

ON-LINE, MULTIELEMENT ICP SPECTROMETER FOR APPLICATION TO HIGH TEMPERATURE AND PRESSURE FOSSIL FUEL PROCESS STREAMS

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ABSTRACT: METC is developing a real-time, multielement ICP spectrometer system for application to high temperature and high pressure fossil fuel process streams. The ICP torch operates on a mixture of argon and helium with a conventional annular swirl flow plasma gas, no auxiliary gas, and a conventional sample stream injection through the base of the plasma flame. The base of the torch body is a unique design, allowing process gas at 650°C to be injected into the torch. The RF generator (40.68 MHz) can deliver 10 kW, but the best detection limits have been observed at 5 kW. The detection system is a quartz fiber optic bundle mated to a battery of one-tenth meter monochromators with photomultiplier tubes. A microcomputer controls scanning of the monochromators and data acquisition from the PMTs. The METC ICP system is modular and mobile, allowing the system to be operated in close proximity to any process of interest.

Rising concerns about the potential release of harmful elements into the environment from coal utilization have driven the development of new analytical capabilities. Especially useful to the suite of advanced technologies under development by the Morgantown Energy Technology Center, (METC), would be a process monitor to perform real-time, multi-element trace analysis in a high temperature and high pressure environment. The inductively coupled plasma (ICP) spectrometer has the potential to perform this kind of process monitoring.

The role of the inductively coupled plasma, (ICP) as a process stream monitor for trace elements is only beginning to be realized, although it has been widely used for a number of years as a spectrometric emission source in elemental analysis laboratories. Previous work by other researchers [1] focused on monitoring of liquid phase process streams and looked only at elements at a relatively high concentration. Process monitoring by ICP spectrometry under conditions relevant to METC's advanced technologies has not been previously reported. The principle reason for this lack of progress is the difficulty of sustaining a stable plasma discharge around a high flow of carbon-containing sample gas.

Conventional ICP systems cannot operate at sample flow rates greater than two liters per minute, nor do they operate well with carbon-containing gases in the sample stream. The low flow requirements limit the use of an ICP

argon plasma with particle-laden process streams, since at such low rates particles drop out of the gas stream before reaching the torch. Also, ICP plasmas quench when the carbon-containing gases of fossil fuel process streams are introduced, especially at high flow rates. Our torch design using a mixed gas plasma provides for operation at higher sample flow rates and for stable performance when analyzing samples of varied gas composition.

Prior work sponsored by METC, [2] was only partially successful in achieving this goal. On-line ICP analysis was attempted on a cleaned sample stream from METC's 107 cm diameter, (42 inch) fixed bed gasifier. An extracted gas stream was diluted with argon to 10% and introduced to the ICP torch at a flow rate of 1 l/min. Higher concentrations of gasifier gas extinguished the plasma, as did higher flow rates. The detection limits of this configuration were very poor. Consequently, METC began seeking methods that allow higher sample flow rates and concentrations while maintaining stable plasma conditions.

The conventional ICP excitation source is a plasma sustained at atmospheric pressure by coupling 27.12 MHz radio frequency power to a stream of argon. Almost all ICP systems use argon as the discharge medium, with aqueous solutions of unknowns nebulized into an argon sample stream injected into the argon plasma. This arrangement works well for power levels below 3 or 4 kilowatts, and for low flow sample streams that contain only argon and a small amount of aqueous aerosol.

Figure 1 shows METC's version of an ICP torch and the induction coil that transmits the high frequency power a radio frequency generator to the plasma. Similar to a conventional torch, it differs in some details because of the need to sustain a discharge with a high flow rate of carbon-containing gases in the sample stream. Also, the sample stream, coming from an industrial gasifier or combustor, is expected to vary widely in composition and particle loading on a timescale of seconds.

The torch uses conventional annular plasma gas injection. Auxiliary gas is not needed, and no provision for it is made in this design. The base of the torch is an unconventional construction, rather than the usual teflon, so a hot, high pressure sample line can be directly connected to the torch. The samples line can be maintained at an elevated (process) temperature to protect sample integrity by preventing tar condensation and particle dropout from loss of velocity. The sample injection tube is ceramic, and connects directly to the sample line through a drilled out compression fitting on the base. Graphite ferrules seal the compression fitting. The sample injection tube does not touch any teflon parts, and water cooling in the brass base protects the O-ring and adjacent teflon sections.

The presence of particles and carbon-containing polyatomic gases in the sample stream requires a high minimal power to sustain a stable discharge. Especially so, since the flow rate of sample gas into the discharge must be high to minimize particle dropout. Operation of argon ICP discharges above three or four kilowatts is difficult because the torch overheats. Our earlier work [2] reported configuration factors very close to unity generate a stable discharge with an argon and helium mixed gas plasma, but more recent work has shown that unusually small configuration factors, near 0.8, work well and

facilitate construction and adjustment of the torch. The mixed gas plasma can be used at up to ten kilowatts with a high flow rate of carbon-containing sample gas. Optimum detection limits were found at five kilowatts, and it is not difficult to sustain a stable discharge at this power level. It is also possible to operate with pure helium, but there is no advantage and it is more expensive.

A frequency of 40.68 MHz, (higher than the conventional 27.12 MHz) was chosen for this torch design so the skin depth in the plasma would be smaller. Hence the coupling of power to the discharge is confined to the outer edge of the plasma flame where it is minimally affected by variations in the properties of the injected sample stream.

The torchbox opens from both the top and front, and has dark glass observation windows on two sides. This arrangement greatly facilitates adjustment of the torch and load coil orientation. Two windows on the back side provide optical access for the detection system optics. There is a separate impedance matching network and a Tesla coil in a housing attached to the torchbox. By using screw latches on all the doors and maintaining clean conductive surfaces around the doors and windows, electromagnetic leakage is kept well below safe limits.

The detection system consists of a battery of six one-tenth meter monochromators equipped with photomultiplier tubes. Each monochromator is equipped with a 3600 or 4800 groove/mm diffraction grating optimized for a particular region of the spectrum. The monochromators are all computer controlled, scanned via stepper motor drivers. Two of the eight monochromators are equipped with a red and near infrared sensitive photomultiplier tube, the rest are equipped with an ultraviolet and visible sensitive photomultiplier tube. Photomultiplier tubes were chosen for their excellent sensitivity and dynamic range. Their principle drawback is the need for separate monochromators for each detector, hence the battery of monochromators. Using two different types of photomultipliers also necessitates two independent high voltage supplies. The photocurrent from the photomultiplier tubes is connected to an A/D card in a PC, where the voltage developed across a load resistor is digitized and stored for processing.

The six monochromators are mounted on a platform adjacent to the ICP torch. Light from the plasma is gathered by two $f/2$, 5 cm diameter quartz lenses and focused into two 3mm diameter quartz fiber optic bundles. Each bundle is randomly split into four branches, and one branch is mounted at the entrance slit of each monochromator. The divergence angle of light from the quartz fiber is such that the gratings are nearly exactly filled without any optic between the bundle output and the entrance slit. The photomultiplier tubes are bolted directly over the exit slit of the monochromators.

For purposes of calibration, an aerosol from standard aqueous solutions is injected into the torch sample stream. The aerosol is generated with an ultrasonic nebulizer, which is much more efficient than the common Babington type aerosol generator. The aqueous aerosol is passed vertically through a drying oven to remove all water from the aerosol, and then through a chiller section, which condenses and removes most of the water vapor from the gas flow. Then the dry aerosol is directed through the sample line into the ICP torch. Overall efficiency of the generator is better than 80%.

A single software package to control the monochromators, acquire the data, and to calculate concentrations was written in C by a resident programmer. When the system is started and a new wavelength calibration is needed, the operator uses a low pressure mercury lamp to generate a known spectrum. The software knows approximately where to drive the stepper motors for various mercury lines; it positions the monochromator wavelength near a mercury emission line and acquires a spectrum of that region. Then the software executes a peak search routine and recalibrates its wavelength exactly.

When the system is to be operated, the first task facing the operator is calibration of both wavelength and concentration. Wavelength calibration was described above; concentration calibration is done conventionally, by supplying standard solutions over a range of concentrations and calculating a calibration curve. To measure concentration the software moves the monochromator wavelength to the peak region and acquires data over a small region of the spectrum. Before and after the measurement, the software moves the monochromator wavelength to either side of the line to acquire a background intensity, and calculates the area of the background trapezoid. It requires approximately one-half hour to start up the system and go through a complete calibration routine. Calibrations are reliable for periods of eight hours or longer. Real-time data are collected at one kilohertz and digitally processed to remove artifacts, and then summed and stored at the rate of one data point per second.

One of the principle requirements of our on-line system was that it be readily adaptable to use in the field. This meant that the system had to be modular and mobile. The torchbox, detection system, and calibration system must all be located at the sampling site, since preservation of sample integrity requires that the length of sampling tube be as short as possible. On the other hand, there is no requirement that the radio frequency generator be close at hand, since power can be conducted over tens of meters of coaxial cable without undue difficulty or expense. Also, in many industrial process installations, the site where the sample is extracted is off-limits to personnel when the process is operating, and therefore all the controls and the computer must be remotely located. Figure 2 illustrates the various ICP modules.

The radio frequency generator is contained in a standard 19-inch cabinet, approximately two meters tall. The generator uses vacuum tubes for both stages of amplification and for the oscillator; the final stage is a single tube. This tube is very large and requires a large cooling air flow. Also, the separate vacuum tube stages require their own plate voltage, and therefore the power transformer is large and bulky. For these reasons, this unit is large, and until solid state technology advances, there is no prospect of obtaining a smaller one. There is a small, mobile transformer from which it is powered; the transformer takes 480 volts from a standard welding power receptacle and steps it down to 208 volts to operate the generator. This is convenient, since virtually all industrial facilities are equipped with 480 volt power. The generator also contains a full set of controls for power delivery.

The calibration rig is housed in a two meter high standard 19-inch rack, including the ultrasonic nebulizer, drying oven, cooling jacket, cooler, power supplies, and controllers. All these devices operate from standard low current 110 volt power.

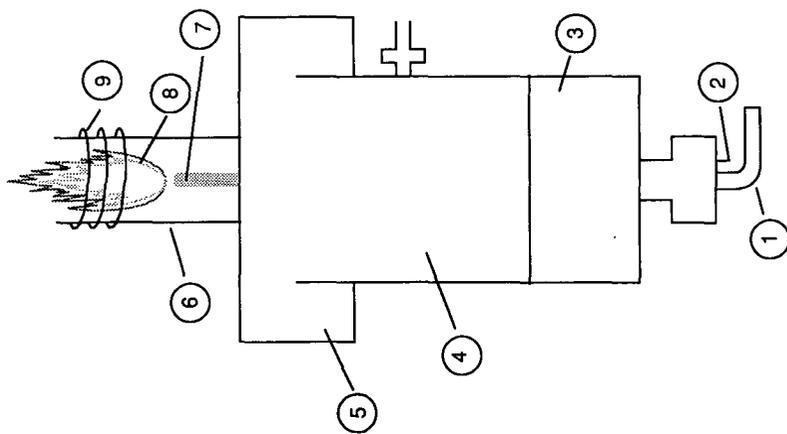
Typically, the computer that runs the monochromators, and the radio frequency power generator are located near each other, so that data acquisition and processing and power delivery are controlled from one location. Additional power controls are located underneath the torchbox to facilitate starting and calibrating the system prior to making measurements on unknowns.

The plasma gas is a mixture of helium and argon. The argon is usually delivered from a large liquid argon tank. Helium is delivered from cylinders on a manifold or from a liquid helium tank. The tanks and cylinders are connected via mass flow controllers and can be remotely located, either near the computer and RF generator or at another convenient location.

