
Session 8b

Hazardous Air Pollutants

**8b.1 Comprehensive Assessment of Toxic Emissions
 From Coal-Fired Power Plants**

CONTRACT INFORMATION

Location U.S. Department of Energy
 Pittsburgh Energy Technology Center
 Office of Project Management
 Environmental Control Division
 Air Toxics and Fine Particulates Control Program

Program Manager Thomas D. Brown

ABSTRACT

The Department of Energy through the Air Toxics Control Program at the Pittsburgh Energy Technology Center (PETC) has been conducting comprehensive assessments of toxic emissions from coal-fired power plants since 1990. The power plants assessed represent an excellent cross section of the combustion and pollution control technologies in current use, with power plants demonstrating advanced control technologies being funded under PETC's Office of Clean Coal Technology. Data from the assessments will be used in the mandated risk assessment being performed by the Environmental Protection Agency. A presentation on the Air Toxics Control Program and results from the assessments will be made at the upcoming Advances in IGCC and PFBC Review Meeting.

A paper will not be available at the time of the meeting. A summary report on the results of the toxic assessments of seven power plants and five Clean Coal technologies will be available in August 1994. If you want a copy of the report, please give me your business card at the conference or write/call at:

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Period of Performance August 1, 1992, to September 30, 1994

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Partitioning	_____											
Modeling	_____											
Verification	_____											
Reporting												

* Project Review Meetings

OBJECTIVES

The Energy & Environmental Research Center (EERC) is carrying out an investigation that will provide methods to predict the fate of selected trace elements in integrated gasification combined cycle (IGCC) and integrated gasification fuel cell (IGFC) systems to aid in the development of methods to control the emission of trace elements determined to be air toxics. The goal of this project is to identify the effects of critical chemical and physical transformations associated with trace element behavior in IGCC and IGFC systems. The trace elements included in this project are arsenic, chromium, cadmium, mercury, nickel, selenium, and lead. The research seeks to identify and fill, experimentally and/or theoretically, data gaps that currently exist on the fate and composition of trace elements. The specific objectives are to 1) review the existing literature to identify the type and quantity of trace elements from coal gasification systems, 2) perform laboratory-scale experimentation and computer modeling to enable prediction of trace element emissions, and 3) identify methods to control trace element emissions.

BACKGROUND INFORMATION

Trace element emissions pose a potential problem to two emerging coal gasification electric power-generating systems: IGCC and IGFC. The potential problems associated with trace elements are the release of substances that are considered air toxics and the degradation of fuel cell efficiency due to contamination with minor elements. In order to develop effective technologies to control trace element emissions within anticipated regulatory requirements and to ensure the efficient operation of fuel cells, the type and

quantity of trace elements emitted from coal gasification-based systems must be determined as a function of system, system conditions, and coal composition.

The fate of trace elements in coals used in IGCC and IGFC systems is closely tied to how the trace elements are associated in the coal and the gasification conditions. Trace elements in coals are associated in several forms, including organic associations, such as salts of carboxylic acid groups and organic coordination complexes, and mineral associations, such as sulfides, sulfates, silicates, phosphates, and carbonates. During gasification, these inorganic elements are partitioned into gases, liquids, and solids. The transformation of these trace elements into the various states and phases depends upon the fundamental characteristics of the elements and their association with minerals and coal particles. Minerals that are not directly associated with coal particles experience a different process environment than minerals that are intimately associated with coal particles during gasification.

In order to predict the form of the inorganic species during gasification, it is essential that detailed information on the distribution of major mineral phases and organically associated inorganic elements be determined. This information is critical since the transformations and interactions during utilization impact the partitioning of trace elements. The primary transformations that occur to major and minor trace species during coal conversion are illustrated in Figure 1. Modeling the transformations using thermochemical equilibrium calculations combined with various chemical and physical constraints to reach equilibrium can be effectively used to estimate the distribution of

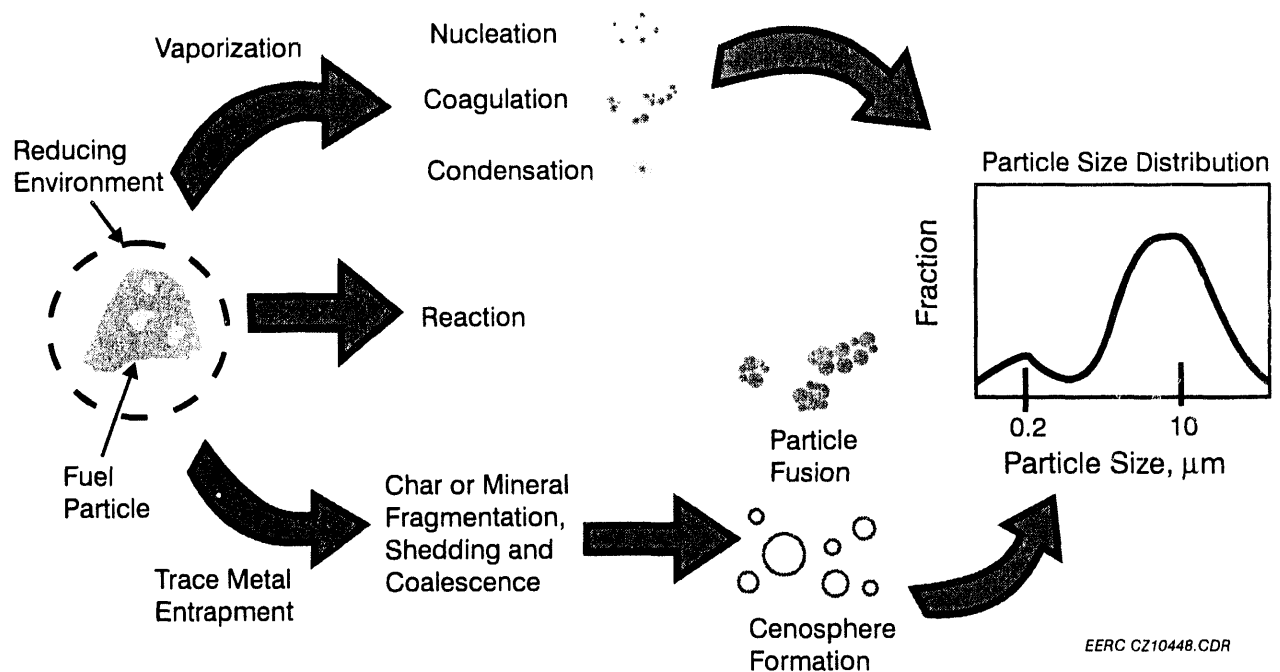


Figure 1. Trace Metal Transformations and Partitioning

gas, liquid, and solid components as a function of gasification conditions.

PROJECT DESCRIPTION

The approach of this project is to identify and model important physical and chemical transformation mechanisms of the trace elements during gasification as a function of coal compositions (trace element abundance and association) and gasification conditions. Identification of the reactions and transformations, coupled with accurate modeling of trace element behavior, is providing essential information for the identification of the form

of the inorganic species. Gasification conditions—such as reducing and oxidizing atmospheres, gas-phase composition, pressure, and temperature—influence the partitioning of the air toxics between various gases, liquids, and solid inorganic components as a function of location in the gasifier. This information will be used to identify the most effective control technology by predicting the form of the trace element as a function of operational conditions. The model will be used to predict the initial partitioning of the metals in the gasifier and their form downstream of the gasifier in the gas cleanup systems.

This project has four work categories: partitioning experiments and analysis, modeling, identification of control technologies, and model testing and verification. The partitioning experiments and analysis have concentrated on the operation of closely controlled experimental equipment to produce the appropriate samples and the analysis/characterization of those samples by state-of-the-art analytical techniques.

A pressurized drop-tube furnace (PDTF) and integrated bench-scale gasifier (IBG) are utilized for the experiments at temperatures from 750° to 1500°C and pressures from 50 to 200 psi. Testing has been conducted for three coals under the following conditions: 1000°–1500°C, 50–200 psi, and 0.5–2.0 O/C ratio. The samples produced in the PDTF and IBG systems have been analyzed using inductively coupled plasma spectroscopy, atomic absorption, x-ray fluorescence (XRF), scanning electron microscopy (SEM), and various other techniques.

The modeling work has concentrated on the modification of two existing codes at the EERC: ash transformations (ATRAN) and thermochemical equilibrium analysis of coals and ashes (TEACH). Both codes are being modified to include specific algorithms associated with trace element behavior. The resultant model is a consolidation of the aforementioned codes into a single program capable of predicting the size, composition, and phase of the inorganic species at a given temperature and pressure. An operational shell is being developed to incorporate the two codes.

The identification of control technologies will be incorporated into the project after most of the testing and modeling is complete, at which time multiple scenarios can be

addressed using the data and models. The model testing and verification will consist of testing the model and assumptions on the transport reactor scaleup facility located at the EERC.

RESULTS

Coal Selection and Characterization

A survey of the trace metals in several coals was performed. The distribution of the seven elements is listed in Table 1. Three coals have been selected for testing: Illinois No. 6, Sufco (Utah), and Pittsburgh No. 8.

Many of the recently developed computer models to predict the particle-size and composition distribution of major and minor elements during coal combustion and gasification were made possible through the use of highly quantitative analytical data on coal mineral composition and size, computer-controlled scanning electron microscopy or (CCSEM) (Steadman and others 1990). CCSEM provides particle-size and composition distribution for the mineral grains in coal. These raw CCSEM data are the primary input to the newest computer models of ash formation.

To determine associations of trace elements with minerals, the standard CCSEM procedure using automated image analysis and energy-dispersive x-ray analysis is performed on the coal. At the completion of each frame of analysis, the operator can locate the specific minerals and reanalyze them with the more sensitive wavelength-dispersive x-ray spectrometer (WDS) to determine trace metal abundance. The WDS data analysis can then be manually compared to the standard CCSEM data to correlate the presence of trace

Table 1. Abundance of Trace Metals in Coals Tested ($\mu\text{g/g}$ dry coal basis)

	Illinois No. 6	Sufco Utah	Pittsburgh No. 8
Arsenic	1.5	0.66	7.80
Cadmium	0.33	0.048	0.10
Chromium	26.0	26.9	18.8
Lead	2.84	0.86	3.87
Mercury	0.067	0.033	0.082
Nickel	15.1	8.35	14.9
Selenium	3.03	1.05	1.41

elements with specific mineral species. A generalized trace element profile can then be created for a number of coals (to be used for data correlations in the model until the more rigorous technique is completed). In addition, the chemical fractionation technique (Benson and Holm, 1985) is being used to support the CCSEM WDS by providing data on the general association of the seven trace metals.

The association of arsenic, cadmium, chromium, mercury, nickel, lead, and selenium were determined for Illinois No. 6, Sufco (Utah), and Pittsburgh No. 8. The associations were determined through a combination of chemical fractionation (Benson and Holm, 1984) CCSEM combined with WDS (CCSEM/WDS) (Galbreath and Brekke, 1994). The summary of the associations are listed in Table 2. This information is combined with the CCSEM data listed in Table 3 and used as input to the TraceTran model to predict the partitioning of trace as well as major and minor inorganic components. Table 3 only reports the abundance of the minerals; size information is also available. Table 4 summarizes the levels of trace metals found in individual minerals.

Partitioning of Trace Metals

The fate and distribution of trace elements as a function of temperature, pressure, and gas composition in IGCC systems are important to the emerging IGCC and IGFC technologies. Laboratory experiments performed in the EERC PDTF and the IBG have been used to determine the partitioning of important trace elements and to enable the prediction of the fate of trace elements in IGCC and IGFC systems.

Testing of all three coals in the PDTF is nearly complete. A parametric study has been conducted on two of the coals to produce solid, liquid, and gaseous products under a range of conditions to determine the partitioning of the trace elements as a function of the association of the trace elements in the coals and of gasification conditions. Based on the literature survey, a standard condition of temperature, pressure, and gas composition was chosen for one test. The other tests were performed with temperature, pressure, and gas composition at values above and below the standard.

Table 2. Trace Element Associations in Coals Examined

Element	Associations
As	Pyrite, arsenates
Cd	Sulfides, clays
Cr	Clays, organic compounds
Hg	Pyrite
Ni	Pyrite, clays, organic compounds(?)
Pb	Pyrite, other sulfides, clays
Se	Pyrite, other sulfides, organic compounds, sulfate

Table 3. Mineral Composition of Coals Used in Trace Element Emissions Program (determined by CCSEM)

	Illinois No. 6	Sufco (Utah)	Pittsburgh No. 8
Quartz	23.3	32.0	14.8
Calcite	0.8	25.0	5.0
Dolomite	0.1	2.9	1.1
Kaolinite	13.8	10.4	21.0
Montmorillonite	3.8	1.3	5.5
K Aluminosilicate	12.2	0.1	20.0
Na Aluminosilicate	0.4	5.6	0.0
Pyrite	26.7	6.6	13.4
Gypsum	5.8	4.3	1.4
Other	13.1	11.8	8.8

The resulting inorganic phases were aerodynamically classified, using a two-stage cyclone system, with a set of impingers/mercury trap for vapor-phase

collection. In some cases, the cyclones are replaced with an impactor. The multicyclone is an Environmental Protection Agency Southern Research Institute five-stage cyclone with the first, third, and fourth stages

removed. The impactor that is used is a University of Washington Mark 5 source test cascade impactor. The cyclone, impactor, and filter were heated to maintain the temperature of the product gas above 100°C to reduce the risk of water condensation during collection. Three size distributions were analyzed to quantify the forms and concentrations of important trace elements. Detailed analysis of the size-fractionated ash allowed for the

Table 4. Trace Element Levels Determined for Individual Mineral Grains in Selected Coals Using CCSEM/WDS ($\mu\text{g/g}$ in mineral grains)

Element	Pyrite	Clays
Ni	100–350	--
As	300–400	--
Se	800–2900	--
Cd	n.d. ¹	--
Hg	80–2700	--
PB	n.d.	--
Cr	n.d.	300–950

¹ Not detected.

determination of size and composition partitioning between the gas and solid phases, since the vaporized components will be concentrated in the smallest-size fractions. The coal and gas flow through the system will be controlled and monitored to allow determination of trace element concentration and mass balance.

A detailed description of the PDTF furnace assembly can be found elsewhere (Benson and others, 1993). Briefly, the PDTF consists of a 2.875-inch-ID alumina tube (55 inches long) with a slightly reduced end, used to support a flow accelerator in a fixed position, nested on top of a tube of the same dimensions (25 inches long). These tubes are concentrically surrounded by a tube of slightly larger dimensions. The tubes are heated externally by high-temperature tube furnaces equipped with Kanthal Super 33 elements. The entire reactor and the heating elements are housed in a water-jacketed pressure vessel. Coal is introduced into the reactor with a carrier gas through a traversing, water-cooled injector located in the center of the tube. Optional secondary air enters the reactor at the top of the tube and flows

through the tube, around the injector assembly. The coal residue and process gases travel down the tube in a laminar flow regime and pass through the accelerator where they are collected by a water-cooled, nitrogen-quenching ash collection probe. Various collection devices can be attached to the collection probe to collect the solids. Size segregation of the ash is obtained by using a multicyclone or impactor in conjunction with a final filter. A bulk filter is used to collect ash for bulk chemistry. A water-cooled deposition probe can also be inserted, in place of the ash collection probe, to simulate the deposition conditions in a utility boiler. The product gases are monitored on-line by O₂, CO, and CO₂ gas analyzers or are intermittently sampled for a gas chromatograph (GC).

The PDTF can operate at temperatures as high as 1500°C and pressures up to 250 psi. Efforts are currently underway to attach an atomic absorption unit to the exiting gas line to acquire on-line mercury analysis from the furnace. Burnouts in excess of 95% with high carbon monoxide/carbon dioxide ratios have been produced under gasification conditions.

In the experimental effort, three coals were run under multiple temperatures, pressures, gas compositions, and residence times. The resultant samples will be collected in a three-stage multicyclone and characterized by using SEM, wavelength-dispersive x-ray fluorescence (WDXRF), inductively coupled plasma (ICP) spectrometry, and atomic absorption (AA).

Tests to determine the partitioning of trace metals into gases, liquids, and solids were conducted in the PDTF. The partitioning was ascertained by determining the fraction in which the material was collected. Metals that are not vaporized during gasification remain in the residual ash and are collected in the size fraction greater than one micrometer. Metals that are vaporized but condense in the system are collected in the submicron fraction. Metals such as Se and Hg may not condense in the system and be emitted in a vapor state. These vapors are collected in the impinger train. The results summarized in this report are for Illinois No. 6 and are focused on the vapor-phase components. Testing was conducted to determine the effect of temperature, O/C ratio, and pressure on the abundance of vapor-phase species. Figure 2 illustrates the effect of O/C ratio on the abundance of As, Cd, Se, and Hg in the vapor phase at 1500°C initial gasification temperature. The results indicate a slight increase in vapor-phase Hg and As. Se showed an even distribution with a slight increase in Se in the vapor phase at higher oxygen levels. The cadmium shows some variation in the abundance with changing oxygen levels. At a 1000°C initial gasification temperature shown in Figure 3, a clear trend in increasing vapor-phase As, Cd, and Hg with decreasing O/C ratios is demonstrated. Se showed the opposite trend, with increasing abundance in the gas phase

with increasing O/C ratio. This trend is likely due to the lower volatility of reduced Se relative to the oxide form as discussed by Dismukes (1994). The effect of initial gasification temperature on the abundance of trace metals in the gas phase is depicted in Figure 4. Figure 4 shows that with increasing temperature, the abundance of trace metals in the gas phase increases.

Predicting Trace Metals Behavior

Predicting inorganic transformations (major and minor components) during coal combustion has long been the focus of many research programs (Zygarlicke and others, 1992; Wilemski and others, 1992; Baxter, 1992). In the program, the techniques that have been applied to combustion have been modified to predict inorganic transformations under gasification conditions. The approach used in this program is to combine inorganic transformation algorithms and the thermochemical equilibrium calculations (Ramanathan and others, 1989, 1991). These techniques have been developed to predict the particle-size and composition distribution of the resulting coal ash particulate, along with the state of the vapor species at selected conditions for major, minor, and trace constituents.

