Trace Element Emissions

Semi-Annual Report October 1994 - February 1995

A. Pigeaud
H. Maru
G. Wilemski
J. Helble

February 1995

Work Performed Under Contract No.: DE-AC21-92MC29261

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

By
Energy Research Corporation
Danbury, Connecticut

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ABSTRACT

TITLE: **TRACE ELEMENT EMISSIONS**

CONTRACT: **DE-AC21-92MC29261**

PERIOD OF PERFORMANCE: 9/30/92 to 7/31/94

ABSTRACT: Many trace elements can exist in raw coal gas either in the form of metallic vapors or gaseous compounds which, besides their action on potentially "very clean" advanced power generating systems such as fuel cells and gas turbines, can also be detrimental to plant and animal life when released into the atmosphere. Therefore, volatile trace contaminants from coal which can also be toxic must be removed before they become detrimental to both power plant performance/endurance and the environment. Five trace elements were selected in this project based on: abundance in solid coal, volatility during gasification, effects on downstream systems, and toxicity to plant and animal life.

An understanding was sought in this investigation of the interactions of these five trace elements (and their high temperature species) with the different components in integrated cleanup and power generating systems, as well as the ultimate effects with respect to atmospheric emissions. Utilizing thermodynamic calculations and various experimental techniques, it was determined that a number of trace contaminants that exist in coal may be substantially removed by flyash, and after that by different sorbent systems. High temperature cleanup of contaminants by sorbents such as zinc titanate, primarily to remove sulfur, can also absorb some metallic contaminants such as cadmium and antimony. Further polishing will be required, however, to eliminate trace contaminant species incorporating the elements arsenic, selenium, lead, and mercury.

EXECUTIVE SUMMARY

The behavior of trace contaminants in potentially very clean and highly efficient, coal-based power generating systems is becoming quite important from environmental, performance, and endurance points of view. The major objective of this program under DOE sponsorship (DE-AC21-92MC29261) has been to investigate the volatilization, partitioning, and emissions of trace contaminants from coal in a gasifier/hot-cleanup/carbonate fuel cell/electric power generating system. While there is a good understanding of the fate of major coal contaminants (e.g., sulfur, chlorine, and nitrogen compounds) in steam-type power generating plants with post-combustion cleanup, only a limited amount of information has been available concerning minor or trace contaminants and toxic species generated from partial or "substoichiometric" combustion the way this occurs in integrated coal gasification power generating systems.

The effort under the present study which was jointly undertaken by ERC and PSI-Technology, consisted of thermochemical calculations, gasification experiments, thermogravimetric experiments, trace element capture experiments, and finally a consideration of various control strategies. The work and results obtained are summarized as follows.

- Thermochemical Calculations: A literature search was conducted to develop the chemical and thermodynamic properties database for different contaminant species over a range of temperatures that might be encountered in equilibrium calculations at various node points in a power plant system. Information from the experimental coal gasification task was used to provide the type and concentration of significantly volatile trace elements generated under gasifier conditions. Concentrations at the various node points along the gas flow path from gasifier to power generating system were then theoretically calculated when starting with the initial contaminant levels emanating from the gasifier. Our thermochemical computations concluded that concentrations of most volatile trace species in the fuel downstream are generally not greatly affected by temperature, but are somewhat more affected by pressure. In the case of zinc it was shown that its concentration could increase considerably if a zinc-based sorbent is utilized for sulfur removal at low pressure.
- Gasification Experiments: Experimental studies of contaminant partitioning and distribution in coal-gas streams were conducted in a variety of facilities at PSIT. These gasification studies were performed with Illinois #6 coal in a laminar flow, drop tube reactor specially configured for the study of contaminant sorption on ash while the facility is operating under approximate Texaco gasifier conditions. Flyash particles produced in these gasification experiments were partitioned and separated by particle size during the runs. The fractions were then separately analyzed over a wide elemental spectrum. About 15 trace elements were found and elemental volatility was inferred from particle size/concentration relationships in cascade impactor and submicron filter separations. Altogether three different sets of gasification experiments each consisting of numerous runs were conducted. The first set was an initial screening test to establish the five most significant volatile elements that remain substantially gaseous at high temperature. These elements became the main focus of this program.

The second and third sets of runs were operated to further establish the effects on elemental volatility due to different oxygen, temperature, and ash filtration conditions. The five most significant trace contaminant elements from these coal gasification experiments were found to be: arsenic (As), selenium (Se), zinc (Zn), lead (Pb), and antimony (Sb). Also evidence for metallic vapors of cadmium (Cd) and mercury (Hg) was detected, although at rather low concentrations.

- Thermogravimetric Experiments (TGA): Simultaneous trace element removal together with the major amounts of sulfur absorbed in a desulfurization process is a very desirable goal. Numerous experiments were performed in the past to investigate the ability of various desulfurization sorbents to also remove significant trace contaminants; this was done both with the earliest types of Zn-based sorbents and now with the latest most promising zinc titanate sorbent (ZT-4) from Research Triangle Institute. In all these experiments there has frequently been the concern that zinc compounds, even though mechanically strong as regenerable pellets or a coarse fluidizable powder, may still remain thermodynamically unstable in a strongly reducing fuel environment and eventually lose the active zinc constituent above 550°C. It was also shown in this task that only antimony (Sb @ 2 ppmv) and cadmium (Cd @ 7 ppmv) are, respectively, completely and partially removable by zinc titanate. The other elements at their low existing concentration levels cannot be removed to sub-ppm levels. Even sulfur in the form of H₂S, is not absorbed by zinc titanate at levels below 10 ppmv under 500°C stable sorbent conditions.
- Trace Element Capture Experiments: Prior work at PSIT, employing their special experimental facility constructed for this type of study, had shown that aluminosilicates even in the presence of HCl and/or SO₂ from combustion off-gases can react with several of the five above mentioned trace metals and metalloids at high temperature. The effectiveness of such sorbents has now been reevaluated under conditions relevant to coal gas fuel (i.e., in a primarily reducing environment). Trace species capture experiments to recommend future control strategies were performed. Two sorbent compositions, including two types of sorption materials (CaO and a diatomaceous earth, Celatom), at two pressures and at 650°C were studied. The conclusion was that under reducing conditions, Celatom is a rather effective polishing sorbent for As, Se, and Zn. During preliminary testing under reducing conditions at both pressures, considerable fractions of these three elements were removed by this sorbent. And, because the material is not easily water leachable based on arsenic leachability test results, the sorbent is landfill disposable.
- Strategies for Contaminant Control: Utilizing results of our thermochemical calculations and experimental measurements, it appears that with a few further developments it may be possible to assemble a system, using the current state of technology, which can accomplish complete hot-cleaning of typical coal contaminants from most hot coal gas streams. Only a very small amount of the already low-abundance Hg species may remain in the gas phase and cannot yet be efficiently removed by flyash sorption/filtration or by any of the other sorbents studied. However, indications are that Hg may possibly be absorbed by activated carbon.

CONCLUSIONS

From these thermochemical and coal gasification/sorption experiments, it can be concluded that our understanding of the volatility and fate of a number of trace contaminants generated during coal gasification has been considerably advanced. Approximate amounts and types of trace elements at different node points were established as shown in the following figure. It can be observed that Cd, Se, As, Pb, and Zn are removed to some extent by flyash sorption (node b). And, of course, the major amount of sulfur (S) and some Zn and Pb are removed by hot-gas chemisorption under pressure (node c). Further polishing by physical capture (node d) may then be needed to bring H_2S , HCl , and As down to acceptable levels to comply with the anode-side tolerance in fuel cells (also shown in the figure). Thus, final polishing strategies have been recommended which show good promise for removal of most of the significant traces of coal contamination.

APPROXIMATE CONTAMINANT REDUCTIONS DURING COAL-GAS CLEANUP:

Levels of Key Trace and Major Contaminants are Shown at Different Node Points

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1. INTRODUCTION AND BACKGROUND

The goal of this investigation was to study the fate and distribution of the volatile compounds of at least five important, coal-derived trace elements in terms of their reactive and condensable materials and possible gaseous emissions into the environment. The definition here of "trace" does not include the well-known major contaminants of sulfur and chlorine. An understanding of the behavior of the most significant trace contaminants derivable from coal will thus be developed in connection with their actions on, and emissions from, integrated coal gasifier/hot-gas cleanup systems supplying fuel for advanced electric power generation that employs either gas turbines (IGCC) or fuel cells (IGFC).