Future plans for this instrument include field testing on coal combustors and gasifiers, refinement of torch design to increase reliability and minimize maintenance, and development of a CCD array detection system.

References

- [1] M.W. Routh and J.D. Steiner, Spectrochimica Acta 40B, 177 (1985).
- [2] D.L. McCarty, R.R. Romanosky, W.P. Chisholm, Proceedings of the Advanced Research and Technology Development, Direct Utilization and Instrumentation & Diagnostics Contractors' Review Meeting, Pittsburgh, PA, September 6-9, (1988), p. 576 - 585.



- 1. Heated Sample Line
- 2. Compression Fitting
- 3. Base Section
- 4. Teflon Body
- 5. Teflon Nut

- 6. Quartz Tube
- 7. Ceramic Sample Injection Tube
- 8. Plasma "Flame"
- 9. Copper Tubing RF Load Coil

Figure 1. ICP Torch with Load Coil and Plasma "Flame"

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1. Torch Box
2. Access doors
3. Matching Network
4. Matching Network Control Panel
5. Heated Sample Line
6. Emergency Shutoff Control Box
7. Electronic Flow Controls and HV Power Supplies
8. Rotameters and Pressures Gauges
9. Chimney
10. 10 KW Radio Frequency Generator
11. Coax RF Power Cable
12. Mobile 480V to 208V Transformer
13. Chilled Water for ICP Load Coil
14. Ultrasonic Nebulizer, Standard Solution, and Peristaltic Pump
15. 500 °C Heater
16. Power Controller to Heater
17. 0 °C Condensor
18. 0 °C Chiller
19. Containment Vessel for Condensed Water
20. Sample Line to ICP Torch

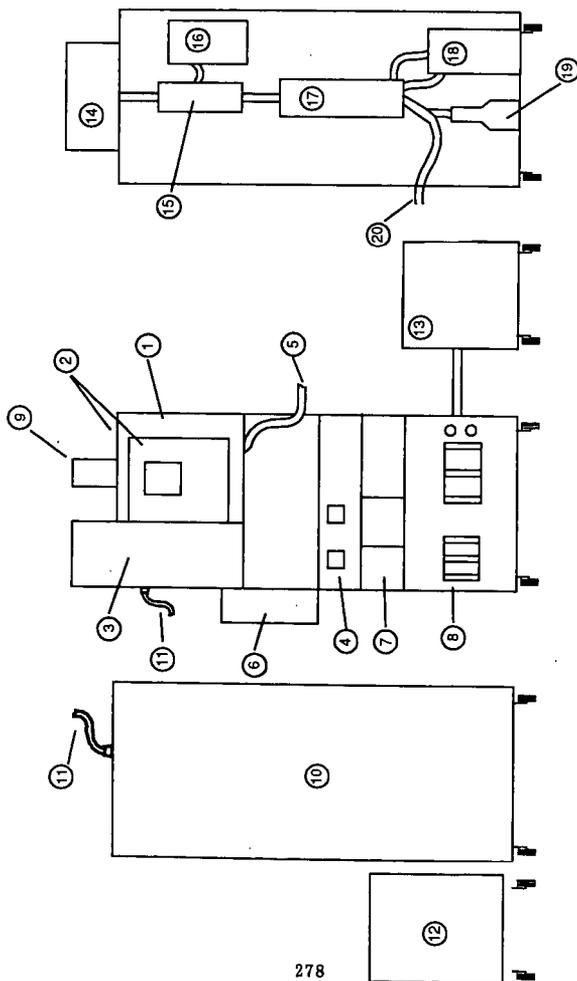


Figure 2. Modular Arrangement of METC's Complete On Line ICP System

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**RECENT ADVANCES IN SAMPLING AND ANALYSIS
OF COAL-FIRED POWER PLANT EMISSIONS
FOR AIR TOXIC COMPOUNDS**

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INTRODUCTION

The new Clean Air Act amendments (CAAs) require the evaluation of potential health effects due to emission of hazardous air pollutants (HAPs) from coal-fired power plant (CFPPs). The amendments also specifically require evaluation of mercury (Hg) emissions from CFPP. Although the CAAs specify these measurements be made, standard reference methods for testing all of the HAP emissions from CFPPs are not available and some of the methods currently being used have not been validated.

Previous studies have shown fly ash from coal combustion may be a potential source of HAPs. Samples for these previous studies, however, were collected using conventional methods which do not allow for the normal dilution and cooling that takes place in a plume. Organic compounds, for example, are typically in the vapor phase at stack temperatures and with conventional methods are collected separately from the particles by condensation and adsorption traps. There is evidence, however, that some polycyclic aromatic hydrocarbons (PAHs) can undergo chemical reactions and/or rearrangements when adsorbed on coal fly ash particles. As a result, samples collected with conventional methods may not be representative of CFPP emissions as they exist in the ambient environment. In addition, there are over a dozen different sampling and analysis methods required to measure HAPs from CFPPs each requiring separate probes and sampling teams. This negates to a great extent the possibility of simultaneous sample collection, greatly increases the cost of sampling and introduces the potential for greater uncertainties in the measurements.

Emission measurements of hazardous air pollutants requires an optimization of sampling and analysis methods. Recent advances in emissions measurements have resulted in major strides towards this optimization process. Two recent advances include the development of a plume simulating dilution sampling system using zero background dilutant for simultaneous measurement of the complete set of hazardous air pollutants and a new hazardous element sampling train.

PLUME SIMULATING DILUTION SAMPLER

Chester Environmental's plume simulating dilution sampler is illustrated in Figure 1. The configuration illustrated is but one configuration that has been used for the simultaneous collection of both gas and particle phase HAPs. An isokinetic sample is drawn into the system through a cyclone preseparator and a heated stainless steel transfer tube. The hot stack gas is drawn from

the transfer tube (similar to a standard Method 5 transfer tube) into the instrument and blending module where it is surrounded by cooled dilution gas.

The dilution gas used for this sampling is nitrogen (N_2) derived from evaporated liquid nitrogen but other mixtures such as an 80/20 N_2/O_2 mixture could be used. This provides a cool, bone-dry dilution gas with zero background for both particulate and vapor phase species. Keystone/NEA has been using evaporated liquid N_2 for dilution gas with its PSDS for air toxic emission testing since 1988. This type of dilution gas is considered essential because of the need to minimize sulfate artifact formation and an oxygen mixture of dilutant gas is considered important to simulate the O_2 concentration in a plume so as not to inhibit the formation of oxygenated compounds.

After blending and mixing, the diluted gas stream passes through an aging chamber. After exiting the aging chamber and before sample collection, the diluted gas stream passes through a section for determining the pressure, temperature, velocity, and relative humidity. The particle and gas phase samples are sampled downstream of this section.

The sample entering the inlet nozzle will pass through the transfer tube and the dilution chamber for dilution, aging, and collection. The transfer tube is maintained at stack temperature to prevent premature condensation. An S-type pitot tube and a thermocouple are installed on the transfer tube to monitor stack gas velocity and temperature. The flow rate through the transfer tube is established by the difference between the total stack pressure at the inlet nozzle and the static pressure in the dilution chamber. This pressure difference, monitored with a magnehelic gauge installed between the upstream port of the pitot and the dilution chamber, is referred to as chamber pressure. The chamber pressure/flow relationship is established by calibration of the nozzle/transfer tube assembly as an integrated unit. The operating chamber pressure will be determined on site using this calibration with the appropriate temperature and pressure corrections for the actual stack conditions encountered.

The dilution chamber facilitates mixing of the flue gas with dilution gas, cooling and aging of this mixture to simulate the dilution processes occurring in a plume, and distribution of the aged mixture to the various sampling devices. The chamber sections can be configured to affect a variety of dilution, aging, and sampling schemes. The chamber flows are balanced by throttling the dilution gas (supplied under pressure) as required to establish the operating chamber pressure (for the specified flue gas flow rate through the transfer tube) while maintaining the necessary sampling device flow rates (withdrawn under vacuum).

A wide range of sampling methods can be used with the PSDS. Particle loading, for example, can be determined by direct filtration and gravimetry. Both the 8 x 10-inch quartz fiber high-volume and teflon filters can be used to provide independent determination of the particle loading. Particle and gas phase elemental compositions are determined using a combination of sampling and analysis methods. The teflon filters are analyzed by x-ray fluorescence and neutron activation analysis for particle phase trace elements and charcoal traps are analyzed by the same methods for gas phase elements. This ultra-sensitive trace element procedure provides low detection limits (down to $0.05 \mu\text{g}/\text{m}^3$) for a wide range of elements. The particulate phase elements measured by this method include Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Sb, Ba, Hg, Pb, U, and Th. Of the four elements expected to have a significant gas phase component at plume-simulated conditions (As, B, Hg, and Se), three (As, Hg, and Se) can be sampled and measured by the charcoal trap method.

The gas concentration in the PSDS is typically reduced by about 30 fold from the stack concentration by dilution. To compensate for this lower concentration, larger volumes are sampled and more sensitive analytical methods used to provide improved detection limits.

HAZARDOUS ELEMENT SAMPLING TRAIN

Current EPA sampling and analysis methods for hazardous elements rely on method 101A for mercury and tentative method 29 for multiple metals testing. Both methods are based on EPA method 5 stack sampling probes and impinger trains. Method 101A uses potassium permanganate in sulfuric acid impingers to extract mercury from a gas stream. Tentative method 29 adds hydrogen peroxide-nitric acid impingers in front of the permanganate impingers to remove other metals. These impinger trains are difficult to run, somewhat dangerous, require complex sample recovery and analysis procedures and are costly. In addition, concerns for the validity of these methods have also been raised and extended sampling periods are required to achieve adequate detection levels.

A method has recently been developed to measure hazardous element emissions that combines activated charcoal impregnated filters (CIFs) and XRF analysis. This method is applicable to all of the elements on the EPA hazardous air pollutants (HAPs) list except beryllium which must be analyzed by inductively coupled argon plasma (ICAP) methods but can be done with the same hazardous element sampling train (HEST). This new, innovative method not only has the ability to measure mercury in CFPP emissions with sampling intervals as short as 10 minutes, but has the potential to achieve order of magnitude better detection limits for mercury and the other HAP elements that are now measured with tentative method 29. ◦

Chester Environmental's HEST is schematically illustrated in Figure 2 to collect both particulate and gas phase samples, and XRF and ICAP to determine elemental concentrations as illustrated with the flow diagram shown in Figure 3.

The sampling train uses a standard in-stack filter probe which draws in an isokinetic sample that passes through a filter pack. The filter pack holds three 47 mm diameter filters. Arranged as illustrated in Figure 2. A stainless steel washer at the filter pack entrance and a stainless steel washer/screen at the exit, hold the three stacked filters in place and prevent sticking to the filter holder O-rings. The first filter collects the particulate phase. Only quartz fiber filters have been used to date but optimum detection limits will be obtained with teflon filters. The second filter is a CIF used to collect gas phase elements. The second CIF is a backup which can be analyzed if there is concern for breakthrough. (To date, in-stack measurements have demonstrated CIF collection efficiencies in excess of 99.7% for total mercury).

The stack gas passes through the filter pack and to a series of impactors to remove water vapor before the flow and volume are monitored.

The filter pack, including the inlet nozzle, are separated from the probe at the end of a sampling period, capped and returned to the laboratory for analysis. In-field sample train rinsing and sample recovery steps are not required by this method. If repeated field tests are required, the filter may be transferred to petri slides and fresh filters loaded in the filter pack. Special filter treatment is not required after sample collection. (Mercury, for example, is not lost from the CIF even after 15 hours exposure to a vacuum of 150 microns of mercury at room temperature).