A computer model to predict the evolution of major, minor, and trace elements during the gasification of coal is being created, based on the algorithm shown in Figure 5. The shaded boxes in Figure 5 represent the inputs required, while the boxes with a drop shadow are the outputs generated from the model. The first task of the model is to determine the associations of the major, minor, and trace elements in the coal prior to utilization. The association of the elements prior to utilization will affect their phase, size,

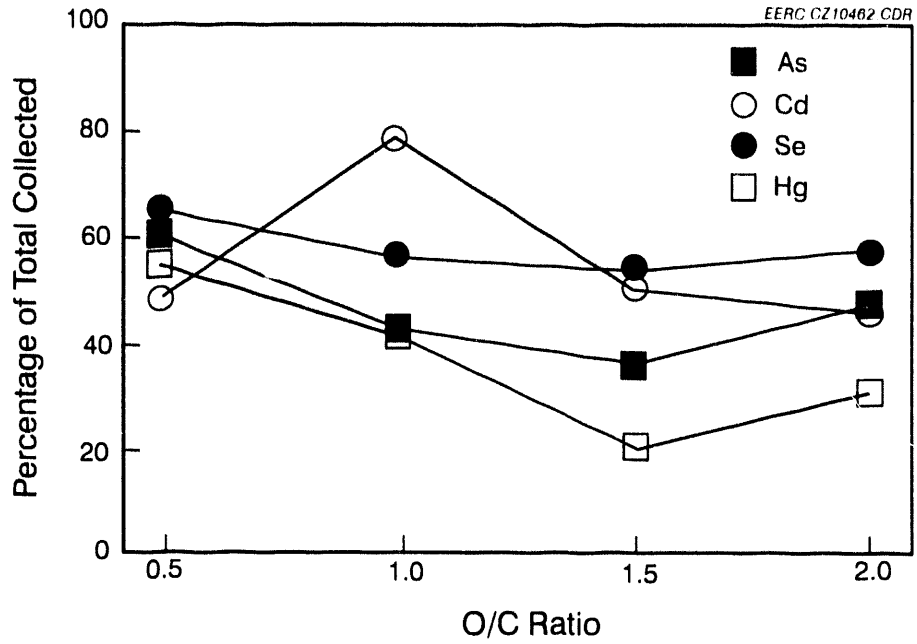


Figure 2. Trace Metal Distribution vs. O/C Ratio for Illinois No. 6

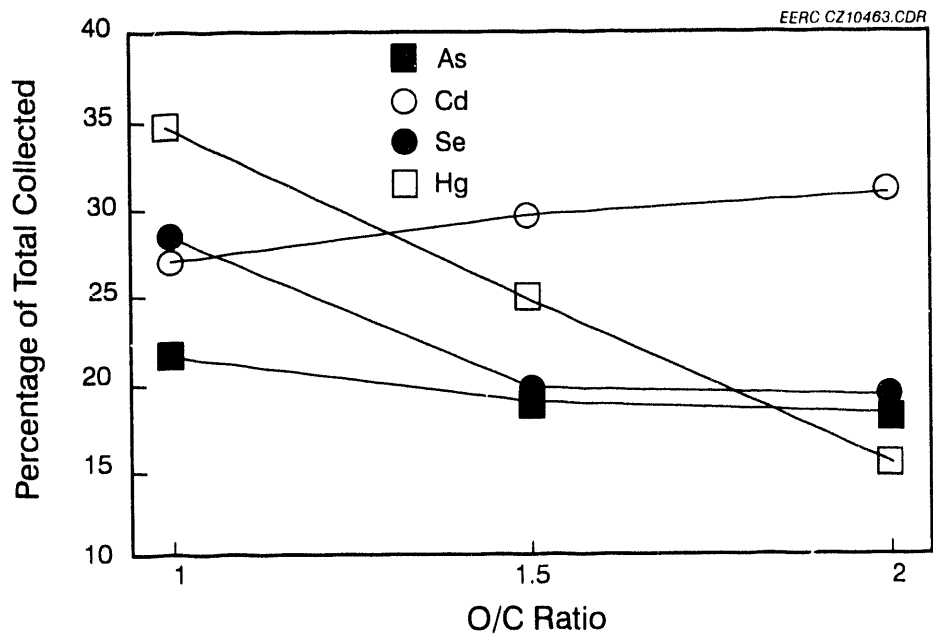


Figure 3. Trace Metal Distribution vs. O/C Ratio for Illinois No. 6

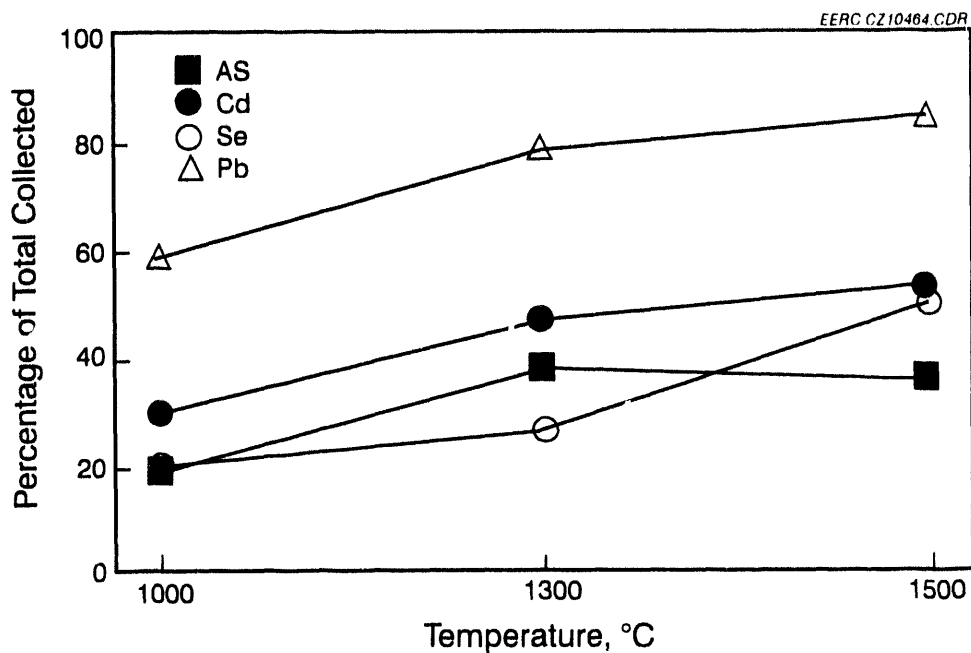


Figure 4. Trace Metal Distribution vs. Gas Temperature for Illinois No. 6

and composition distribution in the residual ash and gas streams. Bulk chemistry, CCSEM/WDS, and chemical fractionation are used as input data.

Once a mass balance is performed around the coal input data, it is necessary to determine which of the inorganic components will be vaporized during the initial gasification process. These calculations will be performed with the use of a thermochemical equilibrium program, TEACH (Ramanathan and others, 1989, 1991), created at the EERC. This code is currently being upgraded to include the appropriate trace element phases. With the exclusion of the vaporized species, the remaining constituents will be processed through algorithms for mineral fragmentation, coalescence of both minerals and organically associated species, and the shedding of resulting particles. Examples of data obtained from the calculations are illustrated in

Figure 6 for major ash components and Figure 7 for trace metals.

The state of the volatile species under given conditions will then be determined, again using the TEACH code. The distribution of Hg species is illustrated in Figure 8.

FUTURE WORK

The future work will involve the following:

- Completing the interpretation of the results obtained from testing Sufco and Pittsburgh No. 8 using the PDTF system.
- Completing the integration of the TraceTran computer code.

Analytical Characterization

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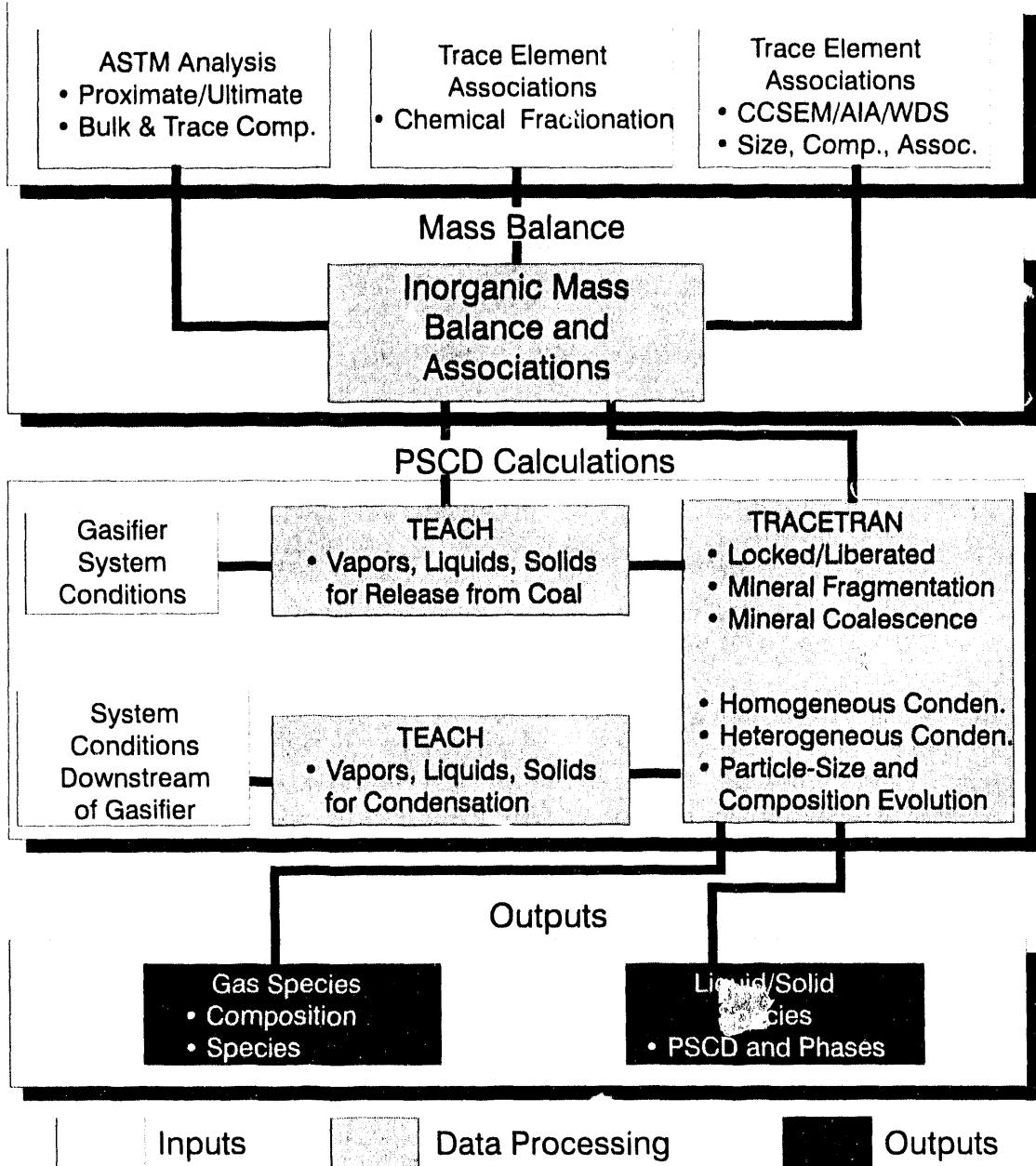


Figure 5. Trace Element Emissions Model Algorithm

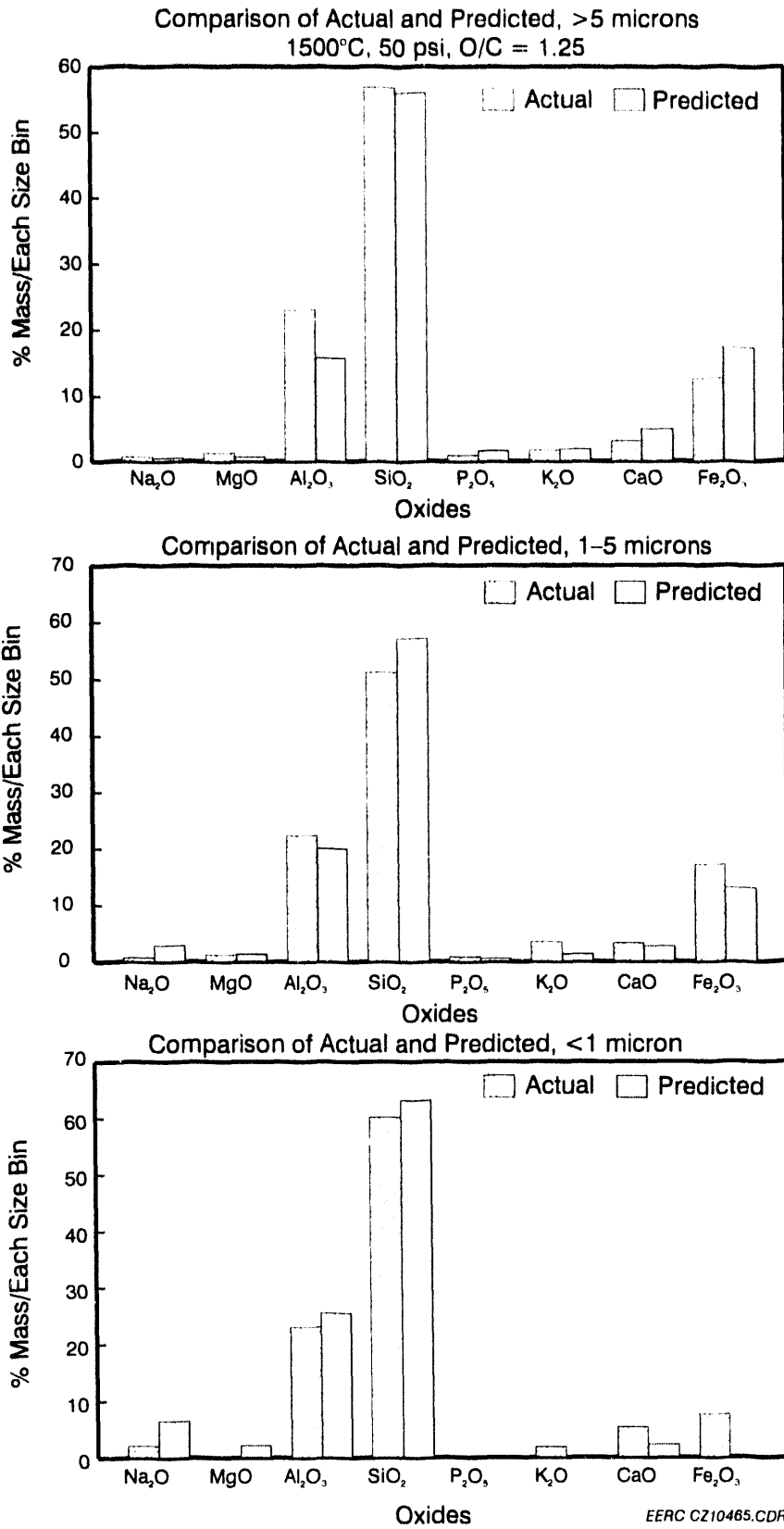


Figure 6. Comparison of Predicted and Actual Particle-Size and Composition Distribution, for Major Elements

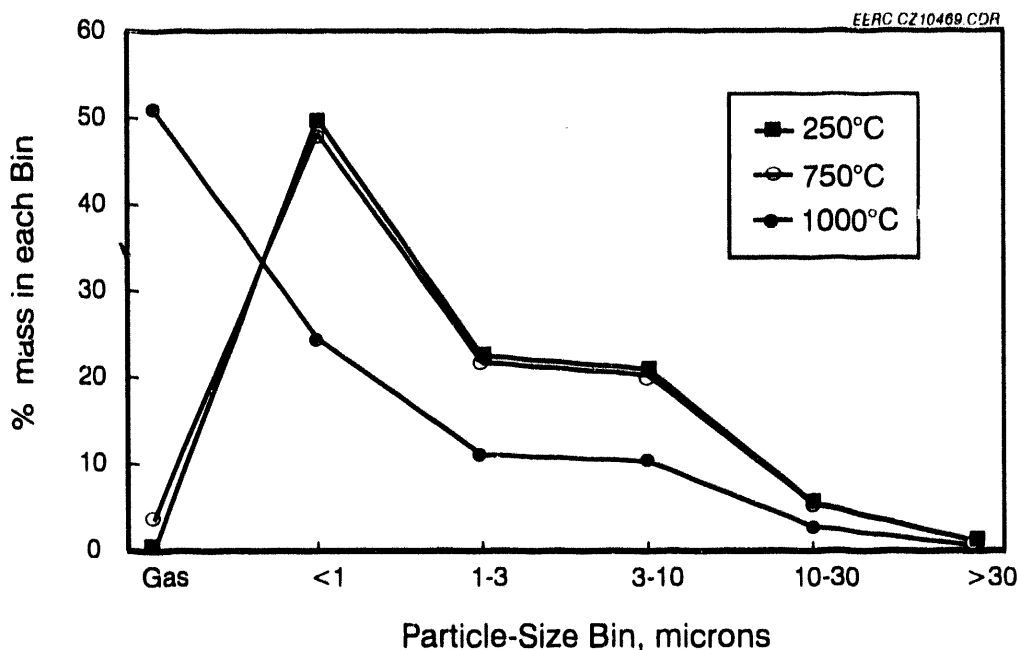


Figure 7. TraceTran Predictions for Partitioning of Pb During Gasification of Illinois No. 6 (O/C = 1.0, pressure = 20 atm)

- Verifying the predictive capability of TraceTran using data obtained from larger-scale systems.