An in-depth understanding of deleterious trace element/contaminant species that may be contained in coal gas, either as metallic vapors or in volatile (molecular) compound form, will provide coal gas users, including electric utilities, with much needed information concerning component decay problems that may have to be faced. Also, the ultimate fate of coal-derived contaminants, besides their action on fuel cell and gas turbine systems, are of great interest in terms of their trace emissions into the environment which could be detrimental or toxic to plant, animal and human life. The data being developed will, therefore, significantly add to our present knowledge of: a) performance/life cycle effects in both advanced and existing power generating systems, and b) the contaminant or toxic load that could be entering the environment when employing coal gasification as a source of fuel gas.

To implement the current study, ERC and PSIT again formed a team to respond to this very important research challenge by conceptually comparing two type of power conversion systems consisting of a gasifier feeding different types of electric power generators. The project's successful completion was enhanced by the complementary abilities of the companies in terms of their past efforts, technical and computational expertise, and the equipment available for simulating individual processes in these systems.

1.1 PROJECT REQUIREMENTS

To achieve the objective of this program, our initial effort was aimed at evaluating and selecting, both theoretically and experimentally, the five most significant, potentially harmful, trace elements contained in an average coal. The major contaminants of sulfur, chloride, and alkali compounds are also present but are not the subject of this investigation. Of current concern, therefore, are the species derived from the minor and trace elements which, due to their volatile nature, may find their way into advanced power plant equipment or end up as emissions into the atmosphere. This project was set up to quantify both the form of compounds, and the overall concentration as elements present at different points in the various integrated power systems. To illustrate, Figure 1.1 schematically shows two types of integrated power conversion plants, IGCC and IGFC, simultaneously connected to the same coal-gasifier/hot-cleanup system.

The fractions of five selected trace elements volatilized in the gasifier and remaining in the gas are to be identified and tracked from coal pile through the power systems and on to possible atmospheric emissions. This will be done by a combination of chemical analyses, thermodynamic calculations, and three types of simulating experiments representing the conditions at different node points as indicated by the circled lower-case letters in the diagram.

Figure 1.1 SYSTEM SCHEMATIC FOR TRACE ELEMENT EMISSIONS FROM IGCC AND IGFC POWER GENERATION SYSTEMS:

Trace Element Species and their Concentrations at Different Node Points were Tracked from Coal Pile to Cleanup to Power Generator and to Possible Environmental Emissions

Before selecting the five most important elements to be studied in-depth, it was decided that scoping studies would first have to be done to determine the most significant trace species being evolved in a typical gasification case. The three criteria that were used for selecting these five elements are stipulated and further discussed in Section 1.6 Criteria for Selection of Five Significant Elements. Because of the ultimate contaminant emissions aspect of this project, the last of the criteria (toxicity and pollution due to contaminant elements) is directly concerned with the list of pollutants and toxic elements that are subject to the Clean Air Act Amendments of 1990, as required by the National Environmental Policy Act (NEPA). The first column in Table 1.1 shows the original ten elements and compounds that were initially investigated at ERC with regard to carbonate fuel cell tolerance. In the second column, these elements are compared to the DOE-METC list of air-toxics of concern in connection with the use of coal as a fuel, and in the third column, the elements are compared to the EPA list of industrial pollutants and toxics. There is considerable correspondence between these lists of contaminants.

Table 1.1 COMPARISON OF COAL-DERIVED TRACE CONTAMINANTS STUDIES AT ERC WITH AIR-TOXIC AND HIGH VOLUME POLLUTANT LISTS:

Depending on Emphasis, there are a Number of Contaminants that show Coincidence
Between the Different Columns Concerning Important Elements

Species Tested in Bench-Scale Carbonate Fuel Cells at (ERC)	METC Portion of Clean Air Act, List of Air Toxics (DOE)	High-Volume Industrial Toxics and Pollutants (EPA)
NH ₃ H ₂ S HCl (Major Contaminants)		HCN SO _x Chlorinated Hydrocarbons
Zn Pb AsH ₃ Cd H ₂ Se Hg Sn	Pb As Cd Se Sb Hg Be	Pb Cd Hg
<u>Constituents Present in Fuel Cells</u>		
SS (Hardware) Co (Electrodes) Ni	Cr Mn Co Ni	Cr Ni
Li ₂ CO ₃ Na ₂ CO ₃ K ₂ CO ₃ LiAlO ₂ (Electrolyte Matrix)		Ketones, Benzene, Toluene, Xylene, Aromatics

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1.2 COAL CONTAMINANTS AND IDENTIFICATION OF DATA GAPS

Coal deposits are an important source of energy in the United States. However, for coal to be widely employed, there exists the need to minimize its potential for environmental pollution. As shown in Table 1.2, both major coal contaminants (i.e., derivatives of sulfur, halide, alkali, carbon and nitrogen) and minor species derived from the inorganic constituents in coal (e.g., Zn, Pb, As, Cd, Hg, Se, Be, Cr, Mn, Sb, Co, Ni, etc.) can provide relatively volatile compounds in the form of sulfides, oxides, and halides as well as their elemental metallic vapors.

A preliminary ranking of the significance of these trace elements/compounds in terms of their presumed effect on the two advanced power systems under consideration, and on the environment, was originally done as illustrated in Table 1.2. However, this initial ranking, without a great deal of background information regarding 10 out of about 30 possible trace species, still provided a formidable list and needed to be greatly reduced, ostensibly by the use of more up-to-date experimental data. Many uncertainties also existed during the inception of the project regarding data gaps in our available files of thermodynamic constants to be used for calculating many of the possible derivative species (not just the volatile elements as such) that might form. Clearly, many complex species can be generated through interaction with each other and with the major coal contaminants of sulfur, chloride, and alkali, or also with the major ash constituents at various temperatures and pressures. Updating our files was, therefore, the beginning of the effort performed under Task 310, which will be discussed in detail in the overviews provided in Section 2.

Table 1.2 POSSIBLE RANKING OF TRACE ELEMENTS IN COAL ACCORDING TO ABUNDANCE/VOLATILITY AND POSSIBLE TOXICITY:

An Initial Comparison Listing was Compiled by ERC and PSI of the Important Coal Trace Contaminants That May Affect the Two Advanced Power Generating Systems

IMPORTANT IGFC TRACE SPECIES				IMPORTANT IGCC TRACE SPECIES			
The three highest ranked trace elements have been studied and modeled together with Cl, S, and Zn for potentially deleterious fuel cell anode effects.				The higher ranked elements together with Cl, S, and Na could be a problem for gas turbine corrosion, tolerance, and emissions into the environment.			
Element	Volatility as Vapors	@ or above	Rank	Element	Volatility as Vapors	@ or above	Rank
As	[AsH ₃ - 3 ppm]	RT-gaseous	1	As	[AsH ₃ - 3 ppm]	RT-gaseous	1
Se	[H ₂ Se - 1 ppm]	RT-gaseous	2	Hg	[Hg(v) - 10 ppb]	RT-gaseous	2
Pb	[PbSe - 1 ppm]	>600°C	3	Cr	[CrCl ₃ - 4 ppm]	>500°C	3
Mn	[MnCl ₂ - 17 ppm]	>625°C	4	Pb	[PbS - 2.6 ppm]	>625°C	4
Be	[BeCl ₂ - 2.5 ppm]	RT-gaseous	5	Se	[H ₂ Se - 1 ppm]	RT-gaseous	5
Cd	[Cd(v) - 0.2 ppm]	>150°C	6	Cd	[Cd(v) - 0.2 ppm]	>150°C	6
Sb	[SbCl ₃ - 0.1 ppm]	RT-gaseous	7	Mn	[MnCl ₂ - 17 ppm]	>626°C	7
Hg	[Hg(v) - 10 ppb]	RT-gaseous	8	Ni	[NiCl ₂ - 3 ppm]	>500°C	8
Cr	[CrCl ₃ - 4 ppm]	>550°C	9	Be	[BeCl ₂ - 2.5 ppm]	RT-gaseous	9
Ni	[NiCl ₂ - 3 ppm]	>500°C	10	Sb	[SbCl ₃ - 0.1 ppm]	RT-gaseous	10

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1.3 THERMODYNAMIC CALCULATIONS

Because of large variations in temperature, pressure and gas composition throughout IGCC and IGFC systems, the systematic experimental determination of the amount of each trace element or compound species in the gas phase appeared prohibitively expensive. As a less costly alternative, thermodynamic analysis can be used to identify the most likely vapor phase and condensed phase species at a number of points within the system. Similarly, it can be used to rapidly examine the effects of such variables as temperature, pressure, and targeted sorbent additions on the partitioning of trace element species among the different possible phases. A version of the SOLGASMIX thermodynamic computational software which had originally been developed and modified at PSIT to also include liquid **ionic** phases besides gases and solids (i.e., the so-called SGM-CIS software) was first considered as it provides for calculation of combined Conformal Ionic Solution behavior and SOLGASMIX free energy minimization. This is because liquid condensed phases are often formed during gasification, and post-gasification, by solid/gas interactions or by condensation when coal gas is being cooled and are, of course, always present in the molten carbonate fuel cell in the form of electrolyte.