Upon receipt in the laboratory, the probe inlet is separated from the filter pack, the filters removed, placed in petri slides and archived. (This method does not require total filter deposit mass to be determined). The filters are removed from storage and analyzed first by nondestructive XRF analysis using a high powered modified Ortec Tefa III analyzer. The complete analysis which requires two excitation conditions (Mo anode and Mo x-ray filter at 50 KV, tungsten anode with Cu filter at 35 KV). The front particulate catch filter is then cut in half after nondestructive XRF. One half of the filter is archived and one half is analyzed for ICAP for Be by ICAP. The entire filter may be analyzed by ICAP if lower detection limits are required. Elemental detection limits of the HEST will range from about 10 to 100 ng/m³.

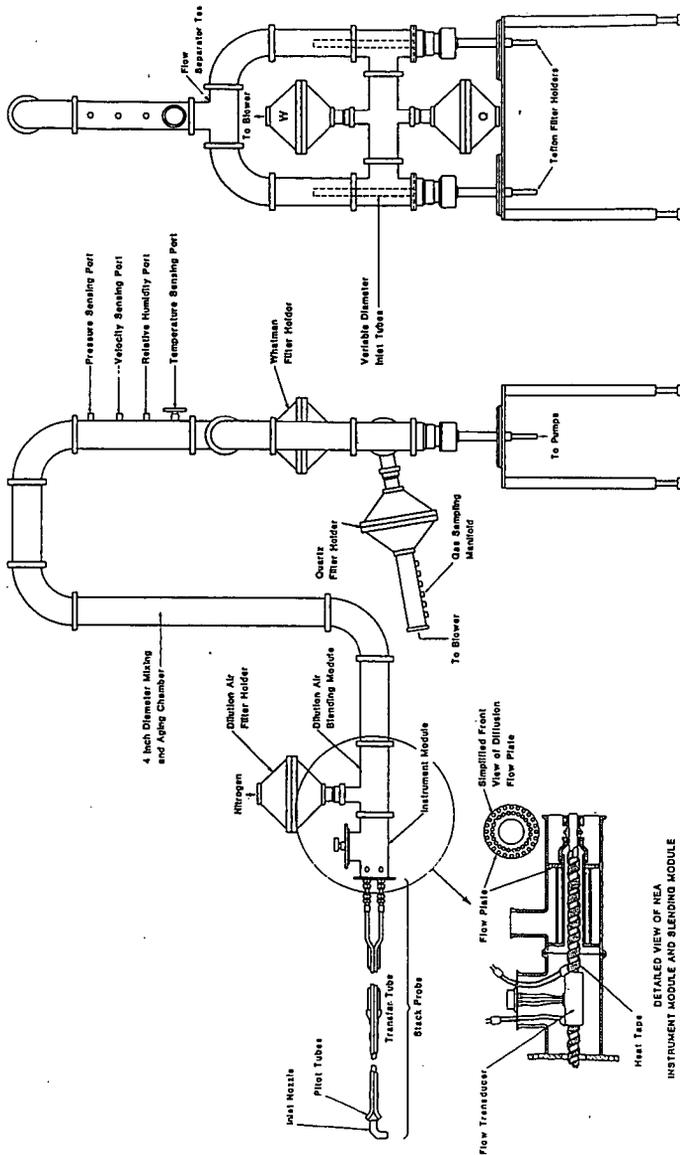
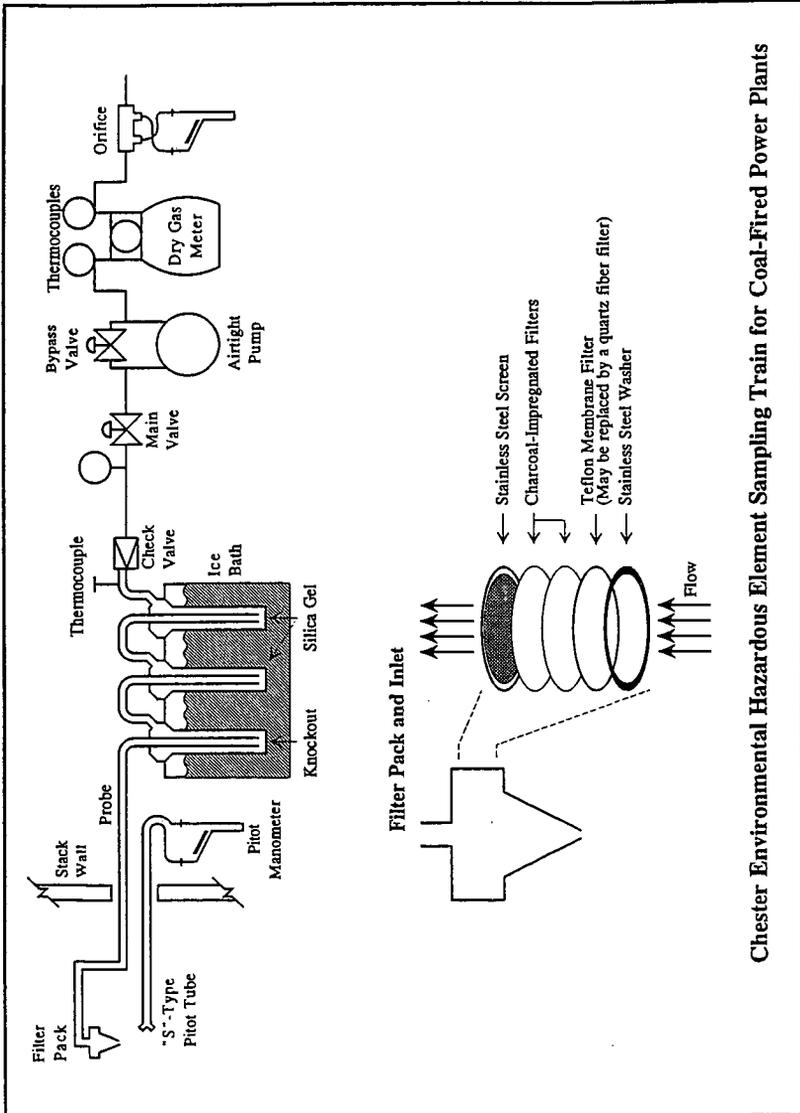


Figure 1. Schematic Representation of the Plume-Simulating Dilution Sampler (PSDS) for Simultaneous Collection of Particle and Gas Phase Hazardous Air Pollutants.



Chester Environmental Hazardous Element Sampling Train for Coal-Fired Power Plants

Figure 2.

CHARACTERIZATION OF HAZARDOUS AIR POLLUTANTS FROM COAL-FIRED ELECTRIC UTILITIES

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ABSTRACT

This paper briefly describes both recent and ongoing studies being conducted to assess the emissions of hazardous and toxic substances from a variety of coal-fired electric utility power generation systems. Recent developments in the analytical methodology required to measure low levels of toxic metals associated with flyash are presented. Also, current and future U.S. Department of Energy plans to augment these assessments are discussed.

INTRODUCTION

The trace elements associated with the mineral matter in coal and the various compounds formed during coal combustion have the potential to produce air toxic emissions from coal-fired electric utilities. The recently enacted Clean Air Act Amendments (CAAA) contain provisions that will set standards for the allowable emissions of 190 hazardous air pollutants (HAPS). These 190 air toxics can be associated with any number of source categories that emit pollutants to the environment. Many of these HAPS could possibly be emitted from coal-fired electric generating stations. Coal-fired electric utility boilers will be studied by the Environmental Protection Agency (EPA) to determine if regulation is appropriate and necessary.

When coal is combusted, trace elements associated with the mineral matter are released in both solid and vaporized forms. Those trace elements not vaporized during combustion will report to the bottom ash stream or exit the combustor as particulate matter. The trace elements that are vaporized during combustion will exit the combustor as gases, condense either as submicron particles, or on the surface of particulate matter in the flue gas stream. The condensation of trace elements on particles results in an enrichment in concentration of specific elements (1), as shown in Table 1.

During the first phase of a two-phase program, the Canadian Electric Association (2) conducted a study to examine air, water, and ash pathways for trace constituents released to the environment from four Canadian coal-fired generating stations. All the major input and output streams of the utility plant were sampled for up to 45 elements in addition to polycyclic aromatic hydrocarbons. Material balances were made based on the average of several runs. Material balance closures to within 20% were found for 37 elements. Closure was not obtained for fluorine, silicon, phosphorus, cadmium, mercury, and boron. Table 2 summarizes the emission of elements which are on the EPA HAPS list from the Canadian Electric Association study of coal-fired power plants. The second phase

of the program dealt with the environmental dispersion and biological implications of the release.

The Electric Power Research Institute (EPRI) has begun to assess the emissions from power plants under the PISCES (Power Plant Integrated Systems: Chemical Emission Studies) program. The first activity consisted of an exhaustive literature review to obtain as much existing data as possible on the emission of chemical species from power plants (3). This data was organized into a database that contains information on both individual power plants and on the chemical characteristics of various streams within those plants. The PISCES literature study also served to identify gaps in the existing data on power plant emissions. The second major activity within the PISCES program is the Field Chemical Emissions Monitoring project which involves the use of a consistent and comprehensive analytical protocol to evaluate all inputs and outputs of the pollution control subsystems and all the process streams at the utility for HAPS. To date, the EPRI study has gathered analytical information at ten utility sites for 24 of the 190 hazardous pollutants listed in Title III of the CAAA.

Conventional air pollution control subsystems have the potential to remove many of the air toxic emissions from flue gas generated from the combustion of coal. However, there is a lack of precise analytical data on the removal of toxics across environmental control devices, such as electrostatic precipitators, baghouses, and wet limestone scrubbers. The relative concentrations of some of the toxic materials could also be increased as a result of using these technologies, or toxics could be formed when chemicals are added to the flue gas stream to increase particulate collection efficiency. Further, some of the more advanced SO₂ and NO_x mitigation technologies involve furnace injection of a sorbent and combustion modification, respectively, and could influence the distribution of toxics between the bottom ash and flue gas streams. To date, little information exists on the effects these advanced technologies have on the amounts of toxic substances formed in the combustion zone.

CURRENT DOE AIR TOXICS INVESTIGATIONS

The Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE) has two current investigations, initiated before passage of the CAAA, that will determine the air toxic emissions from coal-fired electric utilities. DOE has contracted with Battelle Memorial Institute and Radian Corporation to conduct studies focusing on the potential air toxics, both organic and inorganic, associated with different size fractions of fine particulate matter emitted from power plant stacks. Table 3 indicates the selected analytes to be investigated during these studies. PETC is also developing guidance on the monitoring of HAPS to be incorporated in the Environmental Monitoring Plans for the demonstration projects in the DOE Clean Coal Technology Program.

Battelle Memorial Institute

Battelle Memorial Institute and its subcontractor, Keystone/NEA, will correlate the air toxics produced by a laboratory combustor with those from two operating coal-fired electric utility boilers. A characterization of air toxics associated with the surfaces of fine particles and vapor phase constituents of the stack flue gas of the selected coal-fired units will be made. Both the diluted, cooled flyash particles with adsorbed and condensed material on the surfaces and the hot

gas flyash particles will be collected in three size fractions from the stacks. These size fractions are <0.6, 0.6-2.0, and 2.0-0.5 microns.