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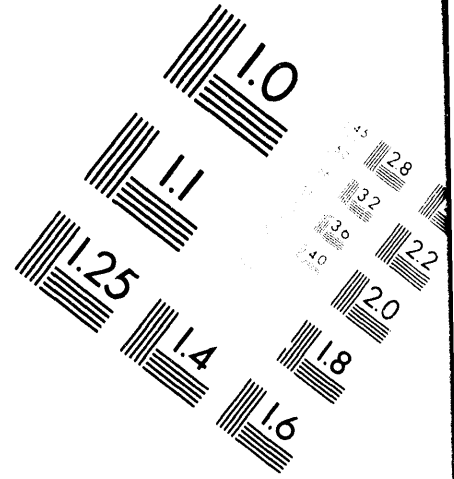
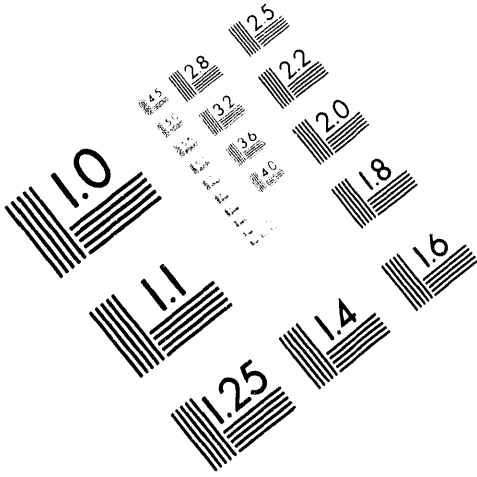
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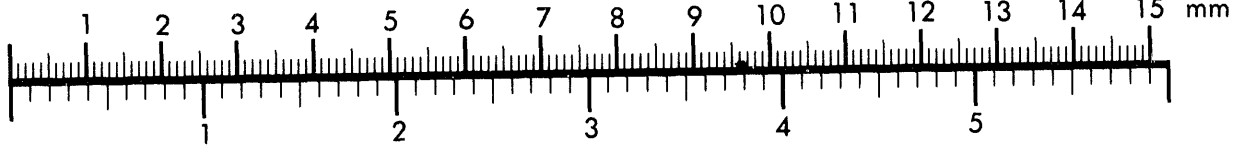
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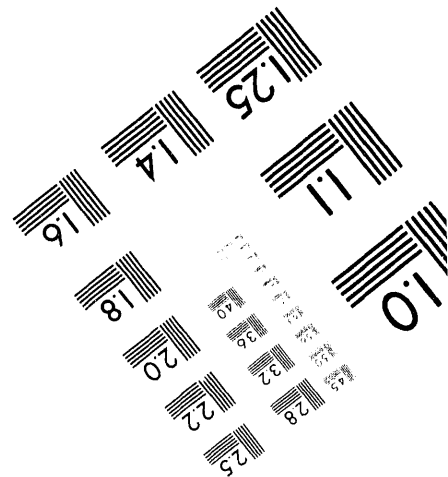
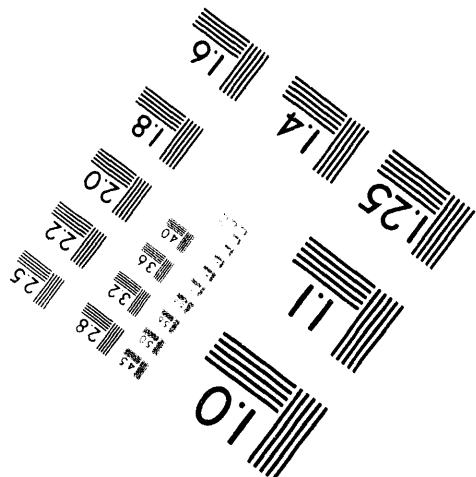
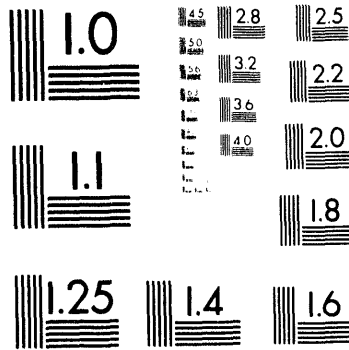
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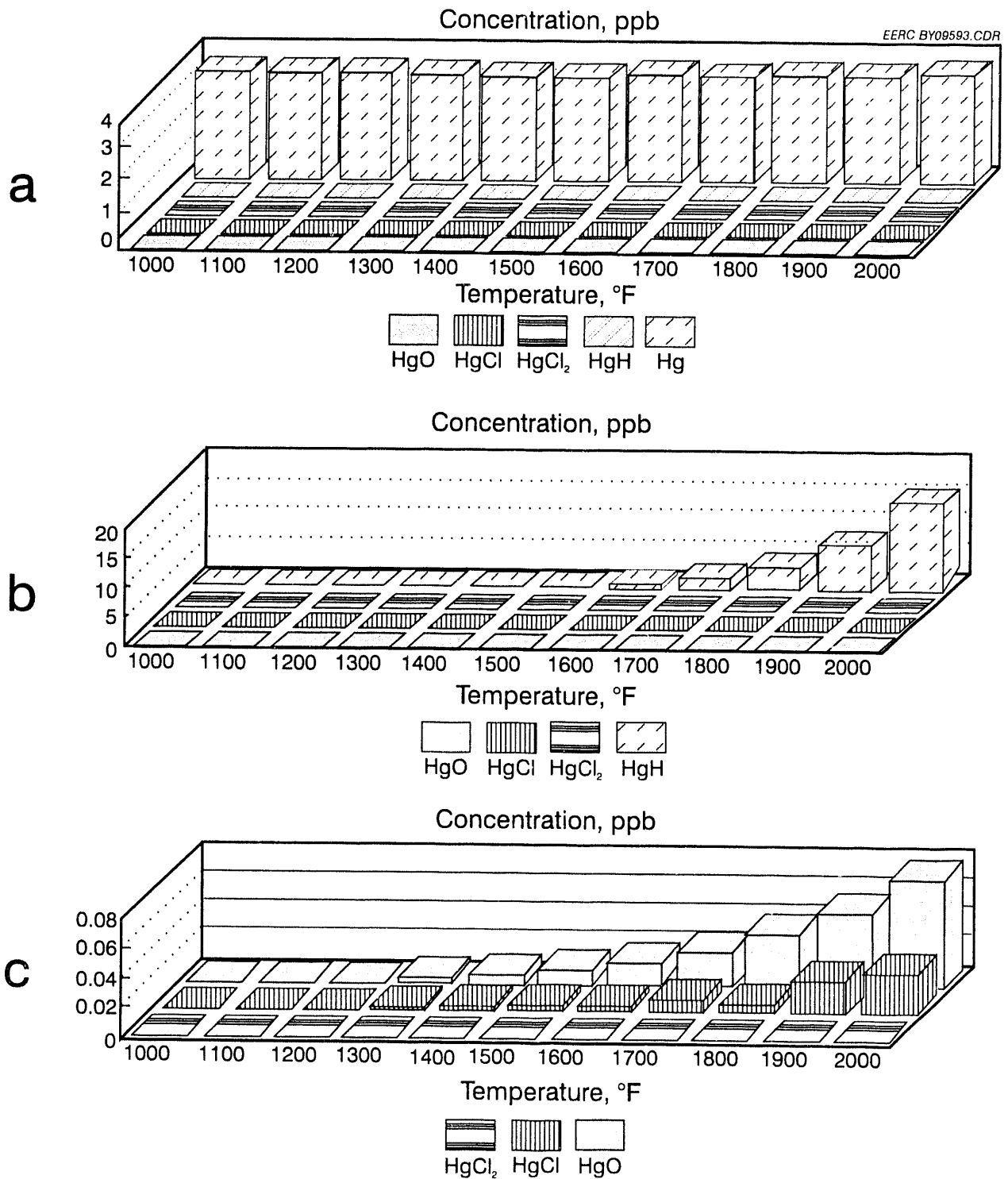


Figure 8. Distribution of Hg Species as a Function of Temperature for Sulfo Coal Using Thermochemical Equilibrium Calculations

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HAP Sampling at Tidd PFBC

CONTRACT INFORMATION

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Period of Performance August 2, 1989 to June 30, 1995

Schedule and Milestones

Program Schedule

	FY1990		FY1991		FY1992		FY1993		FY1994		FY1995	
	1	2	3	4	1	2	3	4	1	2	3	4
Design Specification/ APF Procurement	_____											
Detailed Design	_____											
Test Plan	_____											
Hardware Procurement	_____											
Testing	_____											
Data Analysis	_____											

OBJECTIVE

The objective of this project was to sample process streams of the Tidd PFBC plant and to characterize the HAPs associated with those various process streams. The data are comparable to HAP data collected by DOE and EPRI studies at conventional coal-fired utility plants.

BACKGROUND INFORMATION

Passage of the 1990 Clean Air Act Amendments (CAAA) has dramatically increased the interest in hazardous air pollutants (HAPs) from all sources. Title III of the amendments specifically commissioned a study of the hazards to public health reasonably anticipated to occur as a result of emissions of

pollutants listed in Title III by electric utility steam generating units. A study of mercury must also be conducted by U.S. Environmental Protection Agency (U.S. EPA) and transmitted to Congress. U.S. EPA, the Utility Air Regulatory Group (UARG), the Electric Power Research Institute (EPRI), and the U.S. Department of Energy (DOE) are studying emissions of HAPs at numerous fossil-fuel fired utility plants with various configurations and emissions control systems. U.S. EPA will use these data and health risk assessment models to evaluate the hazards to public health associated with the Title III HAPs. Findings from these studies will be used to determine if regulation of electric utility HAPs is appropriate and necessary.

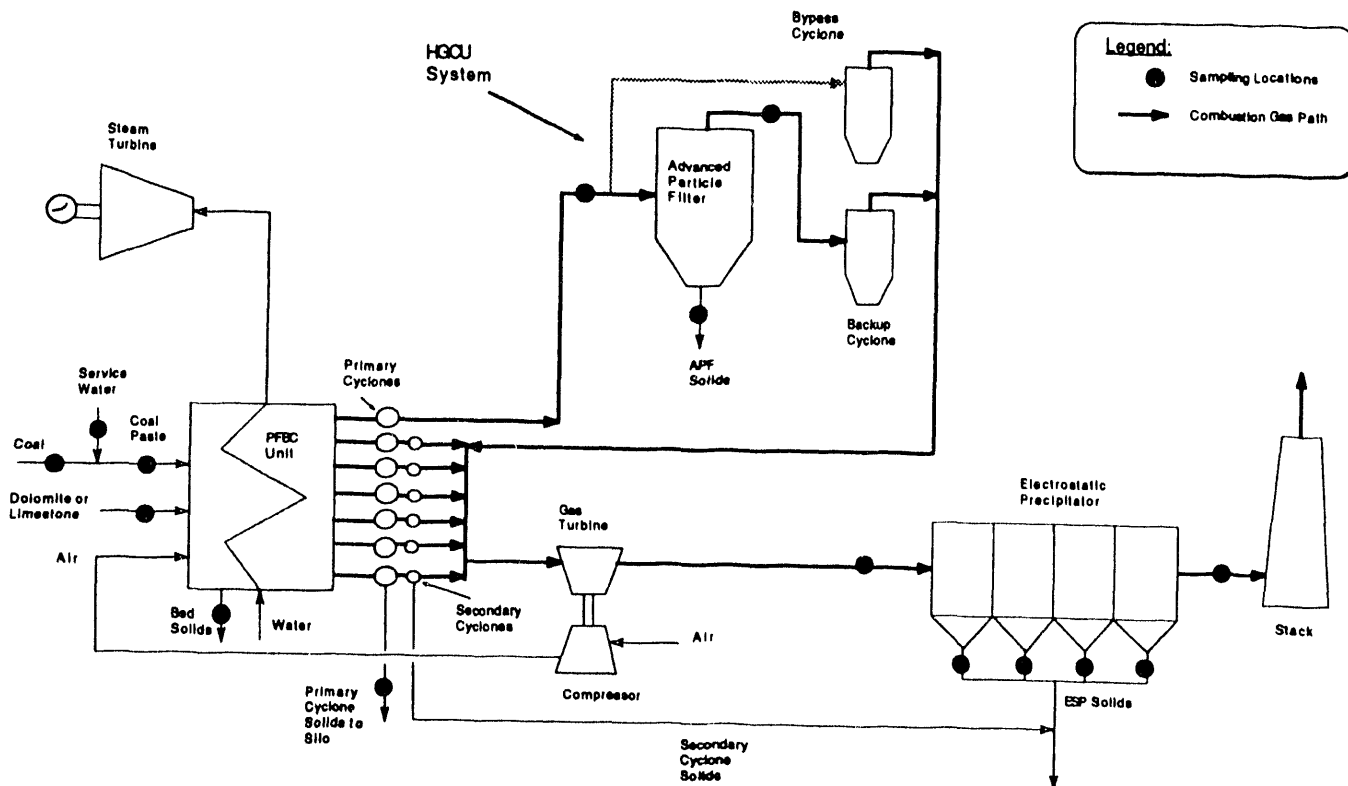


Figure 1. Plant Tidd Process Flow Diagram

The pressurized fluidized bed combustor at Tidd Plant provides a unique opportunity to collect comparable data with the DOE and EPRI studies. A demonstration-scale hot gas clean-up (HGCU) system presents an exceptional occasion not only to evaluate collection of HAPs by the HGCU, but to compare the performance of the HGCU to an electrostatic precipitator (ESP).

PROJECT DESCRIPTION

Twelve sampling locations throughout Tidd PFBC plant were selected to characterize the HAPs in the plant cycle. Sampling was conducted at the input and output of the combustor, before and after the HGCU and before and after the ESP. (See Figure 1).

Seven solid process streams were sampled including coal and sorbent to the PFBC unit and ash from the PFBC bed and ash collection devices. Service water which is mixed with the coal to make coal paste was the only liquid process stream sampled. The four gas stream samples collected were the inlets and outlets of the HGCU and ESP (See Table 1).

Gas Streams Sampling

Each of the gas streams were sampled and will be analyzed for metals, anions, ammonia, cyanide, formaldehyde, volatile organics, semivolatile organics, dioxins/furans, and particulate loading (See Tables 2-1 thru 2-3 and Tables 3-1 thru 3-3). Particulate size

Table 1

Samples To Be Collected at Plant Tidd

Process Stream	Sample Type	Sampling Location
Coal ^a	Solid	Automatic sampler on feed belt to crusher.
Coal Paste	Solid	Paddle belt feeder to storage tank.
Sorbent (Limestone or Dolomite)	Solid	Automatic sampler on east sorbent injector.
Bed Ash	Solid	Entrance to ash storage silo.
ESP Ash	Solid	ESP hopper No. 11 (Nos. 12, 13 and 14 if available).
Primary Cyclone Ash	Solid	Automatic samplers on ash storage silo.
APF Ash	Solid	Sampled upon loading into disposal trucks.
Service Water	Liquid	Tap on service water header.
APF Inlet	Gas	Single 4-inch-diameter port on APF inlet duct.
APF Outlet	Gas	Single 4-inch-diameter port on APF outlet duct.
ESP Inlet	Gas	Five 4-inch-diameter ports on ESP inlet duct.
ESP Outlet	Gas	Two 4-inch-diameter ports on ESP outlet duct.

^a Raw coal samples held for possible analysis pending data quality assessment of coal paste results.

distribution was conducted at the ESP inlet and outlet. All solid and liquid stream samples were collected at the appropriate times to account for residence times within the system so the solid and liquid samples will be representative of gas sampling periods.

One of the most challenging aspects of this program was the gas stream sampling around the advanced particle filter (APF) of the HGCU system. The system operates at approximately 1550°F and 185 psig. The high temperature and pressure at the HGCU system require that a fixed sampling probe be used for gas sampling in the APF inlet and outlet. A schematic of the fixed probe sampling system designed and employed at the APF is shown in Figure 2. An Incoloy 800 tube (1/2" O.D.) serves as the sampling probe and nozzle. This sample probe is contained in a 315 stainless

steel (SS) 4" diameter tube. Cooling air is supplied to the large tube to accomplish cooling of the gas sample from 1500°F to a temperature range of 800-600°F. A flow orifice and sample control valve downstream of the filter are used to control isokinetic sample rates.

RESULTS

Throughout the sampling period, the PFBC unit was very stable and provided steady-state conditions while sampling was conducted. All samples enunciated in Radian Corporation's sampling plan were collected and only minor problems were encountered. Isokinetic sampling was achieved for the samples taken around the ESP and HGCU systems and the samples were also reproducible. Sampling periods for the ESP and APF were 6 to 8 hours to assure sufficient sample was collected for

Table 2-1
Field Sampling Requirements for Gas Streams

Analysis	ESP Inlet	ESP Outlet	APF Inlet	APF Outlet	Field Blanks ^a	Media Blanks ^b	PE Audit Samples
Particulate Loading	3	3	3	3	2	1	1
Metals ^c	3	3	3	3	2	1	1
Anions ^c	3	3	3	3	2	1	1
Ammonia/Cyanide ^d	3	3	3	3	2	1	1
Formaldehyde ^d	3	3	3	3	2	1	—
Volatile Organics ^d	6 ^e	6 ^e	6 ^e	6 ^e	12 ^f	1	—
Semivolatile Organics ^c	3	3	3	3	2	1	—
Dioxins/Furans ^c	3	3	3	3	2	1	—
Particle Size Distribution	3	3	—	—	—	1	—
Hexavalent Chromium ^g	—	3	—	—	1	1	1

- ^a One field blank each is collected at the ESP inlet and APF inlet to assess impact of sample handling at these two locations.
^b Media blanks refer to prepared reagents for impinger solutions, blank VOST tubes, XAD resin cartridges, and blank filters.
^c Both particulate and vapor phases analyzed, separately.
^d Vapor phase analysis only.
^e Two 20 L samples collected per run.
^f One field blank collected per location per run.
^g Particulate and vapor phases combined for single analysis.

Table 2-2
Field Sampling Requirements for Coal, Sorbent, and Service Water

Analysis	Raw Coal	Coal Paste			Sorbent (Dolomite)			Service Water		
	Field Samples	Field Samples	Field Duplicates	PE Audit Samples	Field Samples	Field Duplicates	PE Audit Samples	Field Samples	Field Duplicates	PE Audit Samples
Ultimate/Proximate/HHV	1 ^a	3	1	1	—	—	—	—	—	—
Metals	1 ^a	3	1	1	3	1	1	3	1	1
Anions	1 ^a	3	1	1	3	1	1	3	1	1
Radionuclides	1 ^a	3	1	—	—	—	—	—	—	—
% Moisture	1 ^a	3	1	—	3	1	—	—	—	—

^a Raw coal samples held for possible analysis pending data quality assessment of coal past results.

Table 2-3
Field Sampling Requirements for Ash Samples

Analysis	Bed Ash		Primary Cyclone Ash		ESP Ash (4 Hoppers)		APF Ash		QC Audit Samples
	Field Samples	Field Duplicates	Field Samples	Field Duplicates	Field Samples	Field Duplicates	Field Samples	Field Duplicates	
Metals	3	1	3	1	3 ^a	1	3	1	1
Anions	3	1	3	1	3 ^a	1	3	1	1
Radionuclides	3	1	3	1	3 ^a	1	3	1	—
Carbon	3	1	3	1	3 ^a	1	3	1	—
Semivolatile Organics	3	1	3	1	3 ^a	1	3	1	—
Dioxins/Furans	—	—	3	1	3 ^a	1	3	1	—
Particle Size Distribution	—	—	—	—	12 ^b	4	—	—	—

**Table 3-1
Analyte List for Inorganic Parameters**

Trace Elements	Major Elements
Antimony ^a	Aluminum
Arsenic ^a	Calcium
Barium ^a	Iron
Beryllium ^a	Magnesium
Boron	Potassium
Cadmium ^a	Sodium
Hexavalent Chromium ^b	Titanium
Chromium, total ^a	Ultimate/Proximate Parameters
Cobalt ^a	Carbon
Copper ^a	Hydrogen
Lead ^a	Nitrogen
Manganese ^a	Sulfur
Mercury	Ash
Molybdenum ^a	Volatile Matter
Nickel ^a	Fixed Carbon
Selenium ^a	
Silver	
Vanadium ^a	
IONIC SPECIES	
Chloride (Cl)	
Fluoride (F)	
Phosphates (as Total P)	
Sulfates (SO ₄ ⁻²)	
Ammonia	
Cyanide	

Table 3-2
Analyte List for Organic Parameters

Volatile Organics ^a (Method 8240)	Semivolatile Organics (Method 8270/CARB 429 ^b)	
Benzene	Acenaphthene ^b	2,4-Dimethylphenol
Bromoform	Acenaphthylene ^b	Dimethylphthalate
Carbon Disulfide	Acetophenone	4,6-Dinitro-2-methylphenol
Carbon Tetrachloride	4-Aminobiphenyl	2,4-Dinitrophenol
Chlorobenzene	Aniline	2,4-Dinitrotoluene
Chloroform	Anthracene ^b	2,6-Dinitrotoluene
1,4-Dichlorobenzene	Benzidine	bis(2-Ethylhexyl)phthalate
cis-1,3-Dichloropropene	Benzo(a)anthracene ^b	Fluoranthene ^b
trans-1,3-Dichloropropene	Benzo(a)pyrene ^b	Fluorene ^b
Ethyl Benzene	Benzo(b)fluoranthene ^b	Hexachlorobenzene
Ethyl Chloride (Chloroethane)	Benzo(g,h,i)perylene ^b	Hexachlorobutadiene
Ethylene Dichloride (1,2-Dichloroethane)	Benzo(k)fluoranthene ^b	Hexachlorocyclopentadiene
Ethylidene Dichloride (1,1-Dichloroethane)	Benzoic Acid	Hexachloroethane
Methyl Bromide (Bromomethane)	Benzyl Alcohol	Indeno(1,2,3-cd)pyrene ^b
Methyl Chloride (Chloromethane)	4-Bromophenyl Phenyl Ether	Isophorone
Methyl Chloroform (1,1,1-Trichloroethane)	Butylbenzylphthalate	2-Methylnaphthalene
Methyl Ethyl Ketone (2-Butanone)	4-Chloro-3-Methylphenol	2-Methylphenol (o-cresol)
Methylene Chloride (Dichloromethane)	p-Chloroaniline	4-Methylphenol (p-cresol)
Propylene Dichloride (1,2-Dichloropropane)	bis(2-Chloroethoxy)methane	N-Nitrosodimethylamine
Styrene	bis(2-Chloroethyl)ether	N-Nitrosodiphenylamine
1,1,2,2-Tetrachloroethane	bis(2-Chloroisopropyl)ether	N-Nitrosopropylamine
Tetrachloroethene	2-Chloronaphthalene	Naphthalene ^b
Toluene	2-Chlorophenol	2-Nitroaniline
1,1,2-Trichloroethane	4-Chlorophenyl Phenyl Ether	3-Nitroaniline
Trichloroethene	Chrysene ^b	4-Nitroaniline
Vinyl Acetate	Di-n-octylphthalate	Nitrobenzene
Vinyl Chloride	Dibenz(a,h)anthracene ^b	2-Nitrophenol
Vinylidene Chloride (1,1-Dichloroethene)	Dibenzofuran	4-Nitrophenol
m,p-Xylene	Dibutylphthalate	Pentachloronitrobenzene
o-Xylene	1,2-Dichlorobenzene	Pentachlorophenol
	1,3-Dichlorobenzene	Phenanthrene ^b
	1,4-Dichlorobenzene	Phenol
	3,3'-Dichlorobenzidine	Pyrene ^b
	2,4-Dichlorophenol	1,2,4-Trichlorobenzene
	Diethylphthalate	2,4,5-Trichlorophenol
	p-Dimethylaminoazobenzene	2,4,6-Trichlorophenol

^a These are the volatile organic compounds detected by VOST (Method 8240) that are listed in the Clean Air Act list of hazardous air pollutants.