Equilibrium calculations in general are best applied to ideal gas and condensed phase mixtures. While this is often a reasonable approximation for low to moderate pressure gas systems, it fails to reproduce the experimentally observed high temperature condensed phases when complex molten mixtures that are not necessarily ionized, such as silicates, sulfides, and oxides, are present. Therefore, in this project, equilibrium modeling has been employed using a simple PC-based version of just the SOLGASMIX computational code. This program similarly minimizes a system's free energy to predict the equilibrium phases - vapors, solids of invariant composition, and condensed phase mixtures - as a function of the thermodynamic variables for complex, multicomponent, closed systems. Thus, as applied to our system (Figure 1.1), and realizing that SGM-CIS will likely not do an acceptable job of predicting vaporization of elements inside the gasifier, the normal SOLGASMIX code was only employed to predict partitioning at downstream sites from the gasifier. **Experimental** measurements of trace element partitioning inside the gasifier (i.e., the location where aluminosilicate non-idealities are expected to cause the greatest excursion from ideal behavior), were used to arrive at the initial conditions for the subsequent equilibrium calculations. The SOLGASMIX program was then used to predict downstream partitioning as described in Task 310 of this report.

1.4 GASIFIER OPERATING CONDITIONS

Trace elements being vaporized in an integrated coal gasification system will always depend strongly on the gasifier and coal type that is specified. Therefore, in order to limit the complexity of our investigation, it was decided to primarily obtain data in conjunction with one bituminous coal, Illinois #6, (Table 1.3) and to simulate typical gasification conditions in the isothermal drop tube furnace at PSIT which approaches a normal, but low pressure, oxygen blown, entrained flow, Texaco type gasifier operation (Table 1.4). These conditions, therefore, provide a definite reference operation since the fate, type, and amount of many trace elements volatilized in different gasifiers are a definite function of the time/temperature/transition histories encountered within each different type of reactor.

Table 1.3 COMPOSITION OF ILLINOIS #6 COAL:

A Single, Standard, Bituminous Coal³ was used for the Experimental Work

Elemental, Water, and Ash Analysis	Wt%	ASTM Ash Analysis as oxides	Wt%
C	62.0	SiO ₂	50.6
H	4.0	Al ₂ O ₃	21.6
N	1.1	Fe ₂ O ₃	18.4
O	8.4	CaO	2.1
S	2.9	MgO	1.2
Cl	0.12	Na ₂ O	0.5
Moisture	11.7	K ₂ O	2.1
Ash (non volatiles)	9.95	SO ₃	2.2

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Table 1.4 GAS PHASE COMPOSITION AT GASIFIER EXIT:

Composition of the Major Gases (Non-equilibrium) was Based on, and Roughly Equivalent to Texaco Gasification Conditions⁴. The Significant Trace Species Present at 1 Atm.

After Node: b were Estimated from our Present Work

Major and Minor Species at Exit of Gasifier	Vol%	Trace Species	Approx. ppmv
CO	38.5	As	0.1
CO ₂	8.9	Se	0.1
CH ₄	0.7	Zn	1
H ₂	25.9	Pb	0.06
H ₂ O	25.2	Sb	0.03
H ₂ S	0.9		
HCl	0.03		

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The goal of the gasification experiments was to quantify the partitioning of trace element species between vapor and condensed phases based on Texaco-type, atmospheric pressure, coal gasification, while providing a detailed accounting of the concentrations of each trace element as a function of the ash particle sizes with which they are associated. The gasifier tests for selection of the five most important trace elements were performed in an isothermal, laminar flow, drop tube furnace as illustrated in Figure 1.2, at a wall temperature of 1525°C under atmospheric pressure, gasification conditions. The only coal sample that was used was size-segregated, 80%-200 mesh, Ill-#6 coal, packaged in Ar-atmosphere (provided to PSIT by Tom Erickson (Steve Benson's group³) at the University of North Dakota, Energy and Environmental Research Center). Additional details are provided under Task 320, describing the basis and conditions for the initial work, and the detailed data that were obtained in these and other gasification tests.

Figure 1.2 LAMINAR FLOW, DROP TUBE REACTOR CONFIGURED FOR ASH GENERATION AND CLASSIFICATION:

This PSIT Facility was Used to Determine the Most Volatile of Coal-Contaminant Species

1.5 PARTITIONING UPON INITIAL GASIFICATION

During gasification, trace inorganic species present in coal will partition as vapor and as condensed phase species that become part of, or are absorbed by, the flyash that simultaneously is produced in a wide range of particle sizes. Certain transition elements such as Fe, Cr, etc. that do not become volatile but remain with the major body of coarse ash which consists primarily of alumino-silicates, were also detected but primarily on the first or upper stages of the cascade impactor. Flyash, which forms during substoichiometric gasification of coal in a gasifier, is a complex function of coal type, mineral form, degree of association with trace elements, combustion zone and gasifier exit conditions. In short, it was this concern with the prediction, both of gasification behavior of trace elements from coals of various rank as well as the extent

of different mineral transformations that could occur during gasification, which led to the original desire to obtain better experimental values for the selection of the five most important elements on which to focus.

It is known that species present as vapors or submicron particles are almost impossible to remove from hot product gas streams with just cyclones or electrostatic precipitators, and may even be difficult to remove with ceramic filter matrices. Hence, besides the absorption/condensation of trace inorganic vapors on mineral ash and flyash not being well known, there was also the need expressed to actually identify the distribution of the various trace elements among the different particle sizes of flyash that are generated in the process of gasifying a typical coal. The flyash particle size distribution containing condensed minerals and trace elements, and the particle size dependence governing trace species vapors being absorbed by them, was determined by analysis of samples collected from the various classification levels of a Pollution Control Systems Corporation seven stage, cascade impactor. This unit was installed below the high temperature drop tube reactor as shown in Figure 1.2. Specifics concerning the analyses of the many cascade impactor collected ash samples, and the conclusions that were drawn from the data is provided under Task 320, in Section 2.

The five trace elements that were selected for in-depth study regarding their ultimate fate in downstream cleanup systems according to the three ranking principles of abundance, volatility, and toxicity, are: arsenic (As), selenium (Se), zinc (Zn), lead (Pb), and antimony (Sb). Zn, although of minimal toxicity, is of concern because of its deleterious effects on the fuel cell anode process. Cadmium (Cd) and mercury (Hg) were also detected, but their abundance and volatility are such that they appear of somewhat less concern. Deposited CdO dust, which will eventually be formed in minute quantities along the pipe walls of any integrated coal gas power generating system, is not expected to become an emissions problem. However, mercury (Hg), or oxidized mercury (HgO) vapors in coal gas, even in the absence of chloride concentrations, will remain volatile throughout an integrated system. Both ERC and PSIT are currently addressing the concept of Hg-capture, or sorption, under separate SBIR grants.

1.6 CRITERIA FOR SELECTION OF FIVE SIGNIFICANT ELEMENTS

Our approach for selecting the most important elements, and of course the associated compounds, was to give appropriate weight to the three primary characteristics of a contaminant species that would cause it to be of significant concern. These were: **Abundance** of an element in a typical average coal, **Volatility**, which also includes its reabsorption behavior on any flyash that is simultaneously produced, and **Toxicity**, which affects general pollution of the atmosphere when volatile trace contaminants are ultimately emitted into the environment. As shown in Table 1.5, the most significant trace contaminant/air toxics in coal that were originally identified as remaining very volatile or somewhat volatile at high temperature have been given various weighting factors (+) to represent their early importance in this project.

Thus, by not considering major contaminants and selecting significant elements possessing at least 4 points (+) of adverse ranking consistent with the literature on toxicity, the Clean Air Act, and our gasification experiments, it is seen that the five selected (mostly toxic) elements, indeed, have the greatest probability of being found in the hot filtered effluent from a coal gasifier.