An innovative source dilution sampler will be utilized to simulate plume cooling and collect the diluted, cooled particles that may have an increased concentration of certain toxic substances. The hot gas samples, particulate and vapor phase, will be collected by EPA Modified Method 5 procedures. The differences in the two samples will provide information on the characteristics of the overall composition of fine particles, particularly materials of air toxic concern.

Laboratory studies can be more useful under certain circumstances than full-scale studies because these studies provide the flexibility to examine emissions from developing pollution control technologies (i.e., furnace and duct sorbent injection, flue gas conditioning, and various combustion configurations). The coals used by the two coal-fired electric utilities will be used in the laboratory combustion studies, which will indicate the efficacy of using a well-controlled laboratory-scale combustor to simulate emissions from a full-scale unit. Additional results from the Battelle laboratory combustion work will include the further development of more advanced sampling methods for collection of flyash and vapor-phase constituents from flue gas. The results will also assist DOE and EPRI in determining which toxic substances to sample in future emissions characterization studies.

Radian Corporation

Radian Corporation will collect size-fractionated particles from the stack of a full-scale coal-fired utility boiler and characterize the particles for both bulk and surface chemical composition. The sampling will take place over two different time periods ranging from three to four weeks. This will enable the collection of fine particles during a high-load season (winter), a lower-load season (spring), and load swings. Particulate samples will be collected from the stack effluent under both hot-stack and dilution-cooled conditions.

A source dilution sampler will be utilized to simulate the cooling and dilution that the flue gases and particles experience while entering the atmosphere at the stack exit. A relationship will be sought between the chemical materials found and the size of particles. Also, the effects of cooling and dilution upon the surface condensation of volatile species will be evaluated and characterized. In addition, the carbon content of the particulate matter will be determined in an attempt to correlate any organic compounds found on the dilution-sample particulate with the amount of carbon in the flyash.

To date, Radian has evaluated several sample preparation and analysis procedures in order to select two bulk-composition and three surface-leaching techniques to use on the size-fractionated flyash samples collected from both the hot stack gas and the cooled stack gas from the dilution sampler. To accurately evaluate these methods, a coal flyash was selected that is certified by Brammer Standard Company for 29 trace metals ($\mu\text{g/g}$) and 8 major metals (wt.%), and is sieved instead of ground to produce a homogenous sample of ash particles less than 80 microns in size. Metals targeted for analysis and low detection limits were arsenic, barium, beryllium, cadmium, chromium, copper, cobalt, lead, manganese, mercury, molybdenum, nickel, selenium, and vanadium. These metals were chosen because of their known toxic properties, presence on the CAAA's list of hazardous

substances, or suspected occurrence in flue gas streams from coal-fired utility boilers.

Total composition of the flyash particles was determined by neutron activation and glow discharge mass spectrometry (GDMS). Acceptable recoveries, defined as 80-120% of the standard's certified value, were obtained by neutron activation analysis for Ba, Co, Cu, Mn, and V. Chromium and arsenic recoveries were only slightly outside this range at 124 and 127 percent, respectively. The reproducibility was acceptable (less than 20% relative standard deviation, RSD) for all the target elements except Cd, Cu, and Hg. Cadmium, lead, and beryllium were not detected by neutron activation. GDMS analysis provided acceptable recovery (80-120%) for two elements, chromium and copper. Recovery of the remaining elements was biased low and ranged from 16 to 86% recovery. The reproducibility was acceptable (<20% RSD) for all target analytes except molybdenum and cadmium, which were not detected.

The primary focus of the methods evaluation plan was to determine methods that could leach or dissolve metals from the surface of flyash particles. The five leaching agents studied were chosen based on either selectivity for the metals of interest, the method's similarity to chemical or biological processes, or as modifications of an established method. The five methods were 1) a nitric acid digestion technique that indicates the maximum amount of material available from the alumina-silica flyash matrix (EPA Method 3050); 2) an acetic acid leaching solution prepared according to the Toxicity Characteristics Leaching Procedure to a pH of 4.93 to simulate environmental availability; 3) a simulated gastric fluid made from HCl, pepsin, and NaCl buffered to pH 1.2; 4) a simulated lung fluid prepared from phosphate buffered (pH 7.5) saline solution containing bovine serum (albumin) and dextrose; and 5) a chelating agent specific for arsenic and chromium consisting of buffered (pH 4.4) ammonium pyrrolidine-N-dithiocarbamate solution.

For all five methods, 100 mg of the certified flyash was treated. The three analytical techniques used for the analysis of the leachate samples included inductively coupled argon plasma emission spectrophotometry (ICP), graphite furnace atomic absorption spectrophotometry (GFAA), and inductively coupled argon plasma mass spectrometry (ICP-MS). Results of the ICP, GFAA, and ICP-MS analysis of these leachate samples provided a clear indication that the analytical method's sensitivity and precision are very important. ICP-MS provided lower detection limits than ICP or GFAA for all the matrices tested. ICP-MS has the advantage of detecting elements from Be to U (mass 9 to 238) with quantitation levels of 20 ng/mL to 0.1 mg/mL. Detection limits for 14 metals in this evaluation ranged from 0.002 to 0.13 ng/mL. The detection limits are 10 to 100 times lower than ICP or GFAA. By ICP-MS, the RSD for nitric acid digestion samples was <20% for all target elements except Cd (34% RSD), Cu (25% RSD), and Pb (36% RSD). These diluted samples had elemental concentrations less than 3 ng/mL for all target analytes. With respect to the ICP and GFAA analyses, only arsenic (1% RSD), beryllium (7% RSD), chromium (120% RSD), copper (27% RSD), lead (59% RSD), nickel (40% RSD), selenium (1900% RSD), and vanadium (5% RSD) were detected. Similar results were obtained on the other leachate samples, except the simulated lung fluid sample whose increased viscosity presented sample aspiration problems, indicating the superiority of the ICP-MS technique.

The nitric acid digestion, gastric fluid, and acetic acid leach are the three methods chosen based on the performance criteria when analyzed by ICP-MS. ICP-MS

provides lower detection limits and improved precision than previously obtained by conventional ICP or GFAA methods.

FUTURE TOXIC EMISSION STUDIES

A collaborative effort has been initiated by the DOE, the Utility Air Regulatory Group (UARG), EPRI, and the EPA to expand the study of hazardous pollutant emissions from utility boilers. This effort will involve measurements at a number of power plants having different boiler designs, NO_x control methods, particulate control devices, and SO₂ removal systems (wet and dry). From these measurements, the EPA expects to predict the potential air toxic emissions from coal-fired boilers in 1995 and 2000 (after controls are installed to meet the requirements of the acid rain title of the CAAA). Measurements from plants firing bituminous or subbituminous coal will be used to evaluate the entire range of existing power plant configurations and will form the basis for this study.

DOE has issued a solicitation for proposals to assess selected hazardous/toxic pollutants from a number of utilities that utilize different pollution control and process subsystems while burning either bituminous or subbituminous coal. The power plant configurations addressed in this solicitation are given in Table 4. Objective of this solicitation are to determine the removal efficiencies of pollution control subsystems for selected pollutants and the concentrations of pollutants associated with the particulate fraction of the flue gas stream as a function of particle size. A further objective is to determine mass balances for selected pollutants for a variety of different input and output streams of the power plants and subsequently for the entire power plant.

Results from all the DOE studies will provide input to the congressionally mandated study being conducted by the EPA to assess the impacts of the listed HAPS emissions from coal-fired electric utilities, as required in Title III of the CAAA of 1990. In addition, the data will provide a basis for evaluating the potential effects of air toxics regulation on existing pollution control and auxiliary processes being utilized at electric utilities and on the commercialization of technologies demonstrated under the Clean Coal Technology Program.

REFERENCES

1. D.G. Coles, R.C. Rahaini, J.M. Ondov, G.L. Fisher, D. Silberman, and B.A. Prentice, "Chemical Studies of Stack Fly Ash from Coal-Fired Power Plant," Environmental Science and Technology, Vol 13, 4, April 1979.
2. J.C. Evans, K.H. Abél, K.B.Olsen, E.A. Lepell, R.W. Sanders, C.L. Wilkerson, and D.J. Hayes, "Characterization of Trace Constituents at Canadian Coal-Fired Plants - Phase I," Contract Number 001G194, Canadian Electrical Association, January, 1985.
3. F.B. Meserole and W. Chow, "Controlling Trace Species in the Utility Industry, paper presented at the conference Managing Hazardous Air Pollutants: State of the Art, Washington, D.C., November 4-6, 1991.

Table 1. Comparison of Elemental Concentrations in Size-Classified Flyash Fractions (Concentrations in $\mu\text{g/g}$ unless indicated by %)

Element	Fraction 1, 18.5 μm	Fraction 2, 6.0 μm	Fraction 3, 3.7 μm	Fraction 4, 2.4 μm
Aluminum, %	13.8	14.4	13.3	13.9
Barium, %	0.168	0.245	0.31	0.41
Calcium, %	2.1	2.23	2.3	2.36
Iron, %	2.51	3.09	3.04	3.2
Magnesium, %	0.47	0.56	0.60	0.63
Potassium, %	0.74	0.80	0.82	0.81
Silicon, %	29.6	28.0	27.5	26.8
Sodium, %	1.22	1.75	1.81	1.85
Sulfur, %	0.101	0.304	0.425	0.711
Titanium, %	0.62	0.74	0.73	0.77
Antimony*	2.6	8.3	13.0	20.6
Arsenic*	13.7	56.0	87.0	132.0
Beryllium*	6.3	8.5	9.5	10.3
Cadmium*	0.4	1.6	2.8	4.6
Cerium	113.0	122.0	123.0	120.0
Cesium	3.2	3.7	3.7	3.7
Chromium*	28.0	53.0	64.0	68.0
Cobalt*	8.9	17.7	20.3	21.8
Copper	56.0	89.0	107.0	137.0
Dysprosium	6.9	8.5	8.1	8.5
Europium	1.0	1.2	1.2	1.3
Gallium	43.0	116.0	140.0	178.0
Hafnium	9.7	10.3	10.5	10.3
Lanthanum	62.0	68.0	67.0	69.0
Lead*	73.0	169.0	226.0	278.0
Manganese*	208.0	231.0	269.0	309.0
Neodymium	45.0	47.0	49.0	52.0
Nickel*	25.0	37.0	43.0	40.0
Rubidium	51.0	56.0	57.0	57.0
Samarium	8.2	9.1	9.2	9.7
Scandium	12.6	15.3	15.8	16.0
Selenium*	19.0	59.0	78.0	198.0
Strontium	410.0	540.0	590.0	700.0
Tantalum	2.06	2.3	2.5	2.7
Terbium	0.90	1.06	1.10	1.13
Thorium	25.8	28.3	29.0	30.0
Uranium	8.8	16.0	22.0	29.0
Vanadium	86.0	178.0	244.0	327.0
Tungsten	3.4	9.0	16.0	24.0
Ytterbium	3.4	4.1	4.0	4.2
Zinc	68.0	189.0	301.0	590.0

NOTE: These data were taken from Reference 1.

*Denotes element is contained on EPA HAPS list.