^b These semivolatile organic compounds will be analyzed in the gas samples by CARB Method 429 using high resolution GC/MS.

Table 3-3
List of Radionuclides

Gamma Emitters
Actinium-228 @ 338 KeV
Actinium-228 @ 911 KeV
Actinium-228 @ 968 KeV
Bismuth-212 @ 727 KeV
Bismuth-214 @ 609.4 KeV
Bismuth-214 @ 1120.4 KeV
Bismuth-214 @ 1764.7 KeV
Lead-210 @ 46 KeV
Lead-212 @ 238 KeV
Lead-214 @ 295.2 KeV
Lead-214 @ 352.0 KeV
Potassium-40 @ 1460 KeV
Radium-226 @ 186.0 KeV
Thallium-208 @ 583 KeV
Thallium-208 @ 860 KeV
Thorium-234 @ 63.3 KeV
Thorium-234 @ 92.6 KeV
Uranium-235 @ 143 KeV

analysis. Preliminary indications are that particulate collection efficiency of the APF is over 99.9%. An interesting observation of the APF sampling shows some removal of SO₂ across the APF. Inlet sampling at the APF required some adjustment to the sampling train. Higher than expected particulate loading required an additional alundum filter and a fiber filter to be added to the sampling train to assure full collection of the particulate and prevent contamination of other non-particulate parameters.

Analysis of the samples collected during this project is proceeding throughout the summer. The first draft report is expected by September 1.

FUTURE WORK

No additional HAP sampling of this nature is planned at PFBC.

REFERENCES

1. Sampling and Analysis Plan for Hazardous Air Pollutants at Tidd PFBC Demonstration Plant, 1994, Radian Corporation, Austin, Tx, DCN 93-633-021-01, RCN 633-021-01-01.

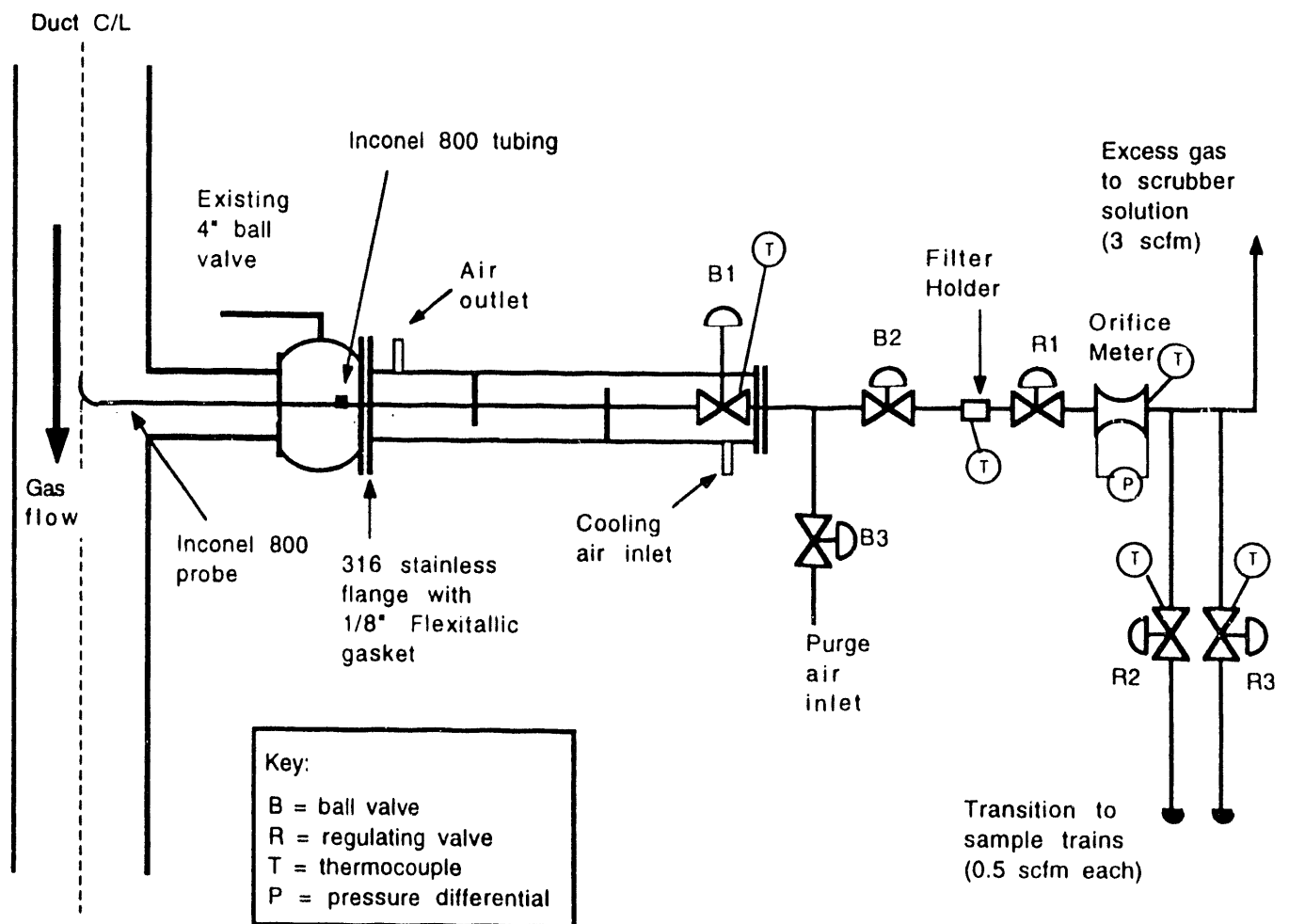


Figure 2. APF High Pressure Sampling System

INTRODUCTION AND BACKGROUND

Behavior of coal contaminants toward potentially "very clean," highly efficient, integrated power generating systems, is becoming increasingly important from both a system's performance and endurance, as well as an environmental point of view. The overall project under this contract is entitled "TRACE ELEMENT EMISSIONS," and the goal is to investigate the fate and downstream effects of "trace" contaminant species during and after coal gasification.

The work has been performed in connection with the effects of trace elements on two advanced, coal gasifier with hot-cleanup, electric power generating technologies: viz., on Integrated Gasification Combined Cycle (IGCC) and on Integrated Gasifier Fuel Cell (IGFC) systems. A reasonably good understanding exists of the fate of major coal contaminants (i.e., sulfur, chlorine, alkali and nitrogen compounds) after coal combustion in steam-type power generating plants

with back-end cleanup. But only a limited amount of information exists concerning minor or trace contaminants and toxic species deriving from coal-gas, which may affect fuel cell and/or turbine systems. Attention is also paid to possible differences in 'toxic' emissions into the environment from these trace elements; especially in connection with integrated, substoichiometric, or mild gasification as compared to direct, high temperature, complete combustion of coal.

Thus the present study is a follow-on to several contaminant investigations at ERC (each time in cooperation with PSI-Technology Company) regarding the "Effects of Coal-derived Trace Species on Performance of Molten Carbonate Fuel Cells".¹ To implement the current study, ERC and PSIT again formed a team to respond to this research challenge with a side by side comparison of the two power conversion systems (i.e., a dual energy plant) consisting of one gasifier feeding two types of electric power generators. As shown in Figure 1, a variety of

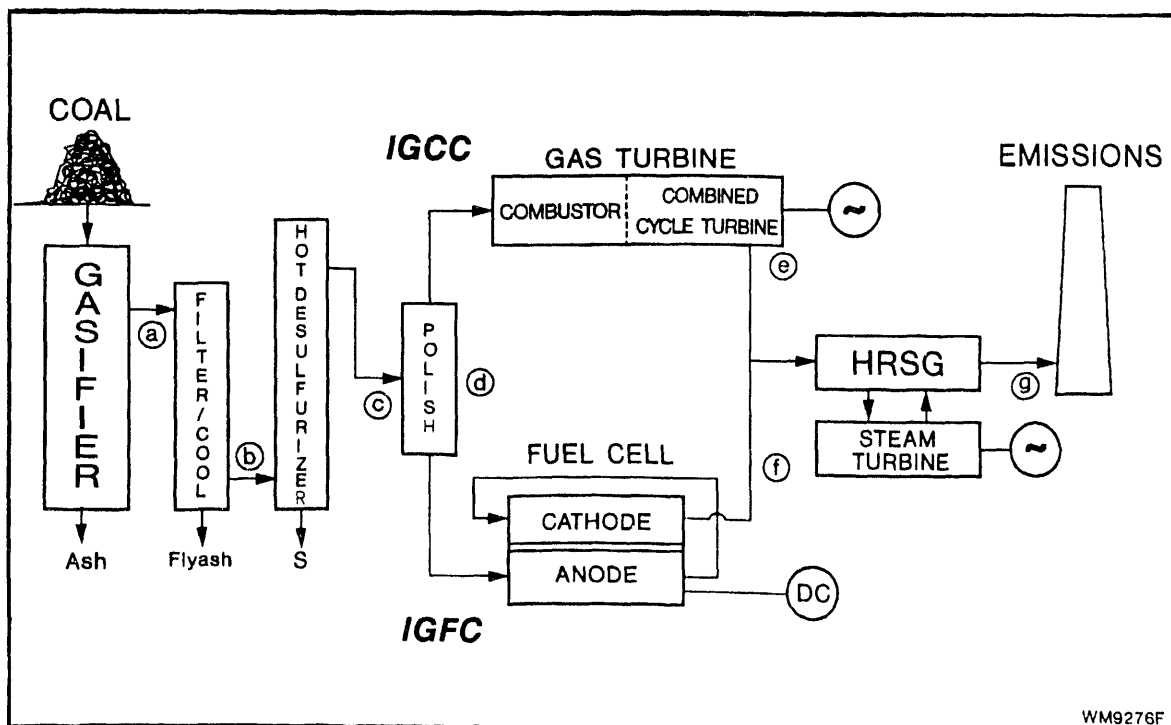


Figure 1. Integrated System Schematic For IGCC & IGFC Power Conversion Configuration for Comparison of the 2 Emerging Technologies as to Trace Element Effects.

node points between the gasifier and hot-cleanup subsystems and power convertors, were targeted as to the contaminant levels remaining at these locations. An understanding of what was required to achieve successful completion of this effort, such as technical expertise and past experience with the subject systems, as well as available equipment for simulating the relevant processes, was well represented by the two companies and the background² they possess in this area.

Selection of 5 Most Significant Trace Elements

Before the five trace elements that were to be studied in depth were selected, it was decided that a scoping experiment should determine the most significant elements being actually evaporated in typical coal gasification. Table 1 presents the information initially available in the form of an overview ranking contaminant elements by weighting factors (+) according to the

Table 1. Ranking of Coal Contaminants in Terms of Abundance, Volatility, and Toxicity
As, Se, Sb, Zn, and Pb, Were Selected as Most Significant Elements to be Studied.

ERC's Original Contaminant Ranking List showing gaseous concentrations (ppmv) in coal-gas if all species are vaporized as acid gases, halides, and metal vapors between 600° and 1000° C	UND-EERC ³ In Illinois #6 Solid Coal (wppm)		UND-EERC Highest Potential Vaporization of Elements into Coal- gas estimated from the solid coal data (ppmv)	Preliminary Ranking			
	1st sample	2nd sample		A B D U A N N C E	V O L L A I T T I Y	TOXICITY LISTS	
						EPA 17	DOE 11
<u>Majors</u>							
S 15,000	29,000	55,000	15,600	++++	+++		
Cl 500		470	120	++	+++	+	
Na 300		820	320	++	+++		
<u>Trace-metalloids</u>							
As 3.0	1.7		0.2	+	+++		+
Se 1.0	1.5		0.17	+	+++		+
Sb 0.1		< 1.0	0.07		++	+	+
<u>Trace-metals</u>							
Zn 100		65	9.0	++	+++		
Pb 3.0	3.2	6	0.26	+	++	+	+
Cd 0.2	0.14		0.011		+	+	+
Hg 0.01	0.032		0.0015		+	+	+
Cr 4	19	34	6.0	+		+	+
Ni 3	8.8	24	3.0	+		+	+
Mn 19				++			+
Be 2.3				+	?		+
<u>Additional</u>							
K		2200	512	++	+		
Co 1.5				+			+
Fe		23,000		+++			
<u>Generally Also Present</u>				Ti Al Si P Ca Mg Cu Ga Ge Mo Br			

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criteria of abundance in coal, volatility during gasification, and toxicity with respect to the environment. These early data have generally correlated quite well with subsequent gasification screening experiments, with Illinois #6 coal, that were done to definitively select arsenic (As), selenium (Se), antimony (Sb), zinc (Zn), and lead (Pb) as the five most significant elements to be studied in terms of coal-gas contaminant effects.

PROJECT DESCRIPTION

Thermochemical Calculations

The project was begun by conducting a literature search and developing the chemical properties data base for the different contaminant species that would be needed to compute site-specific thermodynamic equilibria of trace species interactions and possible condensed phase formation. Using this data base and the input from later gasification experiments which provided the types and concentrations of elements under initial gasifier exit conditions, theoretical trace species concentrations were calculated at various node points along the gas flow path from gasifier to power generating system. In this project, equilibrium modeling was conducted using a PC-based version of the SOLGASMIX computer code which minimizes the system free energy at certain locations (nodes) to predict the equilibrium phases - vapors, solids, liquids and condensed phase mixtures - as a function of local variables for complex multicomponent closed systems. In previous studies, the so-called SGM-CIS software was used to provide for calculation of 'Combined Ionic Solution' behavior as part of the SOLGASMIX program to especially account for sorption of trace species in the fuel cell's molten carbonate electrolyte.

Gasification Experiments

Experimental studies of the parameters of contaminant partitioning and distribution in coal-gas streams were begun with gasification studies performed at PSIT with Illinois #6 coal in a laminar flow, drop tube reactor, as shown in Figure 2, which was specially configured for ash classification and analysis. The unit was operated mostly by simulating conditions that occur in an oxygen-blown, Texaco gasifier, but were modified for ambient pressure application. Ash and flyash particles produced in these gasification runs were classified as to particle size distribution immediately after the reactor, and fractions separately analyzed for their elemental content by Neutron Activation Analysis (NAA) and Proton Induced X-ray Emission (PIXE).

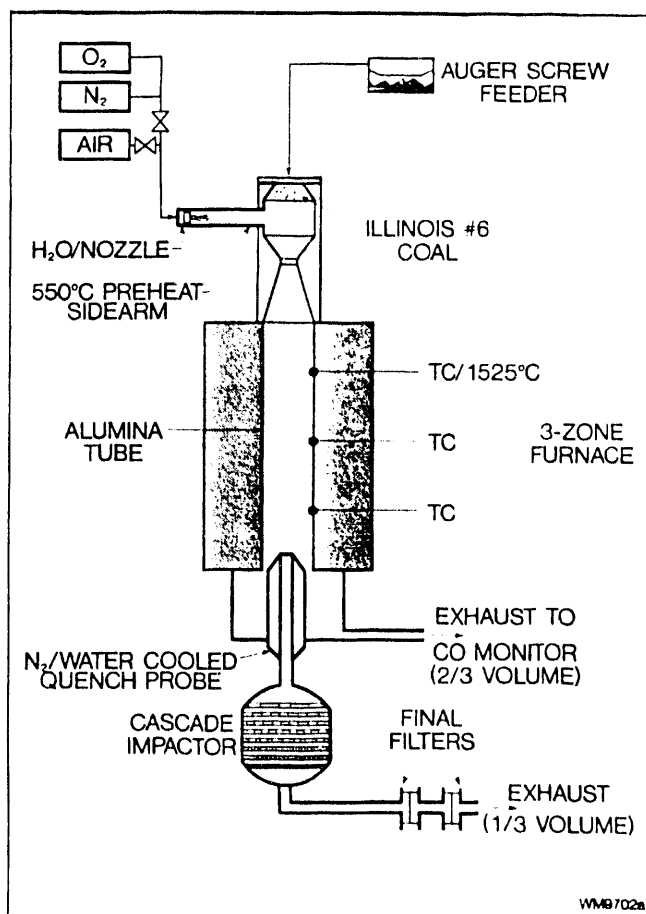


Figure 2. Laminar Flow, Drop Tube Reactor Configured for Ash Generation & Classification

Hence, volatile trace species sorption on both the ash particles produced in the reactor and trapped on the exit filters could be accurately studied for trace elemental content. Three types of gasification experiments were conducted. The first was an initial screening test to establish the five most significant volatile elements that were to be monitored in this work, and the second and third set of experiments were operated to further establish the effects of temperature, different oxygen levels, and hot ash filtration conditions on trace element partitioning.

