed 69% of the total mercury without the additive and from 91% to 95% with the additive. The spray dryer/ESP combination removed 27% to 66% of total mercury without the additive and 78% to 86% with the additive. The higher removals were observed at the lower exit gas temperatures. Although the additive was not specified, it is assumed to be activated carbon.

Several Japanese authors reported 95%-100% mercury removal through use of a wet lime FGD system on the flue gas of a municipal waste incinerator. An oxidizing agent (sodium hypochlorite) was added to the scrubber to solubilize the mercury, which was removed from the scrubber waste water through a reduction, volatilization, condensation and separation process.

Another adsorption mechanism for mercury removal was reported from Germany. A reactor that removes NO_x from flue gas after it passes through an FGD system also removed virtually all mercury in tests. The work was conducted at pilot scale on a municipal waste incineration plant using lignite coke as the absorbent material.

Considerable uncertainties remain in mercury emissions and control. It should be emphasized that the highest removals involved the use of additives on municipal waste incinerator flue gas, not coal flue gas. The ultimate fate of mercury also is undefined. In addition, most old-

er data are suspect given the sampling and analyzing difficulties. For example, because mercury amalgamates with many metals, it is ubiquitous in laboratories and contaminates samples.

Recent reported data, based on better sampling techniques and analytical methods, appear to have resolved some of the uncertainties. The EPRI air toxics sampling program will use new sampling and analytical techniques and the mercury compounds will be speciated.

With continued efforts to acquire better quality data on emissions, the electric utility industry will be in an improved position to develop strategies for its management and to define applicable technologies. END

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