**Aerodynamic cut sizes.

Table 2. Flue Gas Trace Element Releases from Selected Canadian Coal-Fired Power Plants

<u>Element</u>	<u>% of Total Element in Coal Released with the Flue Gas</u>	
Chlorine	49	- 99.0
Chromium	0.1	- 8.7
Manganese	0.1	- 1.0
Cobalt	0.09	- 1.5
Arsenic	0.74	- 9.3
Selenium	3.5	- 73.0
Antimony	0.2	- 2.5
Mercury	79.0	- 87.0
Lead	0.2	- 1.4

Table 3. Compounds and Elements for the Battelle and Radian Air Toxics Studies

Arsenic	Ammonia
Barium	Radionuclides (Ra, Po, U, etc.)
Beryllium	Sulfates
Cadmium	
Chromium	Benzene
Chlorine (as Cl ⁻)	Toluene
Cobalt	Formaldehyde
Copper	Polycyclic Aromatic Hydrocarbons
Cyanide	
Fluorine (as F ⁻)	
Lead	
Manganese	
Mercury	
Molybdenum	
Nickel	
Phosphorus (as PO ₄ ³⁻)	
Selenium	
Vanadium	

TABLE 4.
ELECTRIC UTILITY CONFIGURATIONS

Configuration	Coal Rank	Particulate Control	SO ₂ Control	NO _x Control ¹	Coal Preparation	Cooling Tower (Water) Streams
1	Bituminous	ESP	None	None		
2	Bituminous	ESP	Wet FGD	None		
3	Bituminous	ESP	Wet FGD	All	Yes	Yes
4	Bituminous	Baghouse	None	All		
5	Bituminous or Subbituminous	Baghouse	Wet or Dry FGD	All		
6	Bituminous or Subbituminous	ESP	Dry FGD	All		
7	Subbituminous	Baghouse	None	All		
8	Subbituminous	ESP	Wet FGD	All		

¹ All designation includes low NO_x burners, overfire air, and "other."

SULFUR TRIOXIDE FORMATION IN THE PRESENCE OF
RESIDUAL OIL ASH DEPOSITS IN AN ELECTRIC UTILITY BOILER

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A model is proposed for the catalytic oxidation of sulfur dioxide to sulfur trioxide over vanadium-containing ash deposits on heat exchanger tubes in the convective section of a residual oil-fired boiler. The model includes a global description of the rates of forward and reverse reactions at the deposit surface and mass transfer of the product SO_3 from the deposit surface to free stream. The kinetic parameters for the chemical reaction and the ratio of active deposit surface area to geometric external area are the principal adjustable parameters. Conversion of SO_2 to SO_3 is strongly dependent on the surface area-temperature-residence time distribution in the convective section. The change in surface temperature with increasing deposit thickness accounts for a significant part of the increase in sulfur trioxide content of stack gas which occurs as ash accumulates on convective tubes.

INTRODUCTION

A few percent of the sulfur in residual fuel oil typically appears as sulfur trioxide in the stack gas from an electric utility boiler. Sulfur trioxide is completely converted to sulfuric acid vapor at approximately 500 K (440°F), and condenses as aqueous sulfuric acid at the dewpoint, near 400 K (260°F) (Halstead and Talbot, 1980). Adsorption of the acid on unburned coke particles and reaction with ash increases the particulate matter concentration in the combustion products, when measured by USEPA Method 5. Acid droplets contribute to the visual opacity of the stack plume. The distribution of sulfur oxides among gaseous species, droplets, and particles influences the dispersion, atmospheric reactions, and deposition of sulfate from the plume.

Vanadium, one of the most abundant inorganic impurities in many residual fuel oils, is the active ingredient of commercial catalysts for oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid. The fraction of sulfur oxides emitted as sulfur trioxide from an oil-fired boiler has been observed to increase with increasing vanadium content of the fuel, with increasing excess oxygen in the flue gas, and with accumulation of vanadium-containing deposits on heat exchanger tubes. In the present paper we examine the effect of the deposit surface temperature on sulfur trioxide formation.

Reactions determining the formation and fate of SO_3 in oil-fired boilers are shown as functions of temperature in Figure 1. In the flame and postflame regions, above about 1200 K (1700°F), the steady-state concentration of SO_3 is approximately described by formation and destruction reactions of SO_2 and SO_3 with oxygen atoms (Merryman and Levy, 1971). Detailed discussions of the homogeneous reaction system are given by Cullis and Mulcahy (1972) and by Smith, Wang, Tseregounis, and

Westbrook (1983). The equilibrium distribution of sulfur oxides shifts toward SO₃ as temperature decreases, so the concentration of SO₃ just downstream from the furnace exit is determined by the relative rates of the formation reactions and cooling of the combustion products in this region. Typically 1 mol% of the sulfur oxides are thought to be present as SO₃ in furnace exit gas, i.e. on the order of 10 mol ppm in the products from combustion of 2 wt% sulfur oil. If SO₃ remained at this level, low temperature corrosion, plume opacity, and other problems associated with sulfuric acid would not be too troublesome.

Oxidation of SO₂ is catalyzed by iron- and vanadium-containing ash deposits in the convective section of a boiler. Conversion of SO₂ to SO₃ via heterogeneous reactions is greatest over a relatively narrow temperature range, from about 780 to 980 K (950 to 1300°F) (Wickert, 1963; Reid, 1971). At lower temperatures, formation of SO₃ is limited by the rate of the surface reaction; at higher temperatures it is limited by the equilibrium distribution of sulfur oxides, which increasingly favors the reactants, O₂ and SO₂, as temperature increases. When the heterogeneous contribution to SO₃ formation is significant, problems associated with sulfate and sulfuric acid are more severe. Plume visibility due to acid mist increases as ash deposits accumulate (Reidick and Riefenhäuser, 1980). A model for SO₃ formation in boilers, including both homogeneous and heterogeneous reactions, was developed by Squires (1982). Release of SO₃ accumulated in ash deposits during operation at reduced load was proposed by Shareef, Ramsay, and Homolya (1986) and Shareef, Homolya, and Mormile (1990) to explain the increase in plume opacity associated with increase in load, following a period of low-load operation.

The formation of sulfuric acid vapor and liquid is shown at the bottom left in Figure 1. All four of the major sulfur-containing species, gaseous SO₂ and SO₃, as well as liquid and vapor phase H₂SO₄, may react with metal oxides in the oil ash forming metal sulfates, processes which are shown at the bottom right in Figure 1. Little is known about the relative importance of these reactions, or the relative amounts of sulfate present in particulate matter as metal salts and adsorbed sulfuric acid (Halstead, 1978; Penfold and Smith, 1982). A conservative estimate of the contribution of sulfate to particulate matter would require that one place all of the SO₃ in the particulate, but a conservative estimate of the contribution of acid droplets to opacity would require one to assume that all of the SO₃ forms sulfuric acid mist! More experimental work on the distribution of these species is needed.

MODEL FOR CATALYTIC SO₃ FORMATION

The model is based on the assumption that only ash deposited on convective tubes contributes to SO₃ formation, according to the overall reaction



Ash particles suspended in the gas stream are neglected because their external surface area per unit of flue gas volume is much smaller than that of deposits. Some SO₃ is considered to be present in the gas entering the convective section, but flame and postflame homogeneous reactions are not included in the simulation.

The kinetics of heterogeneous oxidation of SO₂ were reviewed by Urbanek and Trela (1980). A global expression for the rate of formation of SO₃, assuming a rate proportional to the mass fraction of vanadium oxides in deposits, is

$$r_{\text{SO}_3} = k Y_{\text{VO}_x} S_d C_{\text{O}_2}^a C_{\text{SO}_2}^b \left[1 - \frac{C_{\text{SO}_3, s}}{K C_{\text{SO}_2} C_{\text{O}_2}^{1/2}} \right] \quad (2)$$

The factor in brackets accounts for the approach of the rate to zero as the SO₂ concentration adjacent to the catalyst surface approaches its equilibrium value. Under conditions of interest in boilers the extent of reaction is small, so changes in the SO₂ and O₂ concentrations are negligible. When the system is steady, the rate of SO₂ formation at the deposit surface equals its rate of transport from the surface to the free stream:

$$r_{SO_2} = \frac{Sh_t D_{SO_2}}{d_t} A_t (C_{SO_2,s} - C_{SO_2}) \quad (3)$$

Elimination of the unknown concentration at the surface and integration over time, with the boundary condition, $C_{SO_2} = C_{SO_2,o}$ at $t = 0$, gives:

$$C_{SO_2} = K C_{O_2}^{1/2} C_{SO_2} + [C_{SO_2,o} - K C_{O_2}^{1/2} C_{SO_2}] \exp(-k' A_t t) \quad (4)$$

$C_{SO_2,o}$ and C_{SO_2} are the SO₂ concentrations entering and leaving, respectively, a region in which deposit surface temperature and composition are approximately constant. The effective rate coefficient, k' , is given by:

$$\frac{1}{k'} = \frac{1}{Sh_t D_{SO_2}} + \frac{1}{\frac{k S_d}{K A_t} Y_{VOx} C_{O_2}^{a-1/2} C_{SO_2}^{b-1}} \quad (5)$$

The kinetic parameters were estimated from the work of Glueck and Kenney (1968), who observed that the reaction over a vanadium oxide-potassium oxide melt was first order in SO₂ ($b = 1$), and zeroth order in O₂ ($a = 0$). After choosing the kinetic constants, the most important adjustable parameter in the model is the ratio of effective catalytic surface area to the geometric external surface area of deposits, S_d/A_t .

RESULTS

A study of SO₂ formation was conducted by the Consolidated Edison Co. of New York at Arthur Kill Station (Piper and Kokoska, 1983; Shareef, Ramsay, and Homolya, 1986; Shareef, Homolya, and Mormile, 1990). The majority of testing was conducted on the superheat furnace of Arthur Kill Unit 20. This unit normally fires oil containing less than 0.3 wt% sulfur, but the testing for the SO₂ study was performed using oil containing 0.75 wt% sulfur. Measurements of SO₂ were made as functions of load during both transient and steady-state operation. Under steady full load conditions, the level of SO₂ in flue gas varied between 31 and 40 mol ppm over three days of tests. Gas temperatures, tube temperatures, gas velocities, and residence times were calculated for 14 separate tube bundles from the platen superheater inlet to economizer outlet (Piper and Kokoska, 1983; Piper, 1985).

The model described above was used to examine the influence of deposit accumulation on SO₂ formation, considering only the effect of deposit thickness on the surface temperature distribution, neglecting any change in the effective surface area of catalyst which might be associated with deposit growth. The increase in surface temperature with increasing deposit thickness was estimated by assuming that deposit was built on surfaces whose temperatures were fixed at the values calculated by Piper (1985). The deposition rate was assumed to be 1 g/m²-hour, distributed uniformly over the length and circumference of the tubes. Changes in deposition rate with changes in gas, tube, and surface temperatures were not considered. Equation 4 was applied to successive banks of convective tubes, from the furnace exit to economizer outlet. The calculated SO₂ profiles through the convective section after 0, 3, 6, and 12 months of continuous full load

operation are shown in Figure 2. Position in the convective passage is given as a fraction of the total gas residence time. The surface temperature distribution calculated by Piper (1985) is the base case, shown at the bottom of the figure. The calculated thickness of deposits after 12 months of continuous full load operation was 4 mm.

Under the conditions investigated, the temperature distribution is such that the rate of heterogeneous SO_3 formation is low near the entrance to the convective section, then increases, and decreases as the combustion products move downstream. The model properly accounts for the observation that the rate of SO_3 formation peaks in a narrow temperature window, the actual range of temperatures depending on conditions such as mass transfer between the free stream and catalyst surface, concentrations of O_2 and SO_2 , etc. As ash thickness and surface temperature increase, the activity of deposits near the entrance to the convective section decreases as their temperatures move farther from the optimum range. However, the decrease in SO_3 formation rate at the entrance is more than compensated by an increase in rate in the larger surface area, higher gas velocity tube banks in the middle of the convective section, with the result that SO_3 continuously increases with increasing fouling of the tubes. For the assumed conditions, SO_3 at the economizer outlet (far right) increases from 33 to 44 mol ppm over the 12 month period. Changes in surface temperature distribution may therefore be a significant factor in the increase in sulfate emissions with time after cleaning of a unit, apart from any effect of an increase in effective surface area of deposits.