Thermogravimetric Experiments

Numerous experiments to investigate desulfurization sorbents for their additional ability to also remove the 5 selected trace contaminants have been performed at ERC both in the past with

early types of Zn-based sorbents (ZnO and ZnFe₂O₄) and now with the latest most promising zinc titanate sorbent (ZT-4). In all these experiments there has been a concern that generically all zinc compounds, even though they may be made mechanically strong and regenerable, may at too high a temperature be thermodynamically unstable in reducing environment and eventually lose their active zinc constituent. These studies are now being further pursued in a Cahn, TG-131, thermogravimetric apparatus as shown in Figure 3. Studies of equilibrium sorption of the five most significant elements and their interaction species on ZT-4 are currently being performed at 500°C.

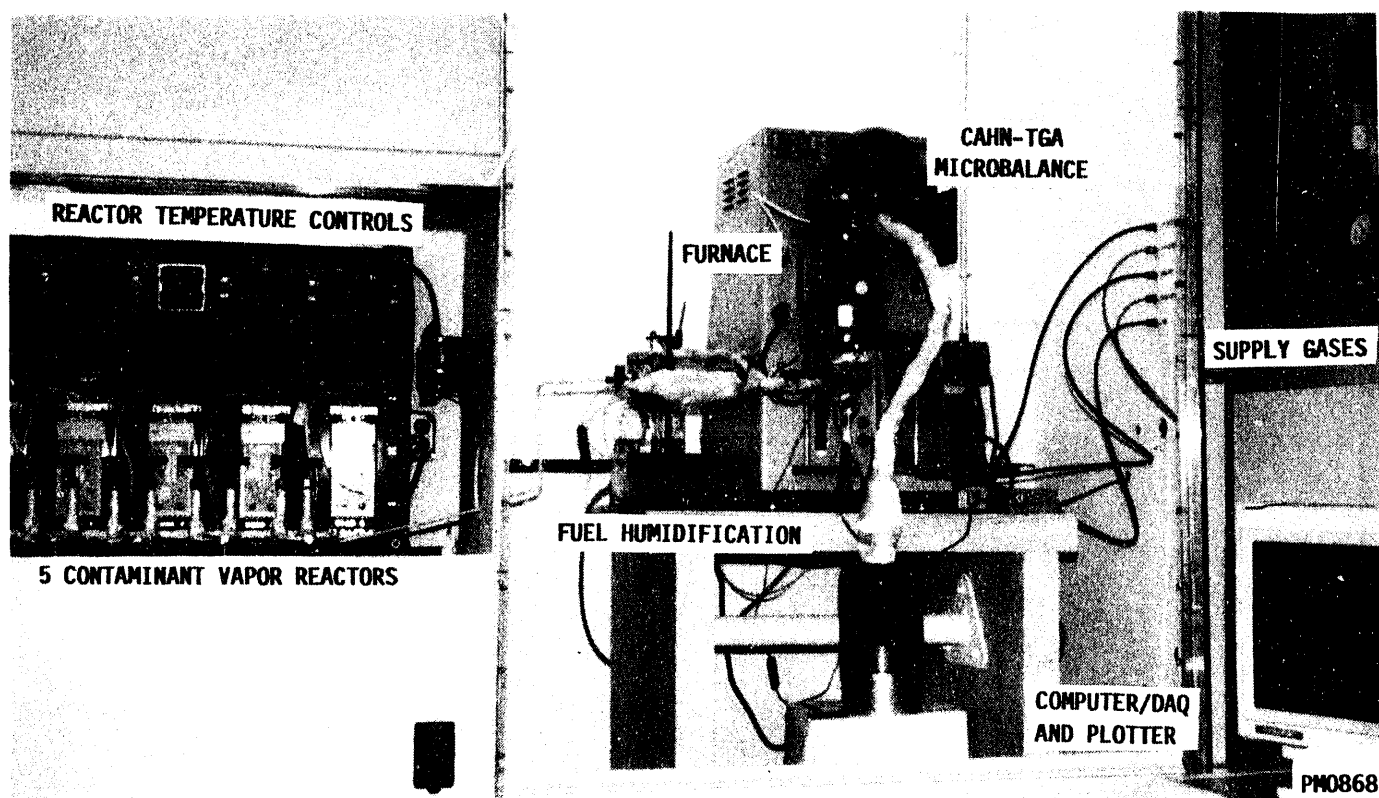


Figure 3. Thermogravimetric (TGA) Sorption Analysis Facility
Combinations of 5 Trace Elements Simultaneously, Plus H₂S and HCl, can be Handled.

Trace Element Capture Experiments

Prior work at PSIT has shown that aluminosilicates (perhaps as alkaline earth compounds) can react with several of the selected trace metals and metalloids at very high temperature (i.e., post-combustion) and in the presence of HCl and/or SO₂. The effectiveness of these sorbents is now being evaluated under conditions relevant to gasifier fuel conditions (i.e., in a strongly reducing environment) to be able to recommend useful, pre-combustion, control strategies. Trace species capture experiments with the five contaminants to be investigated are currently being performed by studying a number

of different materials in PSI's Trace Capture Reactor as shown in Figure 4. Low concentrations of trace contaminants are generated in this equipment in simulated coal-gas flow and immediately afterwards tested for absorption on various sorbents.

RESULTS & DATA

Thermodynamic Analysis

Because of the large variations in temperature, pressure, and gas composition throughout the IGCC and IGFC systems, the actual experimental determination of different amounts of each trace element, either neat or as binary interaction compounds, in gaseous or condensed form at the different node points, would have been prohibitively expensive. Therefore, as was also done in previous fuel cell studies, we have again resorted to thermochemical computation methods before performing the selective experiments representing an actual situation. Effects of the different variables on the partitioning of trace species among the different phases, including sorbent materials and other equipment components, can be quickly determined if the basic free energy data for all the species are available. For example, at 550°C and at 3 different pressures, computations were done for the high temperature incoming gaseous trace contaminant concentrations after node:b to become the lower temperature contaminant levels after node:c when the gas has been scrubbed in the presence of excess Zn₂TiO₄, as shown in Table 2. This clearly illustrates that merely by calculation very important conclusions can be quite rapidly drawn, such as the large amount of zinc that may be removed in the presence of HCl at the lower desulfurizer temperatures.

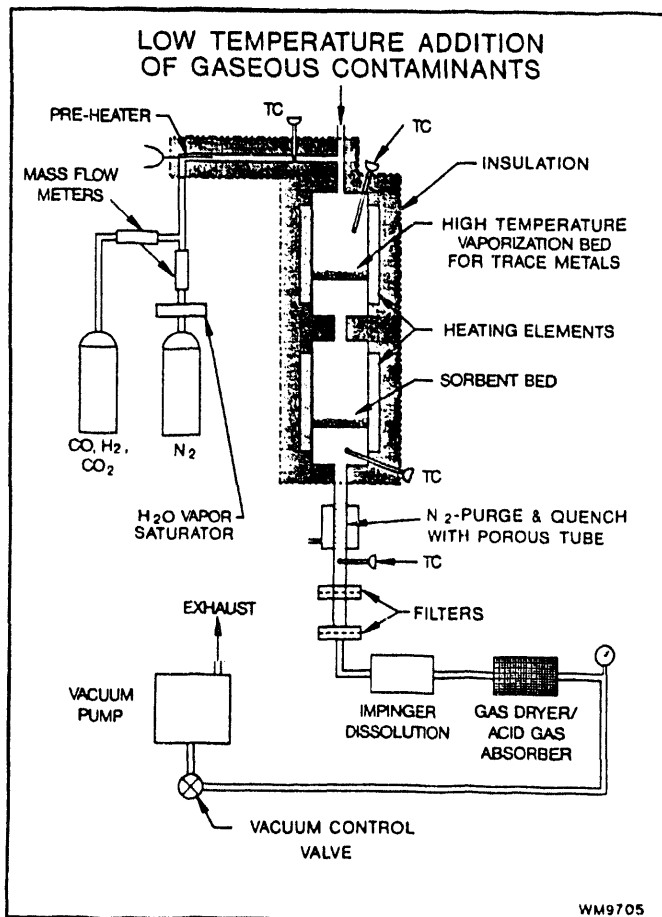


Figure 4. In-Line Element Capture Reactor
Tests of Absorption of Generated Trace Species Can Be Rapidly Performed.

Table 2. Effects of Temperature, Pressure and Presence of Zn₂TiO₄ Sorbent on Gas Equilibria
Thermodynamic Calculation Provides Important Insights into 'Fate' of Trace Element Species.

Species	@ 827° before Sorbent Addition, Node:b			@ 550° C after Sorbent Addition, Node:c		
	1 atm	3 atm	10 atm	1 atm	3 atm	10 atm
As ₂	46.5	41.6	30.8	41.2	31.5	20.8
AsH ₃	5.6	15.6	40.1	12.3	18.8	24.8
As ₄	-	-	-	6.9	12.2	17.7
Sb	6.1	3.7	2.1	-	-	-
Sb ₂	11.7	13.0	14.1	7.0	4.6	2.8
Sb ₄	-	-	-	5.7	7.5	8.9
H ₂ Se	98.5	98.9	101.8	122.5	130.7	137.2
ZnSe	-	-	-	-	-	-
Zn	984.1	985.9	1005.7	247.2	46.3	7.5
ZnCl ₂	1.0	3.1	12.1	1077.8	993.1	951.7
ZnS	-	-	-	-	-	-
Pb	9.9	9.5	8.7	10.8	4.0	0.9
PbCl	1.0	1.7	2.9	38.4	31.0	18.1
PbCl ₂	-	-	-	24.0	43.0	60.9
PbS	48.1	48.2	49.3	0.3	0.2	0.1
% increase (decrease) in gas phase zinc before/after desulfurization due to presence of bulk Zn ₂ TiO ₄				8%	(20%)	(30%)

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Gasification Testing

Knowing that inorganic contaminant elements and compound species present as vapors or as submicron-condensed particles, are extremely difficult to remove for analysis (from hot product gas) when using just cyclones, electrostatic precipitators, or even ceramic filter matrices, the approach taken was to combine several methods to provide gradual condensation, absorption, and (cold) submicron filtration to trap most of the trace element species vaporized from coal. During gasification, inorganic trace species will partition

as both vapors and as condensed phase species that become part of, or adsorbed on, the ash and flyash particles (e.g., mostly alumino-silicates) that are produced at the same time in a wide range of particle sizes. Thus, by simultaneously cooling and allowing the condensing trace species to adsorb on ash particles while also segregating the ash particles by size in a cascade impactor, it was possible to use this flyash as an analytical aid in identifying the time/temperature histories (and therefore volatility) of many of the trace element species that are of interest both qualitatively and quantitatively.

As shown in Table 3, once species were segregated on the 7 cascade impactor stages (representing d_{50} particle ranges of $10\mu\text{m}$ down to $<0.3\mu\text{m}$) and then on 2 submicron filters, it was clearly evident which elements were not present as

volatile species (e.g., Fe, Ni, Mn, Cr, etc) and which had remained volatile toward the end until being adsorbed at the lowest temperature finest filtration stages (e.g., As, Se, Sb, Zn and Pb).

Table 3. Composite NAA and PIXE (wppm) Data of Filter and Impactor Stage Ash Analysis
Combined Data from 8 Experimental Runs Have Elucidated Relative Trace Element Volatilities.

ELEMENTS	Cascade Impactor Stages, wppm				Polycarbonate Filter wppm	Final Filter Activated Carbon
	1	3	5	7		
<u>Majors</u>						
S	1900	-	-	1900	37,000	-
Br	120	2	11	-16	1240	0
Na	2700	4700	-	0	-400	0
K	7500	-	1500	66	1600	-
<u>Minors</u>						
As	2	5	-	11	28	0
Se	3	6	-	9	-51	0
Sb	-	1	-	4	12	0
<u>Trace Metals</u>						
Zn	~130	450	1300	~785	~5600	17,000
Pb	-	-	250	300	2500	-
Cd	1	2	-	1	2	-
Hg	-	1	-	1	1	2000
<u>Metals</u>						
Ni	590	-	140	95	140	-
Fe	~71,000	~61,000	19,000	~570	~1200	0
Mn	350	-	100	4.4	-	-
Cr	~765	430	280	~24	52	0

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TGA - Runs

The concern in our TGA-sorption experiments with regard to baseline stability of sorbent material before introducing the various trace element species, has led to several initial runs with H₂, 20% humidified H₂, and with simulated coal-gas of a nominal composition (i.e., 26% H₂, 38% CO, 25% H₂O, 9% CO₂). Alternating temperature ramping (50°C steps starting at 400°C) and isothermal equilibration periods of ~12 hours, were used to investigate the baseline stability of zinc titanate, as shown in Figure 5. A susceptor with titanate sorbent evenly distributed in 5 levels or pans (average of ~1.2

gram per pan), was used to follow the weight changes of the sorbent material for total run periods of up to 72 hours. It is seen that at the max. 500°C temperature, the material remains sufficiently stable to follow low level weight increases that we expect to observe in connection with trace species absorption of a number of trace elements on this sorbent. These runs are currently in progress.

Trace Element Capture Testing

Tests are in progress but insufficient data are available at this time.

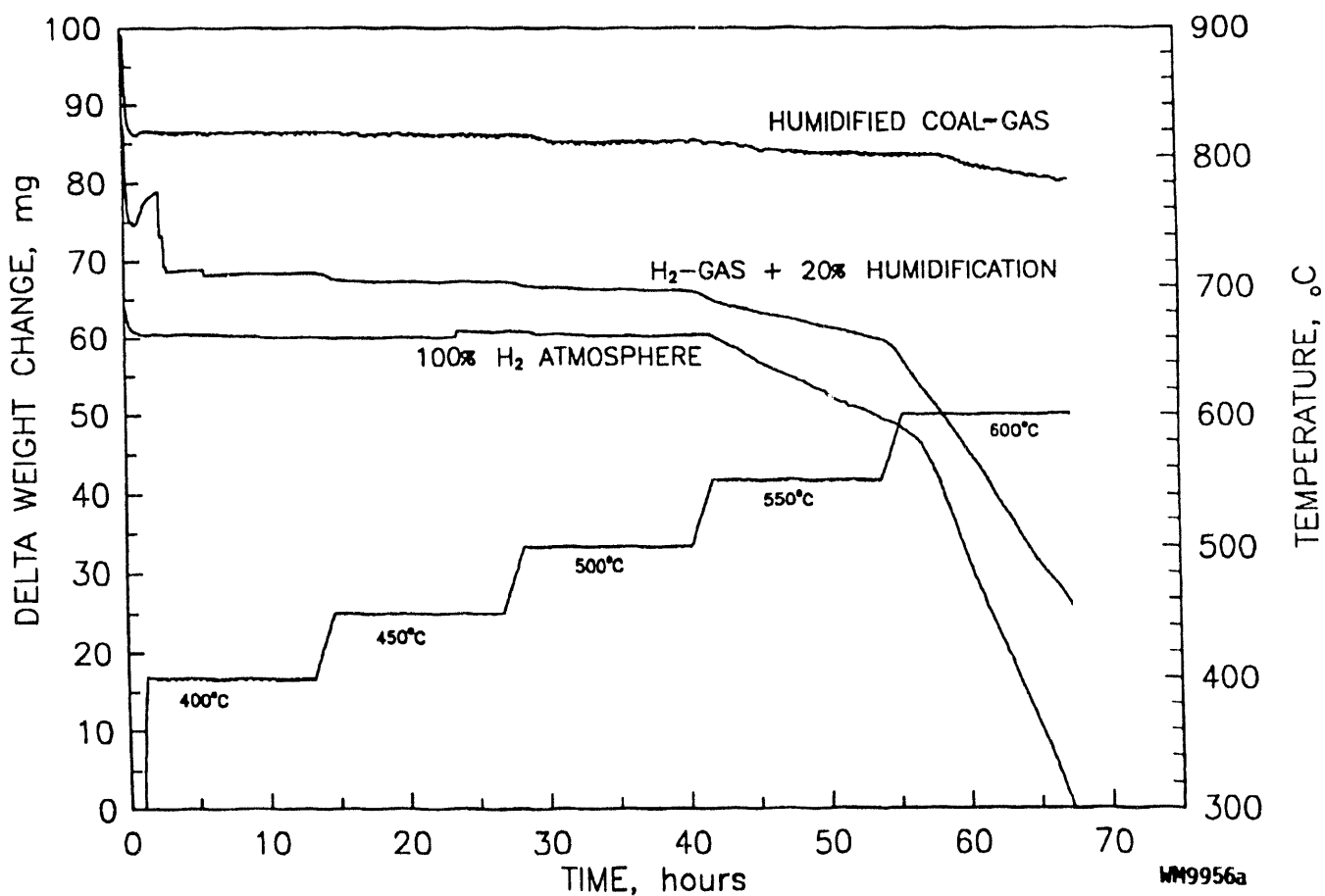


Figure 5. TGA Experimental Runs with (~6 gram) Samples of Sorbent Examination of Effects of Temperature and Humidity on Stability of Zn₂TiO₄ in Reducing Atmosphere for Trace Element Sorption Studies.

FUTURE WORK

To sum up this present investigation of the 'fate' of contaminants at various sites that are of concern to evolving integrated power systems, it is seen that the five most significant trace elements generated by coal gasification, have been identified. And also, that a pattern for their control and removal at high temperature is evolving. However, since only limited theoretical calculations were done within the scope of the current program and experimental con-firmations are also needed, there are still a number of areas where future work in a follow-on program is recommended. For example:

Thermochemical Calculations

The power of our computer research technique has become well established and together with additional modeling would further advance the general ability to quickly predict trace element behavior and effects on IGCC and IGFC systems.

Three specific areas requiring calculational effort are at: 1) *The Gasifier*. Formation of complex aluminosilicates with the 5 trace elements, and correlation with experimental partitioning data as a function of existing gasification conditions. Clearly, the ability to develop a model that better defines aluminosilicate formation from different coals, and which is gasification conditions specific, would be of great use to tailor the type of gasifier and operating conditions needed for optimum integration into power conversion systems; 2) *Hot-Gas Cleanup*. Interaction of trace elements with other than zinc titanate desulfurization sorbents should be considered. Modeling of contaminant interactions with zinc titanate sorbents using equilibrium thermochemistry has been successful. Similar calculations should now be done for other sorbents to determine the utility of a variety of likely desulfurization materials that could also be

beneficial for trace contaminant or metal vapor removal; 3) *NiO-cathode on O₂-rich side of Matrix*. Interactions of trace elements in this part of the carbonate fuel cell, after anode exit-gas is recycled (and oxidized for CO₂ recovery) and trace species become reexposed to the molten carbonate electrolyte, are still a concern that has not yet been addressed.

Gasification Experiments

In our current program, the concentration of trace elements as a function of ash particle size sorption was measured primarily for volatility determination. Only limited experiments were conducted to start assessing the effects of gasification conditions and temperature on changes in trace element volatilization. Results indicate that trace element vaporization is dependent on gasifier stoichiometric conditions, where the amount of an element vaporizing decreases with increasing partial pressure of oxygen in the system; this also increases the ash particle temperature. To explore this interaction in more detail and to determine whether gasification conditions can be optimized to improve trace element capture, a detailed study examining trace element partitioning as a function of gasification stoichiometry, pressure, and other parameters, should be considered.