Table 1.5 OVERVIEW OF COAL CONTAMINANTS IN TERMS OF ABUNDANCE, VOLATILITY, AND TOXICITY FOR RELATIVE RANKING:

Preliminary Parameter Shown here were the Initial Guide for the Project from Different Background Sources and Government Agency Listings of Toxic Elements

ERC's 1992 Contaminant Ranking List (†) shows the element's estimated gaseous concentrations (ppmv) in coal-gas between 600° and 1000° C	UND-EERC ³ Analysis of Illinois #6 Solid Coal (wppm)		UND-EERC Data Converted to Highest potential gaseous concentrations that may exist in coal gas (ppmv)	Preliminary Conclusions			
	1st sample	2nd sample		A B D U N C E	V T O I L L A I T Y	TOXICITY (cf. Table 1.1)	
						EPA LIST	DOE LIST
<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 Ca Cu Ga Ge Mo Br			

† estimated from Finkelman⁵ (1992), and other investigators

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1.7 FATE OF VOLATILE CONTAMINANTS DURING DESULFURIZATION

The fate of the five volatile trace contaminants in cleanup subsystems such as filtration units, turbine expander, hot-gas desulfurizer and/or polishing equipment (Figure 1.1), has been investigated. Besides using thermogravimetric TGA-measurements to determine the equilibrium sorption of trace species on desulfurizer sorbents, a good deal more information has also become available recently concerning efficiency of ceramic candle filters, the use of expansion turbines

(providing cooling) and the problems that may be inherent in zinc ferrite or other zinc containing sorbents for the hot, regenerative, desulfurization process that will be required as the primary step in coal gas cleanup. There is now a concern that zinc compounds, although initially found to be good sulfur sorbents, may generically have only limited life because of Zn-volatilization when used in too high a temperature (reducing fuel) environment. Namely, previous thermogravimetric (TGA) experiments operated at ERC with ZnO and zinc ferrite as sorbents have shown that zinc, as part of sorbent material in almost any oxidized form (i.e., typically ZnO, which has no apparent vapor pressure @ 550°C), does have a considerable vaporization tendency even at 550°C. This is because in the reducing environment of a coal gas fuel, zinc compounds can become reduced metallic Zn which at this high temperature has a partial pressure of >1000 ppm depending on the hydrogen/water ratio in the fuel and the total gas pressure. The fundamental sorption experiments that were done in this connection have employed a Cahn, TG-131, thermogravimetric apparatus as illustrated in the photograph of Figure 1.3.

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Figure 1.3 THERMOGRAVIMETRIC ANALYSIS APPARATUS AND FACILITY:
This TGA Microbalance Facility Includes Complete Instrumentation for Contaminant Blending, Coal Gas Simulation, Humidification and Data Acquisition to Obtain Equilibrium Absorption Information on Sorbents

The objective of these equilibrium measurements of desulfurizer weight change during exposure to coal gas atmosphere with and without ppm-levels of contaminants present, was to: a) investigate the activity of various sorbent materials toward other than sulfur trace species, b) establish the baseline stability of sorbent materials in hydrogen fuel-gas containing different levels of inert gas, humidity, and CO₂-content at varying temperatures and, c) test any interactions regarding sorption behavior toward minor trace elements when included with one or

more of the major coal gas contaminants such as S, Cl, and/or alkali species. The experiments that were done in this respect will be further discussed under Task 330. They have provided valuable insight into the basic reactivity not only of the volatile trace elements that are being removed, but also into the chemical stability of the zinc sorbents themselves.

1.8 EFFECTS ON IGCC AND IGFC SYSTEMS

To assess quantitatively the amount of trace species emitted in stack gases from the two integrated power systems, the inlet conditions to the power converters must first be identified and the transformations of trace element species that occur within each power system (i.e., turbine or fuel cell) must be defined. In the case of an IGCC turbine system directly connected to a gasifier, the high temperatures (above $\sim 800^{\circ}\text{C}$) and dilute concentration of the trace solids and gases entering the combustor will strongly suggest that upon actual combustion, (re)vaporization of any condensed species will occur. Hence, little interaction of volatile trace species is expected with the combustor or turbine components. It is noted, of course, that reduced sulfur (H_2S) and nitrogen (NH_3) compounds upon very high temperature combustion can form the environmental pollutants of SO_x and NO_x . However, only the condensable alkaline, halide, and sulfide species, when present in fairly large concentrations, are considered actual corrosives in turbines which will, besides reacting with the rotating components, also pass through these systems. Therefore, of the five trace species selected, the ultimate emission levels at node 'g' (if no further condensation in the HRSG occurs) will be mostly dictated by the concentrations of trace elements entering the turbine combustor after final hot-gas cleanup and polishing (e.g., at Node c or d).

For the IGFC system, however, significant interaction of the five selected trace elements is expected with the different system components. This is based on a number of recent research projects at ERC that culminated in the overall work report that was finished in 1992¹. It was found that out of the ten trace and major contaminants, as provided in Table 1.1, four showed significant interaction effects, two showed minor interactions, and the rest had no effect on the **anode** side of the carbonate fuel cell. During that initial work, four types of models were developed to predict carbonate fuel cell endurance in terms of the current/voltage decay when low tolerance species are present. However, what has not yet been studied are the reactions that occur **after** the anode exit gas is catalytically oxidized (or combusted) for recycling to the **cathode** compartment where it is needed for CO_2 conservation. A detailed summary of trace contaminant concentrations (and their interaction mechanisms) for which the molten carbonate fuel cell has low tolerance on the anode side is shown in Table 1.6.

This table, developed during several previous projects,^{1,6} shows that the trace elements and compounds to which the cell has very little tolerance (antimony was not yet tested), corresponds to the same five elements selected for our current work. Of course, the major contaminants of sulfide and chloride, which during the previous investigation were included in the effort, are currently not the focus of our study. However, these major contaminants are an important aspect of the present work because H_2S and HCl can form volatile metal salts and thus may enhance the volatility of a number of additional trace metals that then become of possible concern (e.g., Zn, Pb, Cd, Cr, Ni, etc.) which must be taken into account.

Table 1.6 EXPERIMENTAL CARBONATE FUEL CELL TOLERANCES:
Three Categories of Qualitative Tolerance Levels have been Observed for Individual Contaminants when they are Supplied to an Isothermal, 650°C Bench-Scale Carbonate Fuel Cell

CONTAMINANTS (COAL-GAS, ppm)	REACTION MECHANISM	QUALITATIVE TOLERANCES	CONCLUSIONS
NO NOTICEABLE EFFECTS			
NH ₃ (10,000)	$2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$	~ 1 v/o NH ₃	No Effects
Cd (5)	$\text{Cd} + \text{H}_2\text{O} \longrightarrow \text{CdO(s)} + \text{H}_2$	~ 30 ppm Cd	No Cell Deposits
Hg (1)	(Hg Vapor Not Reactive)	35 ppm Hg	No TGA Effects
Sn (3)	(Sn (l) Not Volatile)	(No Vapor @ 650°C)	No Cell Deposits
MINOR EFFECTS			
Zn (100)	$\text{Zn} + \text{H}_2\text{O} \longrightarrow \text{ZnO(s)} + \text{H}_2$	<10 ppm Zn	No Cell Deposits " 75% Utilization
Pb (15)	$\text{Pb} + \text{H}_2\text{Se} \longrightarrow \text{PbSe(s)} + \text{H}_2$	1.0 ppm Pb (Sat'd Vapor)	Possible Deposits With High H ₂ Se
SIGNIFICANT EFFECTS			
H ₂ S (15,000)	$x\text{H}_2\text{S} + \text{Ni} \longrightarrow \text{NiS}_x + x\text{H}_2$	<0.5 ppm H ₂ S	Recoverable Effect
HCl (500)	$2\text{HCl} + \text{K}_2\text{CO}_3 \longrightarrow 2\text{KCl(v)} + \text{H}_2\text{O/CO}_2$	<0.1 ppm HCl	Long-Term Effects
H ₂ Se (5)	$x\text{H}_2\text{Se} + \text{Ni} \longrightarrow \text{NiSe}_x + x\text{H}_2$	<0.2 ppm H ₂ Se	Recoverable Effect
As (10)	$\text{AsH}_3 + \text{Ni} \longrightarrow \text{NiAs(s)} + 3/2\text{H}_2$	<0.05 ppm As	Long-Term Effects

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1.9 CONSIDERATIONS FOR SYSTEM INTEGRATION

Although the overall strategy for reducing gaseous emissions from electric power plants using coal may be different for the case of IGCC vs. IGFC systems, the final outcome of what is emitted into the atmosphere (at Node: g) must be similar since it has to conform to the Clean Air Act mandates now being promulgated. The important point to note is that the two systems have different tolerances for both major contaminants, such as H₂S, HCl, NH₃, Na, K, etc., as well as for some of the trace elements listed in Tables 1.3 and 1.4. Regardless of these differences, which might appear to favor less stringent requirements for the IGCC system (i.e., @ Node d), it is surmised that minimal trace element cleanup of toxic emissions may still require further gas cleaning at a number of node points in either system.