CONCLUSION

Simulation of the catalytic oxidation of SO_2 to SO_3 over vanadium-containing ash deposits, including chemical reaction between SO_2 and O_2 at the surface and diffusion of SO_3 from the surface to free stream, shows that changes in deposit surface temperature associated with deposit growth may be a significant influence on SO_3 formation. Using conditions in Arthur Kill Unit 20 as a baseline, and assuming deposit growth at the rate of $1 \text{ g/m}^2\text{-hour}$ while firing 0.75 wt% sulfur oil, changes in deposit surface temperature resulting from the increase in deposit thickness were estimated to cause a 30% increase in SO_3 at the economizer outlet over a period of 12 months at full load.

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NOMENCLATURE

- a order of the heterogeneous reaction with respect to O_2 , dimensionless
- A_c geometric external surface area of tubes or deposits, per unit of gas volume, m^{-1}
- b order of the heterogeneous reaction with respect to SO_2 , dimensionless
- C_i concentration of species i , kmol/m^3

- d_t tube diameter, m
- D_{SO_2} molecular diffusion coefficient of SO_2 in combustion products, m^2/s
- k rate coefficient for the heterogeneous reaction between SO_2 and O_2 , the dimensions depend upon the orders of reaction, a and b
- k' effective rate coefficient for SO_3 formation, including surface reaction and boundary layer diffusion, m/s
- K equilibrium constant, in terms of concentrations, for the reaction
 $SO_2 + 1/2 O_2 = SO_3$, $m^{3/2}/kmol^{1/2}$
- r_{SO_3} rate of sulfur trioxide formation, $kmol/m^3 \cdot s$
- S_d effective surface area of catalytic deposits per unit of gas volume, m^{-1}
- Sh_t average Sherwood number for mass transfer between tube or deposit surface and free stream, dimensionless
- t time, s
- Y_{Vx} mass fraction of vanadium oxides in deposits, dimensionless

Subscripts

- o initial value
- s condition at the catalytic deposit surface

REFERENCES

- C. F. Cullis and M. F. R. Mulcahy, The Kinetics of Combustion of Gaseous Sulphur Compounds, *Combustion and Flame* **18** (1972) 225-292.
- A. R. Glueck and C. N. Kenney, The Kinetics of the Oxidation of Sulfur Dioxide over Molten Salts, *Chemical Engineering Science* **23** (1968) 1257.
- W. D. Halstead, The Nature of H_2SO_4 in Deposits of Acid Contaminated Combustion Grits, *Journal of the Institute of Fuel* **51** (1978) 149-153.
- W. D. Halstead and J. R. W. Talbot, The Sulphuric Acid Dewpoint in Power Station Flue Gases, *Journal of the Institute of Energy* **53** (1980) 142-145.
- E. L. Merryman and A. Levy, Sulfur Trioxide Flame Chemistry - H_2S and COS Flames, Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1971, pp. 427-436.
- D. Penfold and A. C. Smith, The Analysis of Carbonaceous Material from Oil-Fired Boilers, *Journal of the Institute of Energy* **55** (1982) 98-101.
- B. Piper, 1985, Arthur Kill 20 SO_3 Model, Appendix B to Shareef, Ramsay, and Homolya, (1986).
- B. Piper and T. Kokoska, Opacity Study - Data to Support SO_3 Formation Analysis, KVB 81-21620-1447, Report prepared by KVB, Inc., for the Consolidated Edison Co. of New York, Inc., 1983.

W. T. Reid, External Corrosion and Deposits, Boilers and Gas Turbines, American Elsevier, New York, 1971, pp. 75-114.

H. Reidick and R. Reifenhäuser, Catalytic SO₃ Formation as Function of Boiler Fouling, *Combustion*, Vol. 51, No. 8, February 1980, pp. 17-21.

G. S. Shareef, J. B. Homolya, and D. J. Mormile, SO₃ Formation over Fuel Oil Fly Ash Deposits, 1990 SO₂ Control Symposium, New Orleans, LA, May 8-11, 1990.

G. S. Shareef, G. G. Ramsay, and J. B. Homolya, Development and Calibration of a Prediction Model for the Formation of Sulfur Trioxide in a Residual Oil-Fired Boiler, Report prepared for the Consolidated Edison Co. of New York, Inc., by Radian Corp., Research Triangle Park, NC, 1986.

O. I. Smith, S.-N. Wang, S. Tseregounis, and C. K. Westbrook, The Sulfur Catalyzed Recombination of Atomic Oxygen in a CO/O₂/Ar Flame, *Combustion Science and Technology* 30 (1983) 241-271.

R. T. Squires, The Kinetics of SO₃ Formation in Oil-Fired Boilers, *Journal of the Institute of Energy* 55 (1982) 41-46.

A. Urbanek and M. Trela, Catalytic Oxidation of Sulfur Dioxide, *Catalysis Reviews, Science and Engineering* 21 (1980) 73-133.

K. Wickert, The Oil-Firing Yearbook, Kopf, Stuttgart, 1963.

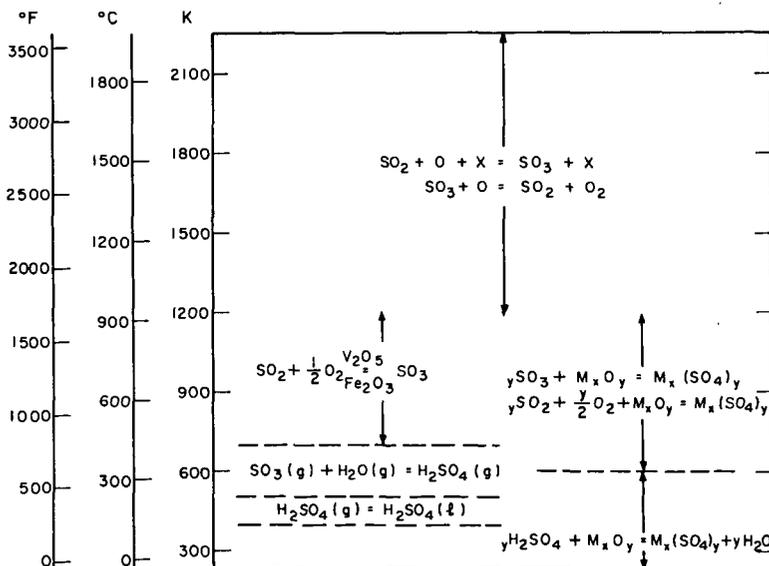


Figure 1. Processes contributing to formation of sulfur trioxide, sulfuric acid, and sulfates in residual oil-fired boilers.

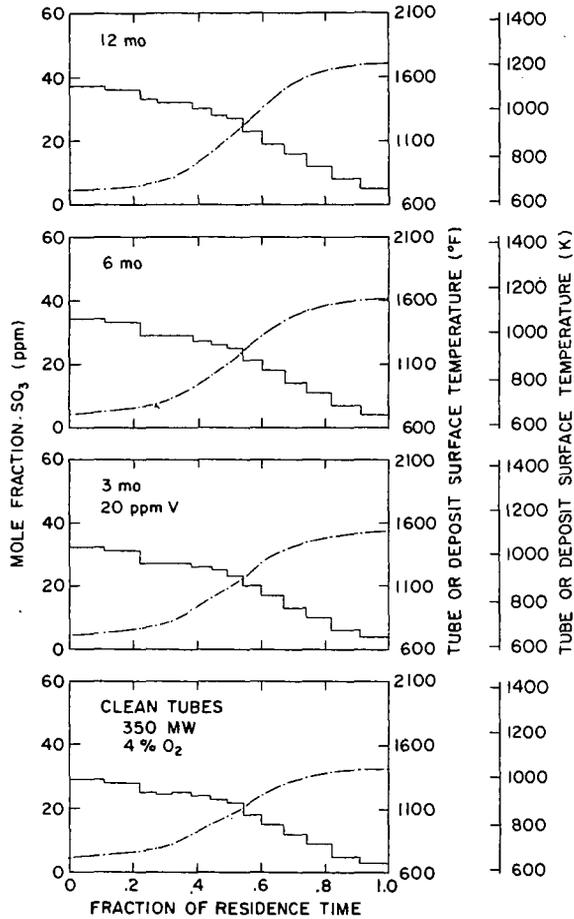


Figure 2. Expected change in SO_3 formation in Arthur Kill Unit 20 as ash deposits accumulate on the convective tubes. Solid line: surface temperature; dot-dash line: SO_3 mole fraction. The estimates are based on the gas temperature-tube temperature-tube area-gas velocity calculations of Piper and Kokoska (1983) and Piper (1985). The fuel oil sulfur content was 0.75 wt%, different from the 0.3 wt% sulfur oil normally fired in the unit. Ash deposits were assumed to grow at the rate of $1 \text{ g/m}^2\text{-hour}$. As the thickness of deposits increases, the formation of SO_3 decreases at the entrance to the convective section because the equilibrium ratio of SO_3/SO_2 decreases with increasing temperature. However, the ultimate mole fraction of SO_3 at the economizer outlet (far right) increases, because the contribution to SO_3 formation from the higher gas velocity, higher surface area region near the middle of the convective section increases.

Precombustion Control of Hazardous Air Pollutants

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KEY WORDS: trace elements, air toxics, coal preparation

INTRODUCTION

The air toxics provision of the 1990 Clean Air Act Amendments (CAAA) requires the Environmental Protection Agency (EPA) to promulgate regulations establishing emission standards for Hazardous Air Pollutants (HAP). Precursors of 13 of the HAPs are found in trace quantities in coal: As, Se, Hg, Pb, Cl, F, Be, Co, Ni, Cr, Sb, Cd, and Mn. The EPA is currently conducting a Congressionally mandated study of HAPs emissions from coal-fired power plants; the results of the study may lead to regulations governing the emissions of specific trace elements from coal. Influenced by the potential risk to coal utilization by possible future HAP emissions regulations, the Department of Energy, in cooperation with coal users and other government agencies, is seeking to evaluate the information on these elements of environmental concern in coal and to examine methods of measuring and controlling these emissions.

One control option is precombustion coal cleaning, which can significantly reduce mineral matter concentration and consequently has the ability to remove trace elements associated with the mineral matter liberated from the coal matrix. Primary factors controlling the precombustion removal of trace elements are the extent of association of the element with mineral matter within the coal matrix and the crushed coal particle size. The finer the coal is crushed, the more mineral matter is liberated and the further the trace elements associated with the mineral matter are reduced in the product coal.

The affinities of coal-related HAP precursors have been discussed extensively in the literature. This paper will review and summarize the literature on trace element affinities in coals, and the ability of precombustion coal cleaning to remove those trace elements from coals.

TRACE ELEMENTS AND COAL CLEANING

Finkelman,¹ in his 1980 dissertation, examined in depth the Waynesburg and Upper Freeport seam coals. In addition, he briefly examined 80 U.S. coals from every major basin and an additional 20 coals from around the world. He relied on a Scanning Electron Microscope equipped with an Energy Dispersive X-ray detector (SEM/EDX) to determine the mode of occurrence. His analysis discusses the problems associated with using float-sink testing as an analytical tool. Finkelman's float-sink data for the Waynesburg and Upper Freeport coals showed that, in general, trace element separation is dependent on mesh size, and, for the trace elements examined, approximately one-half of each trace element found in the whole coal was retained in the fractions with a specific gravity less than 1.50.