Thermogravimetric Experiments

Initial equilibrium experiments of weight loss or gain should usually be considered as a preliminary test in determining a sorbent's stability and its affinity for removing low level gaseous trace species, which can then serve to confirm whatever the thermochemical calculations may have indicated. These TGA-runs can be very simply and rapidly performed, and can also be used to establish the regenerability of materials in different gas atmospheres. Such runs are currently being performed at ERC in connection with a new material and a method for trace element polishing.

Trace Element Capture Experiments

In-line experiments which can closely simulate high temperature contaminant absorption conditions, can elucidate the kinetics of immediate (post-gasification) trace element capture using a variety of materials. Studies of activated sorbents for early removal of the five significant elements are now employing this methodology. In this respect, it is also recommended to expand the test matrix to study early capture of additional elements such as chlorine, cadmium, and mercury species. Another area would be to combine activated sorbents with zinc-based, hot-gas desulfurization (in a single or dual bed reactor) and evaluate the combined effect of also removing trace elements together with sulfur.

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8b.5

Hazardous Air Pollutant Sampling for Advanced Power Systems

CONTRACT INFORMATION

Contract Number

Contractor

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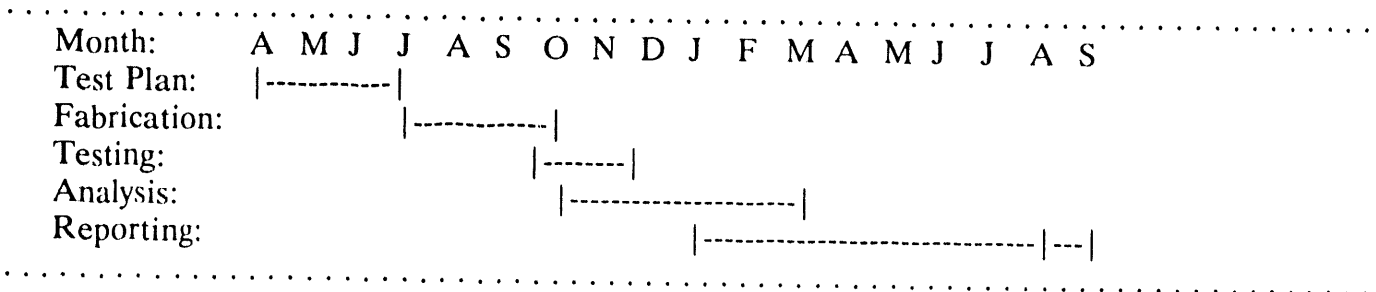
Lori Gould

Period of Performance

June 1, 1994, to September 30, 1995

Schedule Milestones

FY 1994 & 1995 Schedule



OBJECTIVES

This program will characterize an advanced power system to fulfill the following objectives:

- To quantify HAP emissions;
- To determine HAP distribution;
- To define internal control device effectiveness; and
- To characterize the hot, raw syngas.

Two additional project objectives are (1) to compile data in a relational database system to enhance its review and analysis and (2) to determine emission factors for the turbine and incinerator exhaust streams. The project will use innovative sampling techniques, very sensitive analytical techniques, and an enhanced quality assurance/quality control

program.

BACKGROUND INFORMATION

The 1990 Clean Air Act Amendments have resulted in the review of the fate of hazardous air pollutants (HAPs) within and from advanced power systems. HAP assessment has not been conducted at most of the advanced power system demonstration facilities, but efforts have been undertaken recently to conduct HAP data collection.

Both the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) have programs to address HAP data collection for conventional power systems. Radian Corporation has performed HAP measurements to support both the DOE and EPRI programs. Radian has also performed HAP measurements at the General Electric gasification pilot plant and turbine simulator located at the GE Research and Development Center in Schenectady, New York, and at the American Electric Power Tidd Plant, a 70-MW PFBC facility in Brilliant, Ohio.

Many of the sampling and analytical methods used by DOE and EPRI for conventional coal-fired power systems may not be applicable for advanced power systems because of the reducing gas conditions produced by gasification facilities (IGCC or IGFC). The purposes of this paper are (1) to review current programs under which Radian has provided advanced power system HAP assessment in association with DOE and (2) to review methods which will be useful in both conventional and special systems with reduced/fuel environments.

Emphasis will be placed on the work proposed for the IGCC system which Destec Energy Systems operates as the Louisiana Gasification Technology Inc. (LGTI) at Dow's Louisiana Division in Plaquemine, Louisiana.

PROJECT DESCRIPTION

Radian will conduct a HAP monitoring program at Destec's LGTI facility. A schematic of the system, showing sample collection points, is presented in Figure 1.

The program will include preparation of a detailed test plan for HAP determination, determination of the fate of HAPs through the process units at the facility, determination of the effectiveness of control systems at the facility, and collection of HAP data for the hot raw gas exiting the reactor to provide input data to hot gas cleanup research. The program will consist of an 18-month effort from planning through reporting.

The Destec LGTI gasifier is a slagging design, high-pressure, entrained flow system which has been operational since 1987. The unit produces 30,000 MMBtu/day of equivalent syngas while operating on 2,200 tons per day of western subbituminous coal from the Rochelle mine in Wyoming. The unit produces 169 MW equivalent net power. A second demonstration of the technology will be conducted at the Wabash River Coal Gasification Repower Project in West Terre Haute, Indiana. That system, with 262 MW net power, will be the largest single-train coal gasification combined-cycle facility in the United States.

Samples will be collected around the

following process units in the LGTI system:

- Gasifier;
- Particulate removal;
- Gas cooling;
- Acid gas removal;
- Gas turbine;
- Sulfur recovery;
- Sour water stripper;
- Incinerator; and
- Coal preparation.

Consistent with the DOE and EPRI HAP program design, three sample sets will be collected during the test program. The components of interest will include:

- **Hydrocarbons:** C₁-C₆, benzene, toluene, xylenes, aldehydes, and polynuclear aromatic hydrocarbons;
- **Sulfur species:** hydrogen sulfide, carbonyl sulfide, carbon disulfide, dimethyl sulfide, dimethyl disulfide, mercaptans, and sulfur dioxide;
- **Nitrogen species:** ammonia, cyanides, thiocyanates, and nitrogen oxides;
- **Halogen species:** hydrogen chloride and hydrogen fluoride; and
- **Trace elements:** 11 HAPs and 13 other substances.

Table 1 shows the primary differences expected between emitted streams (oxidized environments) and gasification streams (reduced environments). For example, metal oxides, primarily particles, are expected in oxidizing environments, but carbonyls, hydrides, or sulfides might be found in reducing environments. The forms of the various metal species are not

known; organometallic compounds may be present.

Radian will use U.S. EPA reference methods for most emissions streams; however, internal streams will require method modifications, in addition to alternative methods and techniques, to provide accurate data. Specific sampling and analytical issues are discussed below.

Organic Compounds

While a volatile organic sampling train (VOST) can be used for the collection of volatile organic compounds in oxidized environments, reduced sulfur species in internal streams can interfere with instrumental analyses. For the reduced environments, on-site analysis by gas chromatography (flame ionization detection) is used to conduct volatile organic compound analysis. Grab samples can be collected in Tedlar® bags or in glass or stainless steel bombs.

Sulfur Species

On-site GC analysis is also required for sulfur species; in this case, flame photometric detection is used. For some species, direct iodimetric titration is used.

Nitrogen Species

The principal modification to be made when collecting and analyzing nitrogen species from reducing environments is sulfide removal, which is critical. For example, sulfides *must* be removed immediately after collecting samples for cyanide. An acidic solution of lead nitrate or lead acetate is commonly used.

Halogens

The determination of the halogenated species HCl and HF requires no modification in approach. As in oxidized environments, the species are determined as chloride and fluoride, respectively.

Trace Elements

The collection of trace elements requires the use of charcoal (carbon) adsorption and on-line AAS in addition to Method 29, which is used for oxidized environments.

Charcoal Adsorption. Radian has found that charcoal adsorption is efficient for the collection of iron and nickel (as their carbonyls) as well as for arsenic, antimony, lead, mercury, and zinc. Specially cleaned and prepared charcoal tubes are used in series to assess capture and breakthrough; parallel trains are used to compare results by different analytical techniques.

On-Line AAS. In on-line atomic absorption spectrophotometry, a slipstream of the syngas is used as fuel in the flame of an atomic absorption spectrophotometer. Radian has applied this single-element technique for measuring arsenic, nickel, chromium, selenium, cadmium, mercury, lead, and zinc.

Hot Gas Sampling Probe

A unique feature of this program is the requirement to separate and collect particulate matter and vapor at the following conditions:

- 850–1250° F;
- 300–500 psig; and

- High particulate loading.

The sample components must be preserved for quantitative determination.

The design of the hot gas sampling probe is based on probes used by Radian for similar sampling in other projects. The sample gas passes through the probe as the gas pressure is reduced. Particulate matter is either collected or prevented from entering the probe by an in-stack filter or thimble. After passing into the probe, the collected gas is quenched with nitrogen before being directed to the sample collection/analytical device.

CURRENT STATUS

Radian has prepared a detailed test plan for the LGTI HAP monitoring study. The plan has been reviewed by Destec, DOE/PETC, DOE/METC, and EPRI. The detailed plan presents:

- Facility description;
- Approach to HAP testing;
- Methods used to collect, prepare and analyze samples;
- Quality assurance for program data;
- Process data requirements; and
- Data reduction procedures.

In addition, an important aspect of the testing is the collection of hot, raw pressurized gas (gas representative of this gasifier technology), which would be fed to a hot gas cleanup system. Characterization of this stream provides vital stream information for METC's hot gas cleanup program. Radian has prepared a design document for a hot gas probe to be used at the LGTI facility. The probe will allow collection of vaporous and particulate

samples at stream temperature and pressure.

FUTURE WORK

Testing will take place in October and November of 1994. October testing will consist of checkout and verification of the hot gas sampling system. November testing will address HAP monitoring and

sample collection of the system streams. Samples will be transported to laboratories for detailed characterization. Following data assessment and results validation, a report will be prepared for the testing. Although most of the internal streams are considered proprietary data sources by Destec, data review procedures have been defined by Destec, DOE, and EPRI to permit data transfer to those important HAP control programs of DOE and EPRI.

Table 1. Primary Differences Between Oxidized and Reduced Streams

Class	Combustion (Oxidized)	Gasification (Reduced)
Organic Compounds	Very Low	Low - High
Sulfur Species	SO ₂	H ₂ S, COS, CS ₂ , DMS, DMDS, mercaptans
Nitrogen Species	NO _x	NH ₃ , HCN
Metals	Metal Oxide (Particle)	Carbonyls? Hydrides? Sulfides?

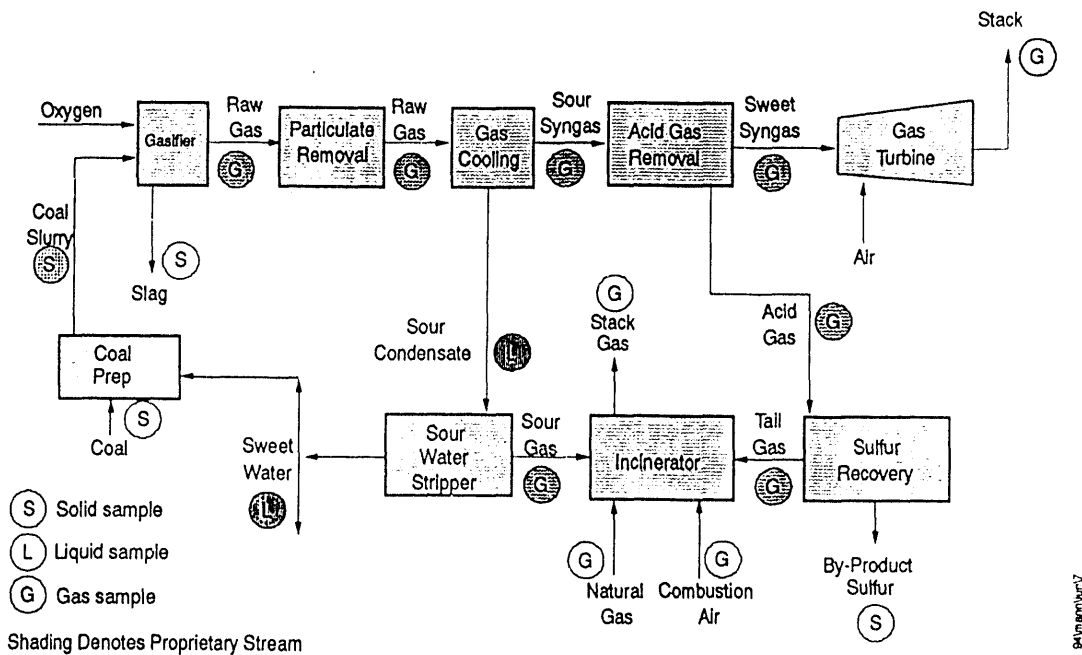


Figure 1. LGTI Gasification System with Sampling Points Shown

8b.6

Instrumentation for Trace Emission Measurements

William P. Chisholm
Morgantown Energy Technology Center

Rising concerns about the potential release of harmful elements into the environment from coal utilization have driven the development of new analytical capabilities. And recent environmental regulations, such as the Clean Air Act and Amendments, demand superior performance from new coal-based technologies as regards their pollution emission potential. In particular, a number of toxic or hazardous trace elements found in coal must be measured and controlled.

Currently available instrumentation for fossil fuel process and combustion monitoring requires sample extraction and remote analysis in a laboratory. This type of monitoring is not adequate for commercialization of many of the advanced technologies under development at METC. In particular, on-line or real-time data, though difficult to obtain, may be necessary for advanced process characterization or control. Especially challenging is the task of sampling and characterizing systems at high temperature and pressure. The inductively coupled plasma (ICP) spectrometer has the potential to perform elemental composition analysis for the purpose of continuous emissions monitoring.

The shortcomings of conventional ICP systems plumbed directly to high-temperature and high-pressure process systems have been previously discussed [1]. In brief, these systems cannot sustain a plasma in a gas stream containing a large proportion of molecular gases, they cannot be connected to hot, pressurized sample lines, and the plasma emission spectrum contains strong interfering molecular bands. The ICP system we are developing addresses all these difficulties.

To enable sampling hot, pressurized sample streams, we have developed a new torch, which is sectioned into several pieces with o-ring seals protected by a cooling fluid. The new torch may be made of an insulating ceramic capable of direct connection to a hot sample line. Our plasma support gas is a mixture of argon and helium. The addition of helium allows the torch to operate at relatively high powers, up to 10 kilowatts. With this power level, molecular band emission is inhibited and the plasma operates stably with sample gas flow rates as high as 90 cubic centimeters per second.

The simultaneous multielement detection system has previously been described in detail [1]. It comprises a battery of small monochromators equipped with 4800-groove per millimeter gratings, and a silica fiber optic bundle optical train.

In order to make the ICP system suitable for field deployment, it was made modular and mobile. The ICP torchbox, the detectors and optics, and the calibration system will be located near the point of sample extraction. The data acquisition system, controlling computer, gas cylinders, and the radio frequency power generator can be located up to 30 meters away. Therefore, the operator and the more sensitive electronics can be in a safe, protected enclosure, while the actual sampling is preformed at a restricted or exposed location.

Given the limitations of typical methods of ICP data analysis, a better way to determine elemental concentration was needed, a method that could account for the interferences and

complications sometimes present in spectra. It was decided that a back-propagation Artificial Neural Network (ANN) might be a tool useful in analyzing this data.

ANNs are computer programs inspired by, and functioning similarly to, biological neural networks. The ANN is trained on a set of ICP data generated with the calibration system, but also including the effects of flow rates, power, easily ionized elements, and spectral interferences. It can incorporate all of these to relate measured spectral intensities to elemental concentrations. Initial experiments have proved promising.

Future work with METC's on-line ICP system will include actual data acquisition from a bench-scale gasifier and further refinement of the current data acquisition and processing software. Also, a two-dimensional array detector coupled to an echelle spectrograph is being developed.

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Session 9a

Sorbents and Solid Wastes

9a.1 Development of Sorbents for High-Temperature Desulfurization in Moving-Bed Systems

CONTRACT INFORMATION

Contract Number DE-AC21-88MC25003

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METC Project Manager Daniel C. Cicero

Period of Performance September 21, 1988 to January 31, 1995

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S	
Sorbent Preparation	_____													
Bench-Scale Mods. and Testing	_____													
Bench-Scale Analysis				_____										
Topical Report*												_____		

* Task Scheduled for FY95

OBJECTIVES

The objective of the option 3 program within this contract is to develop chemically reactive and mechanically durable mixed-metal oxide sorbent formulations that are suitable for moving-bed, high-temperature, desulfurization of coal gas. One optimum formulation will be evaluated in a pressurized 50-cycle bench-scale test. Work on zinc ferrite formulations was performed under the base program (Ayala, 1991).

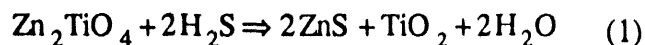
Work on zinc titanate formulations was initiated under the option 2 program (Ayala, 1993) and is continued under the present option 3 program along with testing of other mixed-metal oxides.

BACKGROUND INFORMATION

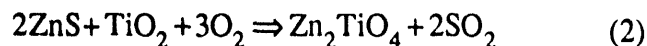
GE is developing a moving-bed, high-temperature desulfurization system for integrated gasification combined-cycle (IGCC) power systems in which zinc-based regenerable sorbents are currently being used as desulfurization

sorbents (Furman et al., 1992). In addition to zinc ferrite, zinc titanate and other novel mixed-metal oxides are being considered as sorbents, particularly for highly reducing coal gases where iron-containing sorbents can potentially undergo excessive sorbent physical degradation. A key to success in the development of high-temperature desulfurization systems is the development of a sorbent for the selected process operating conditions.

Mixed-metal oxide sorbents have been studied quite extensively in the past, including various types of zinc titanates (e.g., Zn_2TiO_4 and $Zn_2Ti_3O_8$) (Gangwal and Gupta, 1993) or as combinations of other metal oxides such as vanadium, copper, manganese, cobalt, tin, and others; see for instance (Lynch and Hepworth, 1993). During absorption from coal gases, H_2S reacts with zinc titanate according to the reaction



Similarly, during regeneration, zinc sulfide reacts with oxygen in the regenerant gas to revert back to the original oxide.

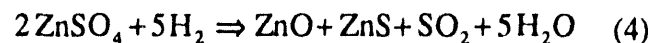


However, the regeneration zinc may lead to undesired side reactions, depending on process conditions, such as the formation of zinc sulfate according to



Zinc sulfate formation is undesired because (a) it results in significant density differences between the starting and ending solid phases that induces mechanical stresses within the pellet, and (b) the sulfate so formed during regeneration reacts with the H_2 and CO in the coal gas in

subsequent desulfurization cycles, that results in the release of SO_2 according to



Although the feasibility of removing H_2S to very low levels (e.g., < 50 ppmv) from coal gases has been shown to be viable in most studies of mixed-metal oxides, one of the major limitations for large-scale use of mixed-metal oxides is the observed weakening and physical deterioration of the pellet and spalling during repetitive use in cycles of absorption and regeneration (Ayala et al., 1993). A need exists to determine best operating conditions that minimize sulfate formation and prevent mechanical degradation.