Each one of the five currently studied elements are considered to be toxic to a greater or lesser extent. Hence, the need may arise for ultimate cleanup of the exhaust gases from any type of system to quite low levels of contamination, and this should occur before (i.e., Nodes c and d) rather than after the fuel gas becomes oxidized (e.g., Nodes e, f, or even g), where removal is often more difficult. In this context with regard to Node: e, it is also important to realize that several of the five selected species, besides being toxic, have decidedly metallic characteristics which upon combustion of the fuel will result in very low volatility (or fully oxidized) species being formed (e.g., ZnO, CdO, PbO₂, etc.). If such species are not removed before complete

combustion takes place, the elements may still have to be removed from hot exhaust gas by additional filtration, preferably before flowing to the HRSG unit to prevent such oxide particles from depositing on internal heat exchanger surfaces. At any rate, toxicity of such hot or cold particulate dusts on their way to the exhaust stack would mandate removal one way or another. Thus, before stack gas is exhausted at Node: g, additional cleanup and filtration will likely be required in connection with IGCC systems.

With the Carbonate Fuel Cells of an IGFC system, there are other concerns. Interactions of the five contaminants with the fuel cell electrolyte/anode components are known to be significant in comparison to turbine components. It is a simple fact that the carbonate fuel cell's long-term life (because it is such a thorough scrubbing device) is more affected by contaminant content than competing rotating equipment. Because of this intolerance, which often results in fairly rapid performance decay (Table 1.6), it will be necessary to remove the five trace species to a considerable extent before they reach the fuel cell, and this means to sub-ppm levels. However, this also means that only very minor or no further clean up treatment of IGFC exhaust gas is necessary (i.e., @ Node f or g) in order to comply with the mandates of the Clean Air Act. So, on the whole, it is apparent that developing coal gas cleanup methods for the above-mentioned systems should primarily concentrate on the Nodes: b, c, and d.

1.10 TRACE ELEMENT CAPTURE AND CONTROL STRATEGIES

Since considerable trace element volatilization can occur during gasification, it will be necessary to remove various species from the (reducing) high temperatures fuel environment well before they can interact with fuel cells, or at a later point from the oxidizing environment which exists after high temperature combustion so as to prevent emission into the atmosphere. For both systems, however, early removal has the great advantage of the trace species still being in more concentrated form in the gas stream and hence more easily removed by sorbents than when in a dilute, (post-combustion) high temperature form where they are likely to have become converted to difficult to remove condensed phase aerosols or gases as in the case of sulfur or mercury. Prior work at PSIT has shown that aluminosilicates (possibly as alkaline earth containing compounds) in the presence of HCl and/or SO₂, can react with several of these trace metals at high temperature. The resulting reaction products were typically non-leachable materials, suggesting effective capture is possible with such sorbents. However, the effectiveness of these (and other sorbents) has not yet been evaluated under conditions relevant to gasifier fuel (i.e., in strongly reducing atmospheres containing H₂S and HCl). A study of a number of such trace capture reactions with selected sorbents in coal-gas environment has progressed at PSIT as reported in detail under Task 340. Figure 1.4 illustrates the approximate trace capture reactor configuration that is being used in these experiments.

Figure 1.4 TRACE CAPTURE REACTOR FOR GENERATING AND ABSORBING TRACE CONTAMINANTS ON SELECTED SORBENTS:

This PSIT Facility (before modification as shown in Figure 2.11) was Originally Used to Screen Once-through Sorbent Characteristics of Oxidized Contaminants

2. TASK-WISE PROGRESS

The Work Plan as implemented is shown in Figure 2.1.

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Figure 2.1 WORK BREAKDOWN STRUCTURE:
A Carefully Planned Approach was Designed for the
Different Phases of this Contaminant Study

2.1 NEPA AUTHORIZATION

This task, completed shortly after the project began, consisted of ERC and PSIT's submissions of their respective NEPA comments on safety and health issues, and declarations concerning the environmental issues that might be affected by the project's research activities. Permission was granted to both companies in connection with the specific projects and activities as called out under the procedures of the Department of Energy.

2.2 DESIGN OF WORK PLAN

As noted in Section 1 (Introduction and Background) regarding the selection of five trace elements representing the most significant contaminant concentrations in coal-gas, Subtask 210, was initially postponed until more definitive experimental data could be obtained. Namely, there was a concern expressed at DOE/METC that insufficient hard data were available to precisely define the volatile trace species emitted from a typical gasifier or coal source after the gas is initially hot-cleaned by cyclones and candle filters. Accordingly, the work done under Section 2.3.2 (Task 320) provides the conclusions that were originally needed for exactly defining the trace element impacts.

2.2.1 TRACE ELEMENT IMPACTS

The range of trace elements gasified from different coals is extensive and varies with the geographical location of the coal source and the type of gasifier used, as has been shown in a number of previous reports. For example, in 1981 a study was done by TRW⁷ regarding the "Monitoring of Contaminants in Coal-derived Gas for Molten Carbonate Fuel Cells". That study's principle objective was the assessment of instrumentation and equipment useful for monitoring and controlling contaminants during cleanup of coal gas. It also included several tables of the contaminant content identified in different coals and that remain in gasifier product streams. Another study was done in 1983 at Westinghouse⁸ to evaluate gasification and cleanup processes for use with molten carbonate fuel cell power plants, which was also based on the contaminant content in various coals. These listings of type and range of contaminants have now been assembled in major part by a large study entitled: "Trace and Minor Elements in Coal", published as part of a monograph on Organic Geochemistry⁵.

Taking into account recent developments in coal conversion technologies, and the integration possibilities with power producing plants, has given impetus to the current study. A major input, the fuel side tolerance levels of molten carbonate fuel cells, is already available. But the impact of trace species on other power conversion systems is not as clearly defined and remains under study. As noted in Section 1.1, the actual selection of the most significant trace elements that would evolve from a typical gasifier/coal combination and be detrimental to the environment was initially not clear.

2.2.2 IDENTIFY DATA GAPS

The early work on this task of filling the thermodynamic data gaps and documenting the free energies of interaction species occurring between more than 20 trace elements and fuel components was expected to result in a very large number of either gaseous or high temperature condensed phases. The many combinations and permutations of compounds that could be produced from such fuel and contaminant species as the chlorides, sulfides, bromides, oxides, and hydrides, reacting with trace metals such as beryllium, potassium, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, cadmium, and mercury - besides the 5 that were later on selected, namely arsenic, selenium, antimony, zinc, and lead - would have been an enormous task. Therefore, initially the gaps in thermodynamic documentation concerning for example Be, Mg, Mn, Co, Cu, Mo, Al, Ca, Ge, Br, etc. were not immediately pursued.

Nevertheless, as detailed in Section 2.3.1, a good deal of progress was made initially by creating a fully computerized, thermodynamics data base as a preprocessor program to execute many multicomponent, thermochemical equilibrium calculations using the SOLGASMIX software code over a wide range of temperatures and pressures. A commercial software database called TAPP (Thermochemical And Physical Properties by ES Microwave, Inc.) was very helpful in this regard. For most of the species found in JANAF, BKK, and Mills, the TAPP data base also lists the coefficients used for fitting the Gibbs free energy values as a function of temperature, while it also contains a number of species not found in any other major compilation, including JANAF.

2.2.3 PRIORITIZE EXPERIMENTS AND MODELING

The Work Plan design of this project was to begin the investigation by addressing a number of questions such as:

- A) The role of gasified coal as a source of significant Trace Element concentrations which when vaporized under entrained-flow gasification conditions would be of definite concern if emitted into the environment,
- B) How do gasification conditions, including the production of high temperature ash and fly ash particles, influence the initial volatilization and later recondensation and absorption of important trace contaminants from coal gas,
- C) What subsequent fate befalls unabsorbed, mostly volatile, trace elements and their species in downstream pollution control devices,
- D) Can current, hot-gas cleanup technologies reduce volatile trace element content to tolerable levels for different power generating systems, and maintain legally acceptable limits for emission into the atmosphere, and
- E) If inadequate removal of trace contaminants occurs using current hot-gas cleanup techniques, are there better methods available?

As previously mentioned, it was decided that one of the first tasks must entail a screening experiment to answer Question B so as to quickly select a manageable number of elements and species for in-depth study during this effort. This meant doing coal gasification experiments with a standard³ coal and studying the subsequent filtration/sorption of contaminants on different size ash and flyash particles cogenerated in the process. Besides the actual **volatility** assessment that this approach would permit, it would also define the most significant elements to be studied (as judged from their relatively **abundance** in coal), and indicate where definite concern regarding **toxicity** might exist, thus also answering the concerns of Question A.

Next, the thermochemical evaluation task to investigate Question C in terms of the predicted types of species to be compared with experimentally found trace element levels, such as remain in coal gas flowing through downstream pollution control devices, was performed. This was initially designated as Task 310, but Task 320 clearly became one of higher priority.