Finkelman summarized the literature that evaluated float-sink studies. His summary covered 12 float-sink studies involving a number of trace elements in several specific gravity fractions and whole coal samples for over 60 coals.

Finkelman briefly reviewed a number of studies that discussed the use of various leaching agents, including HCl, HF, HNO₃, and pyridine. His summary suggests that organic affinity index determinations may be exaggerated due to experimental error and indicates that a common error in each study is the assumption that the leaching was quantitative. In his discussion of correlation of trace elements, several studies on coals from around the globe are cited. His conclusion was that correlation coefficients do not necessarily reflect the mode of occurrence, but rather a common original source of the element. For example, Hg and As have very high correlation coefficients for pyrite and for each other. Finkelman's SEM/EDX experiments found that Hg and As are in solid solution with pyrite, (probably as sulfides) thus suggesting that the Hg and As had a common source. For any given trace element, there does not appear to be any coefficient that indicates a correlation between that trace element's concentration in coal and any other coal constituent's concentration that can be applied to more than one coal.

In summarizing his findings on the trace elements in coal, Finkelman states:

- Most trace elements appear to have an inorganic association in most high-rank coals.
- The organic complexing of trace elements, however, is not unimportant.
- Even in any one coal, the mode of occurrence can vary.

According to Gluskoter² and Ruch et al.³, organic affinity numerical values change with particle size distribution of the coal. The reason for this interpreted behavior is due to the misuse of the term "organic affinity." Gluskoter and Ruch developed the organic affinity index as a single numerical value to replace washability curves in an effort to simplify comparison of trace element reductions among different coals. Some researchers have misinterpreted the term to imply that trace elements may be chemically bound to the organic matrix, i.e., as in organometallic complexes, porphyrins, etc., but the vast majority of the organically associated trace elements in coal are very fine mineral particles that are dispersed and are difficult to liberate and separate. Examining the inorganic material frequently referred to as syngenetic, authigenic, or inherent mineral matter, Nicholls⁴ noted that some elements appear to be predominantly dispersed in the organic fraction, that is, the concentration of the element is constant with rising ash content. This suggests that those trace elements were present when the plant material was deposited prior to coalification and not introduced through later mineral deposition.

Kuhn et al.⁵ examined the trace elements of Davis, Blue Creek, Pittsburgh, Illinois No. 6, Rosebud, and Black Mesa coals. They examined the trace element concentrations of whole coal and float-1.40 sp. gr. fractions for 33 elements and the effects of acid leaching with HNO₃, HCl, and HF, and reactions with lithium aluminum hydride (LAH) on demineralization. They also examined Cr in five specific gravity fractions of Illinois No. 6 coal. Trace element concentrations and organic affinities were determined. With regard to the trace elements that

are potential precursors to HAPs cited in the 1990 CAAA, the following can be extracted from their summary:

- Be and Sb are consistently associated with the organic matrix.
- As and Cd are found with pyrite and can usually be substantially reduced with pyrite by gravity methods.
- Hg, Pb, and Mn have a high degree of inorganic association and are removed rather easily by conventional coal cleaning.

Akers^{6,7} examined conventional coal cleaning as a control method for trace elements. Akers' studies may be summarized by the following:

- Upper Freeport coal was found to be relatively high in As, Cd, and Cr. Conventional cleaning reduced As, Ba, Cd, Cr, F, Pb, Hg, Ag, and Zn by at least 50%. A significant reduction in Ni also occurred. An increase in Se concentration (ca. 30%) was noted.
- Conventional cleaning of Rosebud/McKay subbituminous coals showed significant reductions in As, Ba, and Ni. Small reductions of Cd and Se were observed. The Cr concentration was reported as increasing from 6 ppm to 10 ppm.
- Conventional cleaning of samples from the Croweburg seam indicated significant reductions in As, Ba, Cd, Cr, Pb, Ni, and Zn. In some cases, but not in others, reductions in F, Hg, and Ag correlate with ash reduction.
- A comparison of advanced coal cleaning to conventional cleaning was made with Sewickley seam coal. The Custom Coals International process (density separation of fine coal) was found to provide further reduction of all trace elements, except Hg, which is in disagreement with Kuhn's⁵ findings that Hg is readily removed with the ash. In one example, As was reduced from 14 ppm to 4 ppm (70%).
- Physical coal cleaning is effective in reducing the concentration of many trace elements, especially if they are in high concentration. Trace element removal is not, however, always proportional to ash removal. Potential changes in plant flow sheets and operating parameters may not lead to reduction in the ash content of the coal but may reduce trace element concentrations. Trace element reduction appears to be coal-specific, relating in part to the degree of liberation and the trace-element-bearing mineral matter. Thus, advanced coal cleaning methods that process more finely ground coals may provide greater reductions than conventional technologies.
- Conventional cleaning of Kentucky No. 11 coal led to large reductions in all trace elements measured.
- The Midwest Ore process, which involves extraction with hot perchloroethylene (PERC) followed by gravity separation in PERC, reduced nine trace elements by two-thirds or more.

White et al.⁸ prepared a very extensive report for the EPA that covered the entire coal utilization cycle, including a review of the literature on the following topics: occurrence of trace elements in U.S. coals; organic affinity studies, including the PETC Study⁹; photomicrographic studies; conceptual models for trace element modes of occurrence; coal washing, particularly partitioning of trace elements; and leaching of coal wastes.

The report concluded that:

- Organic affinity data are usually acquired by specific gravity fractionation, although acid leaching has also been used. The literature describing characterization and trace element washability of up to 27 elements was reviewed. Organic affinities and trace element concentrations for mineral-matter-free coals derived from reviewing the literature, including the work of Boyer et al.¹⁰, are presented in tables. The Boyer et al.¹⁰ report has a complete bibliography of 1,076 publications covering the fate of trace elements during mining, preparation, and utilization. The report cites earlier key studies by Buroff et al.^{11,12} and Miller et al.¹³, and includes where trace element removal at coal cleaning plants are cited, with a note that mass balances were not done.
- Although a thorough understanding of the response of various coals to sulfur and trace element removal does not yet exist, significant insight has been developed.
- Coals containing dispersed fine-grained minerals or free-swelling clays are more difficult to clean.
- A logical step in the process of better understanding trace element reduction potential is further statistical assessment of existing data.
- A statistical evaluation of existing ISGS and DOE data was performed. Linear correlations and regressions gave correlation coefficients (CC) ≥ 0.70 for the occurrence of several clustered groups of elements: As, Cd, Pb, Sb, and Zn; Al, Si, Ti, K, Co, V, and Cr; Fe and S; F with Al, K, Si, Ti, Cr, Cu, Be, and Ni. Regarding trace element reduction, a large number of elements showed coefficients greater than 0.70 and appeared to suggest that ash removal was more important than the removal of any individual element. Arsenic, Hg, and Fe reductions had CCs between 0.50 and 0.70 for pyrite removal and As, Co, Hg, Pb, Se, and Fe reductions had CCs greater than 0.50 for sulfur reduction. Efforts to correlate trace element reductions with an element's concentration in the whole coal were unsuccessful, except for the elements in the clays, suggesting that abundance of clays, and not the concentration of the element, determines the extent to which the element can be removed. Analysis of trace element removal data indicated elements in coal occur in two groups: 1) those associated with Al, K, Na, Si, Ti, Be, Cr, Cu, Mn, Ni, V, and ash; or 2) those associated with Fe, As, Hg, and pyrite.

- There is considerable disagreement among coal scientists on the methods of analysis and interpretation of the results of trace element studies of coal. A detailed framework for predicting trace element occurrence for a seam based on existing samples and associated geologic, geochemical, or paleoenvironmental data is lacking. Therefore, research priority needs for the coal resource appear to be in interpreting these data on a regional or seam basis. Given the magnitude of the U.S. coal resource base, combined with the extent and variability of existing data, collection and analysis of further samples (except as they relate to the evaluation of new mines and coal-using facilities) will provide little additional information.
- Pyritic sulfur and trace elements associated with pyrite and extraneous clays can be removed with relatively high efficiency by coal cleaning. Other trace elements are generally not removed during conventional cleaning. Variability in cleanability between regions or seams can be explained by the mode of occurrence, but the geologic processes responsible for these variations are poorly understood. Based on available (and in most cases, limited) data, it appears that the removal of most of the common trace elements can be reasonably correlated with the removal of ash and sulfur from coal using standard washability tests. For the chalcophile elements, the removal of sulfur is a better estimator of trace element removal than is the removal of ash. Removal of chalcophile elements from Allegheny formation coals is generally higher than from other U.S. coals. Interior Province coals exhibit significant variation in cleanability. Using a number of statistical techniques on existing washability data, White et al⁵ determined partitioning coefficients describing the relationship between trace element reduction and both sulfur and ash reduction for six major coal-producing regions of the U.S.
- Before additional data compilations on coal characteristics are made, the procedures for evaluating samples must be standardized.
- The trace element washability of forty-four coals was examined and compared to sulfur washability data for 750 coal samples. The authors concluded that specific attention should be given to major coal seams that are currently being washed or which are likely to be washed. Washability and statistical analysis studies similar to those described should be done, including analysis of minerals in the coals.
- Certain trace elements (e.g., V and Fe) have the potential for the catalytic conversion of SO_2 to SO_3 . Because of the increased efficiency by which SO_3 is absorbed onto the surface of fly ash particles, this catalytic effect may be important but has not been extensively investigated.

Conzemius et al.¹⁴ described the partitioning of 75 trace elements, sulfur, and ash in Illinois No. 6 and Upper Freeport coals processed in two dense-medium cyclone plants at sp. gr. of 1.4 and 1.6. Approximately two-thirds or more of Be, B, Cr, Mn, Co, Ni, As, Se, Cd, Sb, Hg, and Pb were removed. Chlorine and radionuclide concentrations were cut approximately by one-half and Mo by one-third.

The ISGS¹⁵ flotation studies on Illinois No. 6 coal have shown average reductions of selected trace elements of 58% and 77% for froth flotation and aggregate flotation, respectively.

Norton et al.¹⁶ described trace element reduction for a Texas lignite. Coal passing a 25- x 9.5-mm (1-in. x 3/8-in.) screen was cleaned by dense-medium cyclone and 9.5- x 0.15-mm (3/8-in. x 100 mesh) material cleaned on a concentrating table. Mercury, Ni, and Pb (3, 29, and 27 ppm in the feed coal, respectively) were reduced to below detectable levels. Selenium concentration was reduced by one-half.

Bechtel National¹⁷ performed a study on microbubble flotation for DOE and reported the trace element analyses for ROM, conventionally cleaned, and deeply cleaned Pittsburgh No. 8, Illinois No. 6, and Upper Freeport coals. The sources for the concentration data reported are not known, and no discussion of the data in the tables was available. The data presented indicate, that, except for arsenic reduced at every stage of processing, the trace element concentrations in the deeply cleaned coal were significantly lower than in the ROM coal, but higher than the conventionally cleaned coal used as the feed to the flotation unit.