PROJECT DESCRIPTION

Program participants are: GE Corporate Research and Development (GE-CRD, prime contractor), GE Environmental Systems, Inc., (GEESI, subcontractor), and Research Triangle Institute (RTI, subcontractor). United Catalysts, Inc. (UCI) and Phillips Petroleum Company (PPC), acting as vendors, provided the sorbent samples for testing.

Sorbents developed for moving-bed systems must comply with a minimum of chemical and mechanical durability performance characteristics in order to be considered acceptable for long-term operation. Among the desired properties, a sorbent must have:

- High chemical reactivity, as measured by the rate of sulfur absorption and the total sulfur loading on the sorbent.
- High mechanical strength, as measured by the pellet crush strength and the attrition resistance.

- Suitable pellet morphology, as given by pellet size and shape to promote good bulk flowability and reasonable porosity to increase reactivity.

RESULTS

During the current year, several zinc-based sorbent formulations were tested in the laboratory, including UCI's zinc titanate sorbents and PPC's Z-Sorb sorbent, a family of proprietary sorbent formulations. Preparation methods for UCI's zinc titanate sorbents have been described previously (Ayala, 1993). Preparation methods for Z-Sorb formulations are considered proprietary to PPC, and only analyses that describe performance in hot gas desulfurization are presented here.

Table 1 shows the physical properties of the sorbents tested in the program. Both L-4103 B2 and T-2535M are zinc titanate formulations (Zn_2TiO_4) fabricated by UCI and contain 2.0-2.5% MoO_3 as pore modifier and 3% bentonite binder. L-4103 B2 was prepared as a laboratory formulation while T-2535M2 was produced as a larger batch (6,000 lb) for use in the GE moving-bed pilot plant in Schenectady, New York.

Formulations labeled Z-Sorb A and Z-Sorb B are standard formulations sold under the trade name Z-Sorb III. The other Z-Sorb formulations were developed for GE with a larger pellet size by PPC for GE's moving-bed system. Formulation Z-Sorb C was supplied as a one-gallon batch for laboratory evaluation, while Z-Sorb E was supplied as a 12,000 lb batch for use in the GE moving-bed pilot plant. One major difference between zinc titanate and Z-Sorb sorbents is their bulk density (Table 1), with Z-Sorb being a less dense material.

Testing of the sorbent formulations and assessment of their suitability for use in moving-bed desulfurization systems was carried out by measuring single-pellet chemical reactivity of fresh and cycled sorbents in a thermogravimetric analyzer (TGA), desulfurization performance in bench-scale reactor tests, and mechanical durability and sulfate formation in the cycled pellets. Details of experimental procedures have been published previously (Ayala, 1993; Ayala et al., 1993)

Table 1. Physical Properties of Sorbent Formulations

	L-4103 B2	T-2535M2*	Z-SORB: A, B	Z-SORB C	Z-SORB E*
Pellet Length, mm	5.0	6.1	3.6-3.9	6.5, 7.3	6.4
Pellet Diam., mm	4.0	4.9	2.6-2.9	6.4	4.3
Pellet Mass, mg	200	214	27-32	280	114
Crush Strength, lb/pellet	23.2	17.1	7.6-7.1	14.9	10.2
Attrition Resistance, %	95-96.6	96-98.5	99.6-99.1	98.3	98.4
Bulk Density, lb/ft ³	107	~100	~60	~60	~60

* Tested at the GE-CRD Pilot Plant also.

Table 2. Conditions for Bench-Scale Testing of Zinc Titanate and Z-Sorb

Cycle Number:	Gas Composition	Temperature
A1-A8 (6 hr)	39% CO, 10% CO ₂ , 30% H ₂ , 20% H ₂ O, 1% H ₂ S	1000 °F
R1-R5	0.5-21% O ₂ , bal. N ₂	1000-1300 °F
R6-R8	0.5-20% O ₂ , 5% SO ₂ , bal. N ₂	1000-1300 °F
R8+1400 °F(2 hours)	20% O ₂ , 5% SO ₂ , bal. N ₂	1400 °F

A- Absorption; R-Regeneration

Fresh Sorbent Chemical Reactivity

Figure 1 shows the comparison of single-pellet chemical reactivity measured by thermogravimetric analysis (TGA) for various zinc titanate and Z-Sorb formulations. Standard conditions for TGA are 1000 °F, 3% H₂S (Ayala, 1993). The weight gained by a single pellet as a function of time is directly proportional to the amount of H₂S absorbed by the pellet according to equation (1). A strong correlation is seen between the pellet size and the relative reactivity of the pellets: the smaller the pellet size (i.e., a higher ratio of pellet surface area to volume) the higher the weight gained as a function of time, as typical of pore-diffusion controlled reactions.

A desirable rate of H₂S absorption in moving-bed desulfurization systems is a TGA chemical reactivity of 50% of theoretical sulfur loading in less than 1 hr for fresh material, an a minimum of 50% in 2 hours for extended cyclic testing. Overall, pellets with an average diameter greater than 6 mm may not be sufficiently reactive for development of large-scale systems.

Bench-Scale Testing

In order to compare side by side the relative desulfurization performance of zinc

titanate and Z-Sorb, an accelerated 8-cycle test in the bench-scale reactor system was performed. L-4103 B2 zinc titanate and Z-Sorb B were loaded in two reactors of the bench unit. The specific objective of the bench test was to determine the limits of operability for the two sorbents under identical conditions, particularly with respect to pellet spalling and mechanical deterioration due to zinc sulfate formation. Conditions for absorption and regeneration reactions are shown in Table 2. Pressure was held constant at 1 atm for both absorption and regeneration. The gas composition for absorption (cycles A1-A8) was chosen to simulate an oxygen-blown gasifier coal gas similar to that proposed for the Tampa Electric hot gas cleanup system program, except for the slightly higher H₂S and H₂O. The H₂S concentration was kept artificially high at 1% to accelerate the testing. Absorption time was held constant at 6 hours for each of the sorbents regardless of the level of H₂S leaving the reactors.

For regeneration, the test conditions were varied to examine their effect on zinc sulfate formation, reactivity and durability of the sorbents. Regenerations R1 to R5 in Table 2 were conducted without added SO₂ (while maintaining the regeneration maximum temperature below 1300 °F). Regenerations R6 through R8 were conducted adding 5% SO₂ to the regenerant gas to simulate the effect of recycled SO₂. In addition,

Table 3. Desulfurization Performance by Sorbents

	L-4103 B2 Zinc Titanate	Z-Sorb B
Max. Sulfur Capacity (lb S/100 lb fresh)	25	20
Pre-breakthrough outlet H ₂ S	<20 ppm H ₂ S	<10 ppm H ₂ S
% Total S (Abs. 5)	6.03 - 8.87	10.62 - 16.17
% of Max Sulfur Capacity	27 - 40	58-88
lb Sulfur/ft ³ of bed	7.3-10.7	7.0-10.7
% Carbon	0.14-0.18	0.14-0.20

after the R8 regeneration the bed temperature was raised to 1400 °F under 20% O₂ and 5% SO₂ to test the response of the sorbents to extremely harsh conditions of accelerated regeneration at high temperatures.

Desulfurization Performance

Table 3 shows the results of desulfurization by zinc titanate and Z-Sorb after the fifth absorption in the bench-scale reactor system. Both sorbents were exposed for six hours to simulated coal gas. Zinc titanate has a theoretical maximum sulfur capacity of 25 lb/100

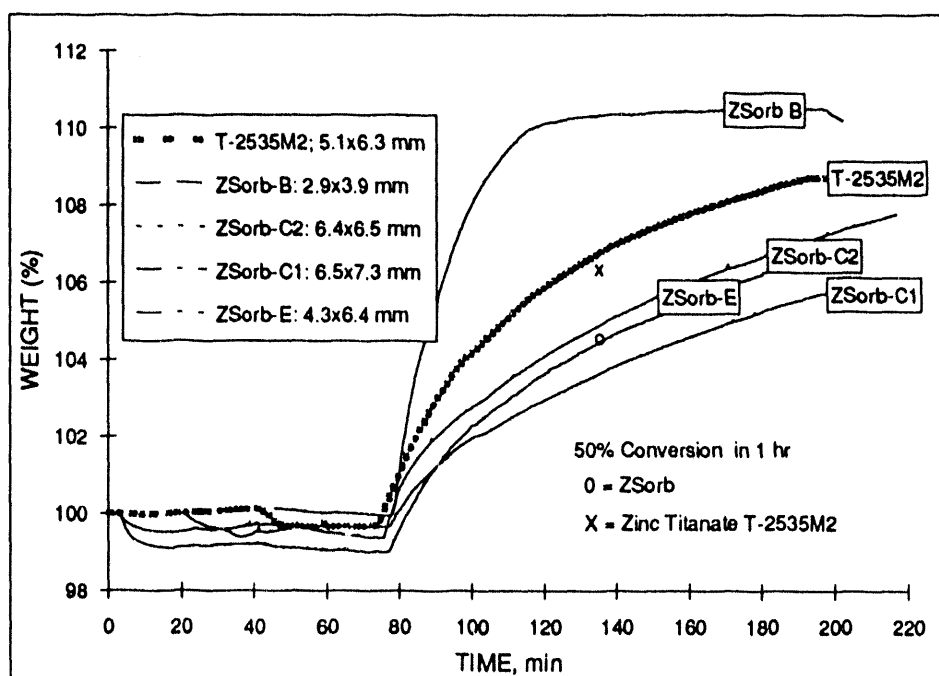


Figure 1. Comparison of fresh pellet TGA chemical reactivity

Table 4. Physical Appearance of Cycled Sorbents

	5th Reg.	8th Reg.	8th Reg. +1400F *
Zn Titanate:			
Pellet Color	white	gray	light gray /yellow
%Cracking	none	none	> 40%
Z-Sorb B:			
Pellet Color	off-white	off-white /yellow	off-white /green
%Cracking	none	none	almost none

* Held for 2 hrs

lb of fresh sorbent while Z-Sorb B has a capacity of 20 lb/100 lb of fresh sorbent. Both sorbents did an excellent job at desulfurization, with H₂S levels leaving the reactor prior to breakthrough of less than 10 ppmv for Z-Sorb B and less than 20 ppmv for zinc titanate. These levels correspond to more than 99% desulfurization (based on 1% H₂S in the inlet gas). Comparison of the total sulfur in the sorbents at the gas inlet and gas outlet locations shows that Z-Sorb B is a more reactive sorbent on a mass basis (comparing 10.6 to 16.2% sulfur in Z-Sorb versus 6 to 8.9% sulfur in zinc titanate). However, after adjusting for bulk densities of the sorbents, both sorbents had a comparable sulfur loading per unit volume of bed between 7 and 10.7 lb sulfur per ft³ of bed. This result is very important for future reactor design because it suggests that a reactor vessel designed for zinc titanate can operate with Z-Sorb under similar process conditions.

Finally, Table 3 also compares the amount of carbon deposits found in both sorbents after

the 6-hr absorption with the simulated coal gas containing 20% H₂O. There is no significant difference in the amount of carbon collected on the sorbents and it appears that cycled Z-Sorb does not catalyze the formation of carbon deposits from the Boudouard reaction ($2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$).

Mechanical Durability of Sorbent Pellets

The level of pellet mechanical deterioration during cycling was assessed, first, semi-quantitatively by measuring the fraction of pellets showing signs of hairline cracking or spalling, and then by measuring crush strength and attrition resistance of the cycled sorbents. Table 4 presents the physical appearance of the sorbents at various stages of testing and shows that zinc titanate suffered severe degree of surface cracking after the 2-hr treatment to 1400 °F (i.e., 8th. Reg + 1400 °F). Z-Sorb B, on the other hand, did not suffer any significant degree of cracking, or very minimal at worst.

The mechanical durability of the pellets was assessed quantitatively by measuring the crush strength (Figure 2) and attrition resistance (based on ASTM D 4058-81 test) (Figure 3). Again, experimental procedures have been described previously (Ayala, 1993). The qualitative observation that zinc titanate deteriorated during the heat treatment to 1400 °F was corroborated by the measurement of crush strength and attrition resistance. Crush strength decreased in L-4103 B2 zinc titanate by almost a factor of two, from 23 to 13 lb/pellet and attrition resistance decreased from 96.6% to 88.0% in the same period. Note that crush strength of the 5-mm diameter zinc titanate is not directly comparable to the strength of the 3-mm Z-Sorb B because of the difference in pellet size and the fact that the pellets, being ellipsoids in shape (i.e., cylinders or spheres with rounded edges), do not have an easily measurable contact

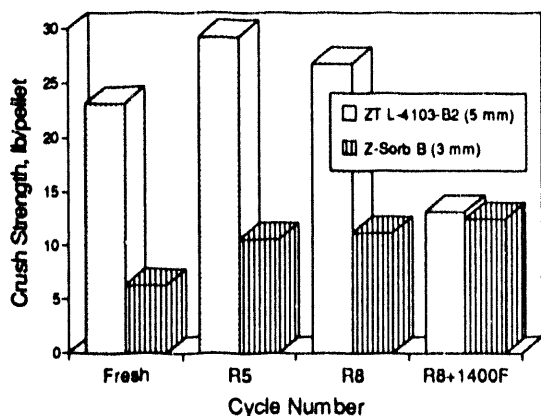


Figure 2. Comparison of Crush Strength During Bench-Scale Testing

line to scale the force per pellet to force per unit length.

Figure 4 shows the corresponding concentration of sulfate sulfur in the sorbents as a function of regeneration cycle for the two sorbents. Zinc titanate underwent mechanical deterioration when the sulfate sulfur level increased from approximately 2% after regeneration R8 to approximately 4% under the 1400 °F treatment. The sulfate sulfur level found in the sorbents correlated very well with the crush strength, attrition resistance, and physical appearance of the zinc titanate through the various

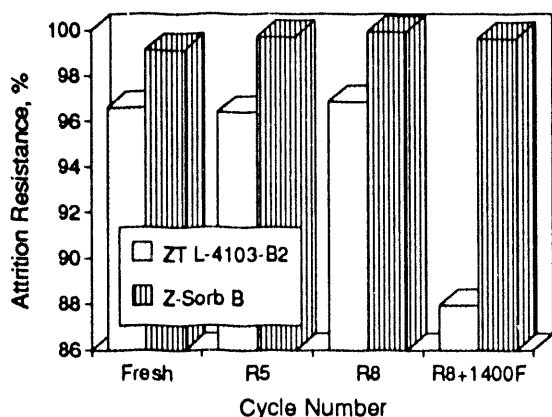


Figure 3. Comparison of Attrition Resistance During Bench-Scale Testing

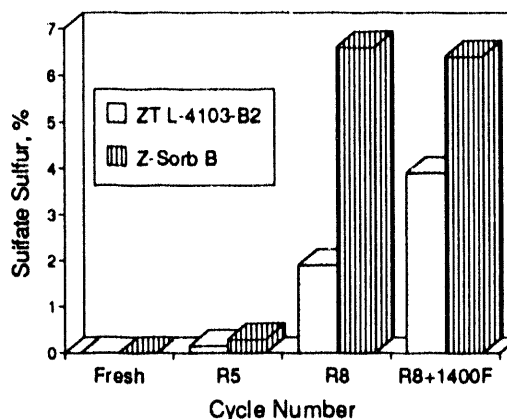


Figure 4. Comparison of Sulfate Formation During Bench-Scale Testing

cycles. On the other hand, Z-Sorb showed that despite forming larger amounts of sulfate sulfur, as high as 6%, did not develop a significant amount of measurable cracks and the sorbent did not lose mechanical strength. The superior mechanical durability of Z-Sorb B compared to L-4103 B2 zinc titanate was clear after the parallel accelerated bench testing of the two sorbents.

The following conclusions can be drawn from the atmospheric testing of L-4103 B2 zinc titanate and Z-Sorb B:

- Reactivity of Z-Sorb B towards H₂S removal from simulated coal gases is comparable to that of zinc titanate when pellets of similar size and shape are considered. The reactivity of the Z-Sorb pellets is a strong function of pellet size.
- Sulfur loading of Z-Sorb B after 6 hours of absorption is higher than that of zinc titanate on a mass basis, but very similar when presented on a bed volume basis. The difference being a result of the lower bulk density of Z-Sorb compared to zinc titanate

- Carbon formation due to the CO dissociation (Boudouard reaction) in cycled Z-Sorb was no different from that of zinc titanate.
- The mechanical durability of zinc titanate deteriorates dramatically under regeneration conditions of high SO₂/air at 1400 °F because of high rate of sulfate formation that produces internal stresses in the pellets resulting in the formation of hairline cracks and spalling.
- Both zinc titanate and Z-Sorb are suitable for operation in a moving-bed system under regeneration conditions below 1400 °F. The higher mechanical durability of Z-Sorb at 1400 °F gives a wider range of operability of the sorbent during pilot plant operation where optimum process conditions are being explored in support of the moving-bed desulfurization system for the TECO Clean Coal Technology Program.

FUTURE WORK

Having determined the conditions for proper regeneration of zinc-based materials, a long-term 50-cycle test of the best Z-Sorb formulation will be initiated in the modified bench-scale reactor system. The test will include:

- Pressurized sulfidation at 10 atm
- Pressurized regeneration up to 7 atm using recirculated gases for closer simulation of the pilot-plant regeneration recycle loop

The objective of the pressurized long-duration test would be to quantify sorbent performance over many cycles (long-term

durability) at one set of selected conditions for absorption and regeneration.

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Fluidized-Bed Sorbents

CONTRACT INFORMATION

Contract Number DE-AC21-88MC25006

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Period of Performance September 21, 1988 to November 20, 1994

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	
Scaleup of Granulation	_____												
Z-SORB Sorbent Testing		_____											
Topical Report							_____						
Life-Cycle Test with ZT-4										_____			
Large Sorbent Batch									_____				
Technology Transfer	_____												

OBJECTIVES

The objectives of this project are to identify and demonstrate methods for enhancing long-term chemical reactivity and attrition resistance of zinc oxide-based mixed metal-oxide sorbents for desulfurization of hot coal-derived gases in a high-temperature, high-pressure (HTHP) fluidized-bed

reactor. Specific objectives of this study are the following:

- Investigating various manufacturing methods to produce zinc ferrite and zinc titanate sorbents in a particle size range of 50 to 400 µm;

- Characterizing and screening the formulations for chemical reactivity, attrition resistance, and structural properties;
- Testing selected formulations in an HTHP bench-scale fluidized-bed reactor to obtain an unbiased ranking of the promising sorbents;
- Investigating the effect of various process variables, such as temperature, nature of coal gas, gas velocity, and chemical composition of the sorbent, on the performance of the sorbent;
- Life-cycle testing of the superior zinc ferrite and zinc titanate formulations under HTHP conditions to determine their long-term chemical reactivity and mechanical strength;
- Addressing various reactor design issues;
- Generating a database on sorbent properties and performance (e.g., rates of reaction, attrition rate) to be used in the design and scaleup of future commercial hot-gas desulfurization systems.
- Transferring sorbent manufacturing technology to the private sector; and
- Producing a large batch (in tonnage quantities) of the sorbent to demonstrate commercial feasibility of the preparation method.