Experimental work on the equilibrium sorption of different trace species by the currently most highly developed desulfurization technique, was then scheduled using the TGA (ThermoGravimetric Analysis) technique to start answering Question D. Finally, to answer Question E, work with non zinc-based sorbents was performed to study other contaminant control methods using a trace element capture apparatus.

2.3 IMPLEMENTATION OF WORK PLAN

This section provides the overall implementation and conclusions of the work plan regarding the theoretical and experimental efforts accomplished in the various subtasks:

2.3.1 THERMOCHEMICAL CALCULATIONS

Calculations using the SOLGASMIX program, both under ambient and high pressure conditions (noting that the experimental work was always done at 1 atm.), were performed using the local gas composition, temperatures and pressures that are applicable at the various node points between gasifier and power conversion units. These points have been indicated by the circled letters in Figure 1.1; tabulation of the conditions corresponding to these different node points are shown below in Table 2.1.

Table 2.1 SUMMARY OF CHARACTERISTIC FUEL-GAS CONDITIONS:

These are the Primary Conditions used for Equilibrium
Calculations at the Various Node Points

Node after	Location & Conditions	Temperature, K	Pressure, atm	Comments
a	Gasifier Exit Gas	1100-1500	1,3,10,40	Uses experimental wt. % of elements vaporized as the initial condition.
b	Cyclone/Candle Filter Exit + Expansion & Cooling	1100	1,3,10,40	Could artificially add other trace capture sorbents for trace contaminant removal with the flyash.
c	Hot-gas Cleanup (desulfurization)	823-923	1,3,10	Zinc titanate or other Zn-based, sorbents. (TGA-testing).
d	Polisher Exit (includes reheating)	823-923	1,3,10	Further halide & trace metal removal w. carbonate melt or liquid Sn(l).
e/g	Turbine and HRSG Exit	1200/373	1	Future may include alumino-silicates or alkaline earth sorbents.
f/g	Fuel Cell Cathode and HRSG Exit	973/373	1	May require other sorbents such as activated carbon.

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2.3.1.1 Conditions for the Calculations

When the complete CO/CO₂ equilibrium of a nominal coal-gas composition is allowed to be established under high pressure conditions, there is usually not enough oxygen available for all carbon species to remain in the gas phase while the temperature is being lowered, as illustrated in Table 2.2. Therefore, thermochemical calculations were first performed to take a

close look at the theoretical condition for soot or carbon formation at different temperatures when the gas is still under high pressure (e.g., condensed carbon being the reference state). It was calculated that at pressures much greater than 1 atm. as above indicated, there may be considerable carbon condensing out of coal gas while the temperature is being progressively lowered.

However, if solid carbon is forced out by simply not allowing it to form at the 923K fuel cell temperature (i.e., by omitting it from the list of species being considered), then the nearest equilibrium composition for the gas phase would be as given in Table 2.3. Comparing the with-, and without-, condensed carbon columns which are at the complete high pressure/high temperature equilibrium, it is noted that the calculated compositions do not differ greatly from each other. But, when these calculated cases are compared to the non-equilibrium, Texaco-type, gas composition provided in Table 1.4, it is seen that the CO/CO₂ ratios and CH₄ concentrations are quite different. This is, of course, because the data for actual gasifier exit gas are non-equilibrium values, but also because low versus high pressure conditions were used where thermodynamically methane production is favored.

Table 2.2 AMOUNT OF EQUILIBRIUM CARBON CONDENSABLE AT 40 ATM:
Theoretical Calculation in Terms of the Original Texaco Coal Gas Composition Used

Temperature, K	% Carbon Condensed	~°C
1500	0	1200
1100	0	800
1000	14	725
923	21	650
823	26	550

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Table 2.3 COMPLETE GAS PHASE EQUILIBRIA AT 923 K, 40 ATM:
These Theoretical Calculation Include the Methane Formation Equilibrium

Species	Vol% with Condensed C	Vol% without Condensed C
CH ₄	12	18
CO	5.2	7.7
CO ₂	34	39
H ₂	11	10
H ₂ O	36	24

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However, regardless of equilibrium pressure or temperature conditions, what is important is that carbon formation or not, these small differences in gas composition and carbon formation must not affect our trace element calculations. To test this, equilibrium calculations for arsenic (which is a significant contaminant in coal gasification) were carried out with and without condensed carbon present. Since arsenic can be present as AsH_3 , As_2 , or As_4 species depending on temperature and pressure, this is an important element to monitor as to its partitioning into different multispecies constituents when calculations are done with/without carbon formation. Figure 2.2 shows the mol fractions of arsenic species calculated with carbon present (closed points) and carbon absent (open points), as a function of temperature (at 40 atm pressure). Even at the lowest temperatures the presence of condensed carbon has very little effect on the distribution or absolute levels of any of the arsenic species. Therefore, all calculations have been conducted using the original gasifier fuel composition discussed previously in Section 1. So, even though for higher pressures (>1 atm) there could be carbon deposition below 1000K (727°C), as far as theoretical equilibrium predictions are concerned, this should not affect trace element calculations.

Figure 2.2 EXAMPLE OF CARBON EFFECT ON As-CONCENTRATION IN FUEL:
Calculated Concentrations of Different Arsenic Species are Apparently
not Affected by Carbon Deposition even at High Pressure

2.3.1.2 Gasifier Exit (Node a)

Calculations were performed for local gasifier exit temperatures up to 1200°C (1500K), at pressures from 1 to 40 atm. Table 2.4 provides an example of the complete list of gases and solids of metals, hydrides, oxides, and salts that have been considered in the equilibrium calculations. Here it should be understood that although only 5 significant trace elements are being investigated, the thermodynamic calculations from here on have all been done in presence of the fairly large chloride and sulfide gas concentrations that are normally associated with coal gas contamination. This is done to realistically assess the behavior of the 5 trace elements (especially the metals) in terms of the different 'species' that can form (e.g., salts, acids, etc.) when they interact with HCl and H_2S at different temperatures and pressure conditions.

Table 2.5 EFFECT OF PRESSURE ON GAS PHASE COMPOSITION AT 1500K:

This Table Provides the SOLGASMIX Calculated Equilibrium Levels
of the Various Species of the Five Trace Elements in ppbv
Concentrations at Node a, Immediately After the Gasifier

First prediction for raw gas at 1 atm*	Vapor Species	1 atm	3 atm	10 atm	40 atm
~200	As ₂	48.2	46.7	41.5	24.6
	AsH ₃	1.7	5.0	15.5	48.5
	AsS	*	*	*	0.5
~70	Sb	29.3	29.2	28.7	26.7
	Sb ₂	*	*	*	*
	Sb ₄	*	*	*	*
~170	Se	2.8	0.9	0.3	0.1
	H ₂ Se	95.3	97.4	98.2	98.5
	Se ₂	*	*	*	*
~9000	Zn	981.0	983.1	984.4	985.3
	ZnS	*	*	*	*
	ZnCl ₂	*	*	*	*
260	Pb	29.4	23.9	21.4	20.4
	PbS	29.2	34.7	37.0	37.6
	PbCl	*	*	*	*

* see Table 1.5, fourth column

* less than calculable

WM9810

2.3.1.3 Cyclone Exit (Node b)

Similar calculations were performed behind the cyclone and candle-filters when the exit temperature dropped to about 800°C (1100K) for the same total gas pressures. None of the elements that are present at 1200°C diminish in total concentration in the gas phase, only other types of molecular forms become evident. As shown in Table 2.6, this holds true except for a major amount of zinc which will condense out as zinc sulfide (ZnS), but this occurs only at high pressure, as shown in the bottom line. Under these post-cyclone conditions, arsenic is still divided between As₂ and AsH₃, but with arsine, especially at the higher pressures, rapidly becoming the more important species. Also, while the gas temperature is lowered from gasifier exit conditions towards the desulfurizer conditions, antimony begins to associate and is now found in the gas phase mostly as the dimer vapor (Sb₂-species) with smaller amounts of monatomic antimony vapor also present.

Similar to what was seen at the higher gasifier temperature, chlorides are again not too important at these slightly lower temperature conditions; however, when high pressure is also maintained, ZnCl_2 begins to be an important gaseous species while most of the metallic Zn vapor starts to condense out as solid zinc sulfide. As for the gaseous lead species, PbS(v) begins to predominate at the lower temperatures, and the metallic vapor, Pb(v) , loses in importance. However, at the higher pressures, some metallic vapor also starts to be converted to a hypostoichiometric form of chloride, PbCl(v) . Monatomic selenium vapor disappears in favor of only hydrogen selenide formation. In summary, not a great deal of change occurs initially toward the lower temperatures except that a small amount of sulfur (where 10,000 ppm is assumed to be present in these calculations) is condensed out by coal-derived Zn(v) , and then only when pressure is very high.