A recent report prepared by Coal Technology Corporation¹⁸ for DOE describes the washability of coal for development of advanced cyclone processes. Four coals, Meigs No. 9, Illinois No. 6, Upper Freeport, and Pittsburgh No. 8, were ground to below 0.15 mm (minus 100 mesh) and deep cleaned using gravimetric techniques at a sp. gr. of 1.5. Deep cleaning of a plant-washed sample of Meigs No. 9 coal resulted in a change in ash content from 12.71% to 6.41%; a major (more than 50%) reduction of As, Mn, and V concentrations; a minor reduction (less than 50%) in Co, Se, and Zn concentrations; essentially no change in the Cd and Hg concentrations and an increase in concentration of Sb, Be, Cr, Cu, Pb and Ni. The ash content of the Illinois No. 6 coal was reduced from 11.05% to 4.7% and resulted in major reductions of As, Cd, Mn, Zn, and Hg concentrations; minor reductions in Co, Pb, Se, Ni, and V concentrations; and an increase in Sb, Be and Cu concentrations. Deep cleaning the Upper Freeport coal reduced the ash content from 23.49% to 4.49%; significantly reduced the Cd, Cr, Co, Pb, Mn, Hg, Ni and Zn concentrations; and mildly reduced Be and V concentrations; and increased the Sb, As and Se concentrations. The ash content of Pittsburgh No. 8 was reduced from 10.31% to 4.36% and provided major reductions in As, Mn and Hg; provided minor reductions in Cd, Cr, Co, Pb, Ni, Se and Zn; and increased Sb, Be, Cu, and V concentrations.

In examining the mode of occurrence and concentration of trace elements in U.S. and U.K. coals, Raask¹⁹ concluded that trace elements in bituminous coals are present chiefly in the mineral matter fraction and, in particular, a large number of chalcophilic elements are present. He also concluded that high-sulfur coals in the U.S. are relatively rich in Cd and Zn, the chalcophilic elements are preferentially removed upon coal cleaning, and between 40% to 50% of Be, Cd, Cu, Pb, Hg, and Zn are removed by reducing the ash content of cleaned coals to below 15%.

Norton et al.²⁰ examined the trace elements in chemically cleaned coals and concluded that hot aqueous carbonate, molten NaOH/KOH, and acid treatments can

effectively remove trace elements from coals. However, they cautioned that corrosion of the reaction vessels may elevate certain trace elements in the treated coals.

A project completed by the EPA's Industrial Environmental Research Laboratory and summarized by Harvey et al.²¹ investigated the distribution of trace elements in the Illinois No. 6 and Illinois No. 5 coals of the Illinois Basin. It was found that elements of environmental concern were present in the following concentrations: Pb (28 ppm), Cr and Ni (18 ppm), Cu (12.5 ppm), As (11 ppm), Mo (9.2 ppm), and Se (2.4 ppm). The other trace elements found in these specific coals average less than 2.4 ppm. From washability tests completed on the same coals, As, Cd, Mo and Pb were found to be trace elements associated with the mineral matter and were typically reduced by 50% or more. Some trace elements (Be, Ni and Sb) appear to be associated with the organic portion of the coal. Reductions in concentration of these elements were more difficult to achieve, their concentrations being reduced by less than 10%. Reductions in concentration of 15% to 30% were noted for several trace elements (Co, Cr, F, Hg, Se and Th) and those trace elements are assumed to be associated with both the mineral matter and the organic portion of the coal.

Researchers at Consol^{22,23} have assembled an extensive database characterizing trace element concentrations of ROM and coal preparation plant products. The database contains over 850 composite samples and 3,400 individual trace element analyses for 225 commercial coals. The Consol researchers concluded that:

- Individual trace elements are weakly to moderately correlated to ash content, but no correlation was noted for sulfur.
- Coal cleaning to remove ash is effective in removing a portion of many trace elements. The degree of trace element removal is often similar to the overall ash rejection.

SUMMARY AND CONCLUSIONS

The literature concerning the trace element concentration of U.S. coals, and coal preparation as it relates to trace element removal, is extensive. The subject has been of interest for at least 40 years and is of vital interest today. A computer search of papers published in the last decade on topics related to the subject readily revealed 200 citations on trace element concentrations in coals and their removal by physical methods. Nearly 100 additional references were found that address chemical and biological methods for removing trace elements from coal. Approximately 100 references were found that deal with the issue of trace element analyses of coal. A considerable amount of the material is contained in EPA reports and the EPRI PISCES Database.

The U.S. coal reserves are reasonably well characterized in terms of their trace element concentrations. However, there seems to be a great deal of inconsistency with regard to trace element washability of coal. As an example, it was noted in the discussion section that some authors report Hg as associated with the organic matrix (difficult to remove) while others report Hg as associated with the mineral matter (easy to remove). Inconsistencies like this suggest that each coal seam must be evaluated individually with respect to trace element washability.

Another example of an apparent inconsistency is the decrease in Cr concentration when Upper Freeport coal was cleaned, while Cr concentrations increased when Rosebud/McKay seam coal was subjected to cleaning. While it is possible that more carbon could be rejected than finely disseminated Cr, in this case the magnitude of Cr concentration increase suggests analytical errors. In reviewing the trace element literature, it is difficult to compare different research findings and determine where the errors may lie. Much of the trace element literature fails to discuss attempts at mass balance closure. Historically, a number of analytical techniques have been applied to trace element analysis of coal and older research efforts may have used analytical techniques which have subsequently been found to be lacking in accuracy. Even when newer methods were used, sampling procedures and sample preparation methods are often not discussed. There exist today analytical techniques which are capable of determining quite accurately trace element concentrations of homogeneous samples. It appears that coal sampling, good sample preparation techniques, and additional analytical standards appear to be the major obstacles to overcome in achieving good trace element analyses of coal.

There is a reasonable correlation between trace element removal during coal cleaning and ash rejection. This is apparently due to the "organic affinity" of certain trace elements. Some trace elements are so finely disseminated throughout the coal matrix that they are not removed by coal preparation methods in common practice. A conclusion based on a review of the literature is that all trace elements can be readily reduced by 40 to 50% by physical coal cleaning and any further characterization that may be deemed desirable should rely on statistical analysis of existing concentration and washability data. Further reductions could be achievable by advanced physical coal preparation methods which separate the mineral matter that has been more effectively liberated by grinding coal to finer particle sizes. To comply with potential regulation of HAPs from coal-fired power plants, it may be desirable to develop methods of removing specific trace elements, such as mercury or arsenic, which would suggest the need for chemical or biochemical coal cleaning methods.

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DISCLAIMER

References in this report to any specific commercial process, product, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. Robert B. Finkelman, "Modes of Occurrence of Trace Elements in Coal," Ph.D. Dissertation, University of Maryland, 1980.
2. H.J. Gluskoter, "Mineral Matter and Trace Elements in Coal," in Trace Elements in Fuel, S.P. Babu, ed., ACS Advances in Chemistry Series 141, ACS, Washington D.C., 1975.
3. R.R. Ruch, H.J. Gluskoter, and N.F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," Environmental Geology Notes No. 74, ISGS, 1974.
4. G.C. Nicholls, "The Geochemistry of Coal-Bearing Strata," in D. Muchison and T.S. Westoll, eds., Coal and Coal-Bearing Strata: American Edition, American Elsevier, New York, 1968, pp. 269-307.
5. J.K. Kuhn, F.L. Fiene, R.A. Cahill, H.J. Gluskoter, and N.F. Shimp, "Abundance of Trace and Minor Elements in Organic and Mineral Fractions of Coal," Environmental Geology Notes, No. 88, ISGS, 1980.
6. D.J. Akers, "Precombustion Control of Trace Elements," Presented at the Sixteenth Annual Conference on Fuel Science, Palo Alto, June 18-19, 1990.
7. D.J. Akers, "Coal Cleaning: A Trace Element Control Option," Preprint for the EPRI Conference on Managing Hazardous Air Pollutants: State of the Art, Washington, D.C., November 4-6, 1991.
8. D.M. White, L.O. Edwards, A.G. Eklund, D.A. Eklund, D.A. DuBose, F.D. Skinner, and D.L. Richmann, Radian Corp., "Correlation of Coal Properties with Environmental Control Technology Needs for Sulfur and Trace Elements," U.S. EPA Final Report EPA 600/7-84-066, June 1984.
9. J.A. Cavallaro, A.W. Duerbrouck, G. Gibbon, E.A. Hattman, H. Schultz, and J.C. Dickerman, "A Washability and Analytical Evaluation of Potential Pollution from Trace Elements in Coal," EPA-600/7-78-038, March 1978.
10. J.F. Boyer, J.P. Constantino, C.T. Ford, V.E. Gleason, and K.A. Rosnick, "Evaluation of the Effect of Coal Cleaning on Fugitive Elements, Phase II, Part III, State-of-the-Art: Fate of Trace Elements In Coal During Mining, Preparation, and Utilization," U.S. Department of Energy Report No. De-AC22-77EV04427, 1981, 263 pp.
11. J.M. Buroff, J. Straus, A. Jung, and L. McGilvray, Environmental Assessment: Source Test and Evaluation Report: Coal Preparation Plant No. 1, VERSAR, Inc., Springfield, Va., U.S. Environmental Protection Agency Report No. EPA-600/7-81-071a, 1981, 287 pp.
12. J.M. Buroff, J. Straus, A. Jung, and L. McGilvray, Environmental Assessment: Source Test and Evaluation Report- Coal Preparation Plant No. 2, VERSAR, Inc., Springfield, Va., U.S. Environmental Protection Agency Report No. EPA-600/7-81-071b, 1981, 290 pp.

13. F.A. Miller, T.L. Bell, R.C. Patyrak, and J.M. Wyatt, Environmental Studies on a Level C Coal Cleaning Plant, Tennessee Valley Authority, Chattanooga, Tenn., U.S. Environmental Protection Agency Report No. TVA/OP/EDT-81/46, 1981, 137 pp.
14. R.J. Conzemius, C.D. Chriswell and G.A. Junk, Fuel Processing Technology, 1988, 19, pp. 95-106.
15. R.B. Read, R.R. Ruch, H.P. Ehrlinger, P.J. DeMaris, D.M. Rapp, L.R. Camp, and J.A. Fitzpatrick, "ISGS Aggregate Flotation Fine-Coal Cleaning Process," Technical Report for January 1, 1983 - August 31, 1986, CRSC.
16. G.A. Norton, W.H. Buttermore, R. Markuszewski, and D.J. Akers, "The Removal and Control of Trace Elements in Coal and Coal Wastes," Proceedings of the EPRI Seminar on Reducing Power Plant Emissions by Controlling Coal Quality, Bethesda, Md., October 27-28, 1987.
17. Advanced Physical Fine Coal Cleaning: Microbubble Flotation, DOE Final Report DE-AC22-85PC81205, Bechtel National, Inc., September 1988.
18. Coal Technology Corporation, Phase I Report, DOE Contract DE-AC222-90PC90177, June 1992.
19. E. Raask, "The Mode of Occurrence and Concentration of Trace Elements in Coal," Prog. Energy Combust. Sci., 1985, 11, pp. 97-118.
20. G.A. Norton, R. Markuszewski, and H.G. Araghi, "Chemical Cleaning of Coal: Effect on the Removal of Trace Elements," Am. Chem. Soc. Symposium Series 319, Fossil Fuels Utilization: Environmental Concerns, R. Markuszewski, and B.D. Blaustein, eds., ACS, Washington, 1986.
21. R.D. Harvey, R.A. Cahill, C.L. Chou, and J.I. Steele, Mineral Matter and Trace Elements in the Herrin and Springfield Coals, Illinois Basin Coal Field, EPA Report No. EPA-600/S7-84-036, 1984.
22. P.R. Tumati and S.M. DeVito, Trace Element Emissions from Coal Combustion - A Comparison of Baghouse and ESP Collection Efficiency, Proceedings of the EPRI Conference on the Effect of Coal Quality on Power Plants, August 25-27, 1992, San Diego, Ca.
23. E.L. Obermiller, V.B. Conrad, and J. Lengyel, "Trace Element Contents of Commercial Coals," EPRI Conference on Managing Hazardous Air Pollutants: State-of-the-Art, Washington, D.C. November 1991.