BACKGROUND INFORMATION

Research Triangle Institute (RTI) is assisting the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) in the development of a fluidized-bed hot-gas desulfurization system employing ZnO-based mixed metal-oxide sorbents for removal of sulfurous compounds (e.g., H₂S, COS, CS₂) at high-temperature (500 to 750 °C [932 to 1,382 °F]), high-pressure (15 to 20 atm) conditions. Desulfurization of hot coal gas in a fluidized-bed reactor offers a number

of potential advantages over fixed beds. Although fixed-bed reactors are operationally simple and provide high sorbent sulfur capacity and zinc utilization and low sulfur breakthrough, they suffer from some serious problems including the need to use hot valves and poor ability to control the temperature during highly exothermic regeneration. Recently, severe spalling and decrepitation of zinc titanate sorbent pellets in fixed beds surfaced as a serious problem owing to the formation of zinc sulfate and subsequent expansion in molar volume during regeneration (Mei et al., 1993). In contrast, fluidizable zinc titanate particles became stronger with cycling and do not suffer from sulfate formation problems (Gupta and Gangwal, 1993). Additionally, fluidized-bed reactors have a number of advantages including easier control of temperature during regeneration, use of small particles leading to faster overall kinetics, and nearly continuous steady-state operation. However, a highly reactive and attrition-resistant sorbent is required, and scaleup and turndown limitations exist for fluidized-bed systems.

PROJECT DESCRIPTION

In this program, regenerable ZnO-based mixed metal-oxide sorbents are being developed and tested. These include zinc ferrite, zinc titanate and Z-SORB sorbents. The Z-SORB sorbent is a proprietary sorbent developed by Phillips Petroleum Company (PPCo).

Design and Construction of an HTHP Bench-Scale Sorbent Test Facility

During the first phase (1989) of this program, a 3-in. ID bench-scale HTHP semi-batch fluidized-bed reactor system was designed and constructed. This reactor operates in a semi-batch mode because the flow of gas phase is continuous while sorbent particles remain in the reactor. This system is capable of operation at up to 871 °C

(1,600 °F) at 20 atm. Any simulated coal gas can be generated in this system using a battery of eight mass flow controllers and three positive displacement pumps (for pumping liquid water to generate steam). This system is equipped with a state-of-the-art computer controlled data acquisition system. A series of gas chromatographs (GCs) and continuous on-line analyzer measure the concentrations of various species in the reactor exit gas such as H₂S, COS, SO₂, CO₂, H₂, CH₄, N₂, CO, O₂. A complete description of this test facility is given elsewhere (Gupta and Gangwal, 1992; 1993).

Development and Testing of Zinc Ferrite Sorbents

Earlier work in this program was focused on preparing fluidizable zinc ferrite particles in 50- to 300- μ m particle diameter range. A number of sorbent preparation techniques were investigated including spray drying, impregnation, crushing the durable extrudates and screening, and granulation.

Of these techniques investigated, granulation proved to be the most successful and a number of zinc ferrite sorbent formulations were prepared using this technique. Testing of these sorbents in the HTHP bench reactor demonstrated that these sorbents possess sulfur capacity and attrition resistance as good as or better than sorbents prepared by crushing and screening. Results of bench-scale testing of selected sorbent formulations are described elsewhere (Gupta and Gangwal, 1991).

With zinc ferrite sorbents, excessive sorbent loss was observed at a sulfidation temperature of 625 °C (1,157 °F). It is thought that attrition of the sorbent in the reactor is primarily due to chemical transformations rather than mechanical forces. Possible chemical transformations responsible for attrition are excessive reduction of ZnFe₂O₄ and iron carbide formation (Gupta and Gangwal, 1991; Gupta et al., 1992).

The applicability of zinc ferrite as a hot-gas desulfurization sorbent, therefore, is conservatively limited to below 550 °C (1,022 °F) and to moderately reducing coal gases, such as low-Btu gas from an air-blown gasifier containing at least 15 percent water vapor. Higher temperatures, as shown in the study, led to excessive sorbent weakening.

Development and Testing of Zinc Titanate Sorbents

To extend the operating temperature and desulfurize highly reducing coal gases, zinc titanate sorbent was developed for fluidized-bed reactors. Following the success of the granulation technique with zinc ferrite sorbents, it was used to prepare a series of zinc titanate formulations in the 50- to 400- μ m particle diameter range. A number of sorbent formulations prepared using the granulation technique exhibited excellent durability, attrition resistance, and sulfur capacity during multicycle testing as described in an RTI topical report to METC (Gupta and Gangwal, 1992).

Based on screening tests, a series of promising sorbent formulations were identified. Further testing of these formulations indicated that ZT-4 sorbent had the best overall performance tested in terms of attrition resistance, chemical reactivity, regenerability, sulfur capacity, and other physical and structural properties. RTI was granted a U.S. Patent on manufacture of fluidizable zinc titanate sorbent (Gupta et al., 1993).

Ten HTHP runs were carried out, each involving 10 sulfidation-regeneration cycles in the bench unit. Bench-scale testing variables included sorbent type, temperature (550 to 750 °C [1,022 to 1,382 °F]), gas type (KRW or Texaco gasifier gas), steam content of coal gas, and fluidizing gas velocity (6 to 15 cm/sec). In all 10 multicycle tests, unlike zinc ferrite sorbents, the sulfur capacity utilization for zinc titanate sorbents at breakthrough was consistently between 40 and 60

percent with very little decline with cycling. The attrition resistance of 10-cycle regenerated sorbent was significantly better than the fresh sorbent in all the runs. The detailed test results are described in an RTI topical report to METC (Gupta and Gangwal, 1992).

Reactor Design Issues

During bench-scale testing, it was demonstrated that sulfided sorbent can be completely regenerated with 1 to 5 percent O₂ in N₂. Sulfate formation was not found to occur at 760 °C (1,400 °F) and 15 atm (220 psia). The inlet temperature could be controlled to reach the required 760 °C (1,400 °F) with any of the oxygen contents tested. Also, regeneration of the zinc titanate sorbent demonstrated stoichiometric formation of an essentially O₂-free, SO₂-containing off-gas according to $ZnS + (3/2) O_2 \rightarrow ZnO + SO_2$. A quasi-steady-state generation of SO₂-containing off-gas was demonstrated indicating that a nearly constant steady-state SO₂ content in the regeneration off-gas of a commercial fluidized-bed system can be obtained. The constancy of SO₂ concentration in the regeneration tail-gas is believed to be essential for economical downstream processing to elemental sulfur or sulfuric acid.

The sulfidation reaction was found to be controlled by intrinsic chemical reaction rather than external or pore diffusion. The apparent activation energy for the sulfidation reaction ranged from 15 to 20 kcal/mol depending on the sorbent composition, indicating that significant reduction in size of the desulfurization reactor can be achieved by increasing the operating temperature. A simple single-parameter mathematical model that assumed well-mixed solid phase and plug flow of gas made a reasonable prediction of the breakthrough behavior in the semi-batch HTHP reactor. Effects of addition of HCl and NH₃ were also investigated on the sorbent performance (Gupta and Gangwal, 1992).

100-Cycle Test with ZT-4

Following the successful multicycle parametric testing of various zinc titanate formulations in the bench-scale fluidized-bed reactor, a life-cycle test consisting of 100 sulfidation-regeneration cycles was carried out to determine the long-term reactivity and mechanical strength of ZT-4 sorbent. This life-cycle test was carried out at 750 °C (1,382 °F) sulfidation temperature, 15 atm (220 psia) pressure with a medium Btu Texaco O₂-blown gasifier gas containing 11,400 ppmv of H₂S. These highly severe sulfidation conditions were purposely selected to provide possible worst-case results of long-term sorbent durability. Regeneration of the sulfided sorbent was performed using 2 to 2.5 percent O₂ in N₂ in a temperature range of 720 to 760 °C (1,328 to 1,400 °F). The amount of sorbent in the reactor was 500 g and a relatively high superficial gas velocity of 15 cm/s was used to ensure good fluidization and to more closely simulate commercial operation. This resulted in a superficial gas residence time of only about 1.24 seconds.

This life cycle test conducted under extremely severe operating conditions, and highly reducing nature of coal gas, demonstrated superior performance of the ZT-4 sorbent. The following were the pertinent findings of this life-cycle test:

- The ZT-4 sorbent consistently reduced the H₂S content of coal gas from 11,400 ppmv to <20 ppmv in a semi-batch bench-scale fluidized-bed at 750 °C (1,382 °F) and 15 atm.
- The sorbent was found to be fully regenerable, with negligible residual sulfate remaining. An oxygen concentration of 2 to 3 percent with N₂ diluent was found to result in adequate regeneration rates with no temperature control problems due to the exothermicity of the regeneration reaction.

- The sulfur capacity of the sorbent at breakthrough of 500 ppmv H₂S ranged from 12.6 wt% in Cycle 1 to 5.8 wt% in Cycle 100 with an average of about 9 percent. Most of the decline in the sulfur capacity occurred during the first 50 cycles.
- The decline in sulfur capture capacity was found to correlate with a decrease in the BET surface area, pore volume, and internal porosity. The best correlation, as expected with small particles, was with the BET surface area.
- X-ray diffraction (XRD) analysis indicated the presence of zinc silicate in the sorbent, which is believed to result from the reaction of ZnO with free SiO₂ released from the distributor material. Zinc silicate is believed to be a potential cause of some of the reactivity loss.
- Attrition resistance measurements carried out in our 3-hole airjet attrition tester indicated that the attrition resistance of the sorbent after 100 cycles of testing was significantly higher (<3% 5-h loss) over that of the fresh sorbent (about 40% 5-h loss).
- No significant sorbent loss (<2%) from the reactor was detected over 100 cycles. The total zinc loss determined by chemical analysis was negligible.

Complete details of the test conditions and experimental results are reported in RTI's recent topical report to METC (Gupta and Gangwal, 1993).

Z-SORB Sorbent Testing

PPCo developed a fluidizable version of its Z-SORB sorbent for testing in RTI's HTHP fluidized-bed bench-scale test facility as discussed previously. A life-cycle test consisting of 50 cycles of sulfidation and regeneration was carried out with PPCo's involvement and guidance

throughout the test to demonstrate long-term durability and mechanical strength. The details of this test and experimental findings are described in a separate paper entitled "Fluidization Studies Using Phillips Z-SORB Sorbent," included in this proceedings volume. A topical report jointly prepared by RTI and PPCo is currently being reviewed and will be submitted to METC by June 30, 1994.

Scaleup of the Granulation Technique

As discussed previously, the fluidizable zinc titanate sorbents (e.g., ZT-4) prepared by granulation technique exhibited superior performance during long-term testing. These sorbents were prepared in a laboratory-scale granulator of 2-L capacity. In order to prepare large sorbent batches for clean coal demonstration plants, the lab-scale granulator was replaced by a 35-L machine. A number of zinc titanate batches were prepared in this machine with the recipe used in preparation of ZT-4.

The physical and chemical properties of the sorbent designated as ZT-4L ('L' refers to the large machine) were compared with those of the original ZT-4. Table 1 shows a comparison of these properties. Figure 1 shows a comparison of the thermogravimetric analyzer (TGA) reactivities of ZT-4 and ZT-4L measured using the standard 1.5-cycle TGA test described in Gupta and Gangwal (1992). It is noteworthy in Figure 1 that at saturation the weight gain is identical for both the sorbents as would be expected owing to their exact chemical composition. The slope of the sulfidation curve in Figure 1, which represents the rate of H₂S absorption, is somewhat greater for ZT-4L compared to ZT-4, indicating a degree of superior chemical reactivity. Examination of physical property data listed in Table 1 for both the sorbents clearly indicates superior attrition resistance of ZT-4L over ZT-4. The difference in the surface areas and the pore size distribution is insignificant.

Table 1. Physical Properties of ZT-4 and ZT-4L

	ZT-4	ZT-4L
ZnO-to-TiO ₂ molar ratio	1.5	1.5
Binder content	5 wt%	5 wt%
Particle size range	100 to 300 μm	100 to 300 μm
Mean particle size ^a	174.6 μm	179.9 μm
Surface area	3.53 m ² /g	3.4 m ² /g
Mercury pore volume	0.2229 cc/g	0.1968 cc/g
Median pore diameter	2,175 Å	1,734 Å
Attrition resistance		
5-h loss	39.7%	17.0%
20-h loss	89.0%	71.0%

^aHarmonic mean.

Other structural properties such as XRD phases and chemical analyses for Zn and Ti were almost identical for both formulations. These data clearly

show that the scaleup of the manufacturing process by a factor of 17.5 was highly successful. The sorbent prepared using the 35-L machine possessed better chemical reactivity and attrition resistance. A large sorbent batch (3,000 kg) employing the 35-L machine is currently being produced.

Technology Transfer

RTI and DOE were granted a U.S. Patent (No. 5,254,516) on October 19, 1993 on the manufacture of the fluidizable zinc titanate sorbents by the granulation technique. Discussions were held with a number of U.S. catalyst manufacturers to commercialize the technology. These discussions culminated in identification of a catalyst manufacturer, Contract Materials Processing, Inc. (CMP), in Baltimore, MD. A contract was executed between RTI and CMP. CMP has extensive experience and facilities for manufacturing large quantities of custom (toll) catalysts and adsorbents for a variety of applications.

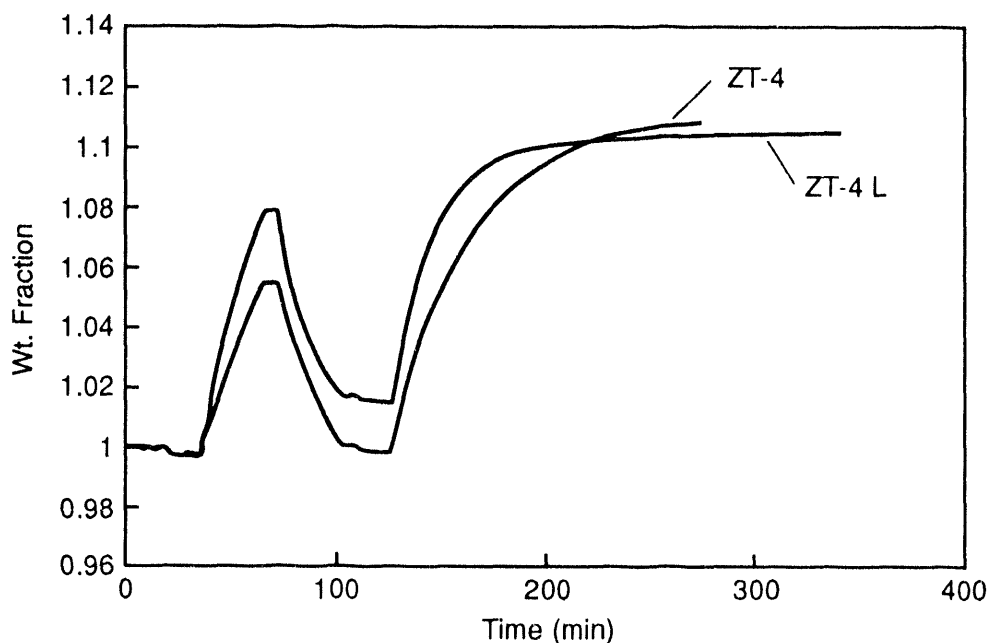


Figure 1. A Comparison of TGA Chemical Reactivities of ZT-4 and ZT-4L

Table 2 shows the cost projections for manufacture of ZT-4 sorbent by granulation independently provided by CMP. Anticipated demand figures were provided by DOE. As can be seen, the current price is \$7.91 based on a relatively small demand and, as demand increases, the price will be reduced to about \$3.20/lb. This price is close to that contemplated by DOE/METC in their projections for future IGCC plants (Schmidt, 1993).

It may be mentioned here that the ZT-4 sorbent was independently tested by the Institute of Gas Technology (IGT) under a contract with Enviropower to confirm the data obtained at RTI. IGT confirmed the RTI performance data on the sorbent.

Plans are under way to test the ZT-4 sorbent with real coal gas at DOE/METC in the fall of 1994 (Portzer and Gangwal, 1994). This test with real coal gas will demonstrate the applicability of the sorbent with other gas contaminants such as NH₃, HCl, heavy metals, and fine particles.

RTI is working closely or having discussions with a number of private companies in the United States and abroad to promote commercialization of

the zinc titanate technology. These include PPCo, Tampella Power/Enviropower, M.W. Kellogg, Texaco and a number of companies in Europe and the Far East.

Production of Large Sorbent Batches

RTI arranged a shipment of 2,000 kg of T-2551 zinc titanate sorbent from United Catalysts, Inc. (UCI) of Louisville, KY, to Enviropower in Finland for testing in the pilot plant. UCI produced this sorbent batch on a "best-efforts basis." Table 3 compares the properties of T-2551 with ZT-4L. Clearly, both the TGA reactivity and the attrition resistance of the ZT-4L sorbent is better than the T-2551 formulation. UCI did not disclose the details of the manufacturing method.

Following successful scaleup of the granulation technique and execution of a business agreement between CMP and RTI as discussed previously, commercialization of this technology depends on the success of upcoming pilot-scale demonstration tests and subsequent large-scale demonstration under the DOE Clean Coal Technology Projects. Under a Cooperative Research and Development Agreement (CRADA) between DOE/METC and Enviropower, CMP is currently manufacturing a

Table 2. Cost Projections for Manufacture of ZT-4 by Granulation^a

Year	Quantity (tonnes) ^b	Cost (\$/lb) (1994\$)
1994	3	7.91
1995	3	7.91
1996	10	7.91
1997	60	5.80
1998	60	5.80
1999	60	5.80
2000	60	3.20
2001 to 2005	60 to 180	<3.20

^a Independently provided by CMP.

^b Tonnes = 1,000 kg.

Table 3. Comparison of T-2551 and ZT-4L

	T-2551	ZT-4L
Chemical composition		
ZnO/TiO ₂ (molar)	1.5	1.5
% S-capacity at saturation ^a	14	22
Attrition resistance (%)		
5-h loss	39.4	17.0
20-h loss	67.8	71.0
Median pore diameter (Å)	8,887	1,734
Mercury pore volume (cc/g)	0.21	0.20
BET surface area (m ² /g)	0.93	3.4

^a Measured in the TGA.

3,000-kg batch of ZT-4L using the 35-L machine. Out of the 3,000 kg, 2,000 kg of the sorbent will be shipped to Enviropower in Finland for pilot-plant testing and the remaining 1,000 kg will be delivered to DOE/METC for testing in their process developmental Unit (PDU). The expected date of delivery of the sorbent is about August 15, 1994.

FUTURE WORK

Preliminary investigation of preparing zinc titanate particles by spray drying indicates that highly reactive and attrition-resistant (better than a fluid catalytic cracking [FCC] catalyst used in petroleum refineries) particles can be prepared at a price of about \$3/lb. Further development of this technique is continuing.

Currently, the 3,000-kg batch of the ZT-4 sorbent is being produced by CMP. A life-cycle test consisting of 50 cycles of sulfidation and regeneration will be performed with this sorbent to provide long-term reactivity and attrition data to Enviropower prior to their pilot-scale tests.

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