Table 2.6 EFFECT OF PRESSURE ON GAS PHASE COMPOSITION AT 1100K:

This Table Provides the SOLGASMIX Calculated Equilibrium Levels
of the Various Species of the Five Elements in ppbv
Concentrations at Node: b After Filtration and Cooling

Species	1 atm	3 atm	10 atm	40 atm
As_2	46.5	41.6	30.8	18.0
AsH_3	5.6	15.6	40.1	76.3
AsS	*	*	*	*
Sb	6.1	3.7	2.1	1.1
Sb_2	11.7	13.0	14.1	15.9
Se	*	*	*	*
H_2Se	98.5	98.9	101.8	112.3
ZnCl_2	1.0	3.1	12.1	26.2
Zn	984.1	985.9	1005.7	325.7
ZnS	*	*	*	*
PbCl	1.0	1.7	2.9	5.6
Pb	9.9	9.5	8.7	6.3
PbS	48.1	48.2	49.3	54.8
% of Zn as ZnS(s)	0%	0%	0%	69%

* less than calculable

WM9811

2.3.1.4 Hot-Gas Cleanup Exit (Node c)

The hot gas cleanup module here is primarily designed to be a desulfurizer at conditions from 550°C to 650°C exit temperature and intermediate pressure. Most of the sorbents considered have always been Zn-based materials. This aspect of hot-gas cleaning will be further

discussed in Section 2.3.3. For the present calculations, zinc titanate was chosen since its experimental use has been well received because of its mechanical strength (if used as a fluidized bed sorbent) and its thermodynamic properties are readily available. As Table 2.7 indicates, titanate and titanite salts of the metals zinc and lead together with the dioxide form of titanium were added to the list of possible solid species that could be present and therefore should be considered.

Table 2.7 POSSIBLE CONTAMINANT SPECIES PRESENT BEFORE NODE c:
List Showing the Stable Gaseous and Condensed Species During Desulfurization

Element	Gas Phase	Condensed Phases
Arsenic:	$\text{As}_2, \text{As}_4, \text{AsH}_3, \text{AsS},$	$\text{As}_2\text{S}_3(\ell)$
Antimony:	$\text{Sb}, \text{Sb}_2, \text{Sb}_4, \text{SbCl}_3, \text{SbH}_3$	$\text{Sb}(\ell), \text{Sb}_2\text{S}_3(\text{s}), \text{Sb}_2\text{O}_3(\text{s})$
Selenium:	$\text{Se}, \text{Se}_2, \text{SeO}_2, \text{H}_2\text{Se}$	$\text{ZnSeO}_3(\text{s}), \text{ZnSe}(\text{s})$
Zinc:	$\text{Zn}, \text{ZnCl}_2, \text{ZnS}$	$\text{Zn}(\ell), \text{Zn}(\text{s}), \text{ZnO}(\text{s}), \text{ZnS}(\text{s}), \text{ZnSeO}_3(\text{s}),$ $\text{Zn}_2\text{TiO}_4(\text{s})$
Lead:	$\text{Pb}, \text{PbCl}, \text{PbCl}_2, \text{PbCl}_4, \text{PbO},$ PbS	$\text{Pb}(\ell), \text{PbO}(\ell), \text{PbO}(\text{s}), \text{PbCl}_2(\ell), \text{PbSO}_4(\ell),$ $\text{Pb}_3\text{SO}_6(\text{s}), \text{Pb}_4\text{SO}_7(\text{s}), \text{PbS}(\text{s}), \text{PbTiO}_3(\text{s})$ $\text{PbSO}_4(\text{s}), \text{Pb}_2\text{SO}_5(\text{s}), \text{PbSe}(\text{s})$
Titanium:		$\text{Ti}(\text{s}), \text{TiO}_2(\text{s}), \text{ZnTi}_2\text{O}_4(\text{s}), \text{PbTiO}_4(\text{s})$

WM9812

Tables 2.8 and 2.9 summarize the primary concentrations of contaminant-containing species as a function of pressure and temperature at respectively 650°C and 550°C. At the hot-gas desulfurizer exit conditions, arsenic is predicted to be distributed between three different molecular species (i.e., As_2 , AsH_3 and with a small amount of As_4). Antimony, at these lower temperatures, becomes associated in dimeric and higher molecular forms (i.e., Sb_2 with a small amount of Sb_4). Selenium is still found predominantly as H_2Se , while the solid $\text{ZnSeO}_3(\text{s})$ does not seem to form. Chlorides, however, are now becoming quite important with major amounts of zinc being removed from the hot-gas sorbent in the form of gaseous zinc chlorides by reaction with Zn_2TiO_4 which as the hot-gas sulfur sorbent is now present in excess at Node c. Thus, under the higher desulfurizer operating temperatures of Table 2.8, loss of zinc from the sorbent as $\text{Zn}(\text{v})$ and $\text{ZnCl}_2(\text{v})$ is being exceeded beyond what would be transferred as original zinc from a gasified coal source (see Table 2.6 for comparison).

Fortunately, at a somewhat lower temperature the zinc vaporization from sorbent is greatly diminished under 550°C (823 K) desulfurization conditions, although both zinc and lead chlorides are still formed as is shown next in Table 2.9. Finally, traces of Pb are now primarily divided between three species (i.e., PbCl , PbCl_2 , and $\text{Pb}(\text{v})$) because $\text{PbS}(\text{g})$ is now no longer the important species it was at Node: b. This is because sulfur is being efficiently removed from the gas phase through formation of complex, solid, zinc sulfide titania (not shown in tables) as a result of the presence of an excess amount of Zn_2TiO_4 being maintained.

Table 2.8 EFFECT OF PRESSURE ON GAS PHASE COMPOSITION AT 923K:

This Table Provides the Equilibrium Levels of Species in ppbv
Concentrations at Node c, After High Temperature Desulfurization

Species	1 atm	3 atm	10 atm
As ₂	45.2	43.2	37.0
As ₄	0.3	0.7	1.7
AsH ₃	11.9	25.1	44.8
Sb	*	*	*
Sb ₂	14.4	14.3	12.2
Sb ₄	0.5	1.3	3.3
Se	*	*	*
H ₂ Se	103.4	114.2	125.6
ZnCl ₂	1,827.0	1,567.5	1,398.1
Zn	21,759.9	4,068.1	622.4
ZnS	*	*	*
PbCl	23.0	34.7	40.8
PbCl ₂	2.3	7.5	21.3
Pb	36.0	25.3	12.3
PbS	0.8	1.0	0.9
% increase (decrease) in gas phase zinc	2200%	393%	50%

* less than calculable

WM9896

While sulfur is removed from the gas phase through the reaction of H₂S to form a solid ZnS(s) titania sorbent complex, the amount of hydrogen sulfide in the gas phase is reduced from about 8700 ppm at the hot-gas cleanup inlet to 8 to 20 ppm at the exit, with the concentration varying somewhat depending on pressure and temperature. As already mentioned, at the higher temperatures and low pressures, the presence of the large amount of zinc-bearing sorbent in the hot-gas cleanup system appears to add zinc vapor to the gas phase in considerable excess to the original zinc vapor derived from the coal source.

The increase or decrease in gas phase zinc shown in these tables is theoretically computed by comparing the results of the calculation at Node c, with a calculation for the same closed system that does not have excess zinc titanate present. Thus, it is shown in these tables that at 650°C (923K), considerable amounts of zinc could be carried over into the gas phase, and this occurs especially when operating under 1 atm conditions. But, at the lower 550°C temperature shown in Table 2.9, and at higher pressures from 3 to 10 atm, some of the coal-derived zinc vapor may actually be retained with the sorbent, probably in the form of ZnS(s) mixed with zinc titanate.

Table 2.9 EFFECT OF PRESSURE ON GAS PHASE COMPOSITION AT 823K:

The Same Type Equilibria in ppbv are Shown at Node c,
but this Time After Low Temperature Sorption

Species	1 atm	3 atm	10 atm
As ₂	41.2	31.5	20.8
As ₄	6.9	12.2	17.7
AsH ₃	12.3	18.8	24.8
Sb	*	*	*
Sb ₂	7.0	4.6	2.8
Sb ₄	5.7	7.5	8.9
Se	*	*	*
H ₂ Se	122.5	130.7	137.2
ZnCl ₂	1,077.8	993.1	951.7
Zn	247.2	46.3	7.5
ZnS	*	*	*
PbCl	38.4	31.0	18.1
PbCl ₂	24.0	43.0	60.9
Pb	10.8	4.0	0.9
PbS	0.3	0.2	0.1
% increase (decrease) in gas phase zinc	8%	(20%)	(30%)

* less than calculable

WM9897

In summary, the five trace contaminants studied in this effort exit the hot-gas cleanup module primarily in the gas phase, although only at parts-per-billion levels when the upstream concentration (i.e., as shown in Table 2.6 exiting at Node b) is also at ppb levels. But compared to the entering concentrations, there are still forms of arsenic, hydrogen selenide, and zinc and lead chlorides that remain in fair amounts in the gas stream without being absorbed by the hot-gas cleanup system at 550 or 650°C. Also, the higher the temperature and the lower the pressure, the more zinc titanate sorbent is predicted to add zinc to the gas stream, resulting in more zinc leaving the hot-gas desulfurizer than is originally entering with the coal-gas fuel.

2.3.1.5 Effect at Gasifier Exit due to Alkali Content in Coal (Node a)

Since chlorine (probably in the form of sodium chloride) has been shown to be important for the speciation of lead and zinc, it is also of interest to assess the effect of sodium itself on the trace element gases in the gasifier exit (at Node a) by performing calculations there at 1500K (~1200°C), but now focusing mainly on lead and sodium species. The amount of sodium used

in these calculations corresponds to the amount of sodium normally found in gasifier ash. But, since most of the sodium in bituminous coal ash is bound to silicates, not much of it is available in the gas phase during gasification. To model this interaction, a solid solution of Na_2O , SiO_2 , and Na_2SiO_3 , as shown in Table 2.10, was included in the calculations in addition to the various contaminants and salts in vapor and condensed phases that would normally be present.

Table 2.10 Pb AND Na METAL SPECIES USED IN EQUILIBRIUM CALCULATIONS:
A List Showing the Stable Condensed and Gaseous Species Included
in our Calculations When Considering Alkali Content in Coal

Element	Gas Phase	Condensed Phases
Lead:	Pb, PbCl , PbCl_2 , PbCl_4 , PbO , PbS	$\text{Pb}(\ell)$, $\text{PbS}(\ell)$, $\text{PbS}(\text{s})$, $\text{Pb}_3\text{O}_4(\text{s})$, $\text{PbO}_2(\text{s})$, $\text{PbO}(\ell)$, $\text{PbSO}_4(\ell)$, $\text{PbSO}_4(\text{s})$
Sodium:	Na, NaO , NaOH , NaCl	$\text{Na}_2\text{O}(\ell)$, $\text{Na}_2\text{O}(\text{s})$, $\text{Na}_2\text{SiO}_3(\text{s})$, $\text{Na}_2\text{S}_2(\ell)$, $\text{NaCl}(\text{s})$
		Solid Solution Phase
		$\text{Na}_2\text{O} + \text{SiO}_2 + \text{Na}_2\text{SiO}_3$

WM9930

As expected, the results of the calculation showed that at 1500K only a very small fraction of the total sodium present in coal is predicted to exit as a volatile species in the vapor phase, namely from 0.003 to 0.013 fraction of the total amount present as given in Table 1.3. The rest of the sodium exists in solid solution with the silica that makes up the bulk of the ash and flyash which is derived from coal. Since a major amount of the lead, which is one of the more toxic but low volatility metals, is also bound up with the gasifier ash, it was of interest to see if the presence or absence of alkali in solid solution in ash had any effect on the nominal volatility of the two most common and important gaseous lead species, Pb and PbS (Table 2.5). Figure 2.3 illustrates that with or without sodium present in our calculations, the effect on the gas phase concentrations of these species is predicted to be very slight at this high temperature and under various pressures.

2.3.2 GASIFICATION EXPERIMENTS

As the details of the coal gasification runs were being developed to obtain data on volatile contaminants and ash solids closely resembling a Texaco coal gasifier output, the methods of operating the drop tube reactor and the techniques for collecting ash and volatile contaminant samples and analyzing them were steadily refined, starting with the initial screening experiments. Several stages of refinement have resulted in two main groups of data being collected during this project. The initial screening experiments consisted of gasification runs with low temperature classification of ash particles in a cascade impactor as the first analysis step of the ash products, which was then followed by a set of final filters as illustrated in Figure 1.2. Gasified product was extracted directly from the drop tube reactor into a N_2 -quenched, water-cooled, sampling probe providing a gas cooling rate of greater than 10^3 K/second before solids were classified and sampled.

Figure 2.3 EXAMPLE OF SODIUM EFFECT ON CONCENTRATIONS OF Pb-VAPOR SPECIES IN GASIFIER EXIT GAS AT 1500K:

As Shown by the Closed Points with Sodium Present, and Open Points without Excess Sodium in the Calculation, there is Very Little Difference Between the Relevant Pb-species Concentrations at this High Temperature (and even at Low Pressure) Due to Alkalinity

In the second group of experiments for purposes of primary ash removal at as high a temperature as possible, a high temperature (tissue quartz) filter, supported by a converging ceramic venturi sampler, was placed between the water-cooled N₂-quench probe and the reactor exit. In this configuration, ash particles were removed from the gasification process at temperatures of approximately 800°C. The purpose was to gain a better understanding of contaminant condensation at later sampling stages without the material being burdened by excessive amounts of ash and fly ash when exiting from the gasifier before being cooled down for classification. This appears to be an important condition since the sudden cooling of the bulk of ash particles to the low impactor temperatures could result in a greater tendency for volatile trace species to be absorbed on them.

Hence, during the second set of gasification experiments, runs were conducted to determine this effect of ash particle temperature on the volatility of trace elements. Temperatures may vary as a result of changes in the oxidation stoichiometry of the gasification process itself. This ash temperature investigation generally came about as a result of the observation that volatility of trace elements under **complete** combustion conditions appears to differ substantially from what was found in our first set of runs using sub-stoichiometric combustion or gasification conditions. The earlier experiments were, therefore, repeated at an oxygen concentration of 40% O₂ in nitrogen delivering the stoichiometric combustion ratio. In these experiments, the particle-containing gas stream was also quenched for particle classification purposes using the cascade impactor with alternate stages greased with Apiezon (Type T) hydrocarbon grease when required for Proton Induced X-ray Emission (PIXE) analysis of samples.

After exiting the impactor, the gases then passed through a polycarbonate filter of nominally 0.2 μ m pore size to collect any remaining, submicron or aerosol particles. This filter was later followed by an additional, activated-carbon, filter of carbon-coated cotton fibers

(Schleiger & Schuell) to absorb all the remaining gaseous contaminant species and traces of elemental (mostly metallic) vapors. Thus, high temperature ash particles from the tissue-quartz filter, and the quenched particles from the different stages of the cascade impactor as well as the polycarbonate filter, and the vapors trapped on the final carbon filter, were all analyzed for their trace element content via Neutron Activation Analysis (NAA).

These NAA analyses of particulate fractions was achieved mostly by taking duplicate samples of the odd-numbered cuts from the cascade impactor and from the two final filters. Moreover, alternate particulate fractions from the cascade impactor, as well as samples from all filters, were also analyzed via Proton Induced X-ray Emission (PIXE), in which case each individual sample was tested three times.

2.3.2.1 Cascade Impactor Particle Classification

The cascade impactor that was used has provided on-line, size classification of all ash particles with diameters greater than $0.36 \mu\text{m}$. The principle and operation of a classification impactor is illustrated in Figure 2.4. Each stage consists of a group of circular holes with uniform diameter (jets). The particulate laden gas stream is accelerated upon passing through the jets and subsequently deflected upon encountering a collection plate below it. Each following stage contains finer jets and more of them. The streaming lines of the flowing gas are thus repeatedly redirected as gas is passed around the collection plates and toward the next stage below. Small ash particles are able to follow the streamlines. Large ash particles with high kinetic energy cannot follow these lines and, therefore, deposit on the collection plates below the large diameter jets. Jets of each successive stage being of smaller diameter again further accelerate the gas which causes smaller and smaller ash particles to deposit. The diameter of ash particles impacting on a given stage is proportional to a particles inertial energy $U^{-1/2}$, where U is the linear velocity of the gas stream for a given jet⁹.

To avoid problems associated with particle bounce and subsequent re-entry into the gas stream, the collection plates for PIXE-analysis are usually covered with a removable kapton foil liner coated with a very thin layer of Apiezon type-T grease. Calibration of this type impactor, utilizing greased impactor stages, has shown good agreement with theory; d_{50} values of particle size distributions for this impactor were determined by density-correcting the manufacturer's calibration curves for the appropriate operating conditions. Particle micron sizes as they occur on the collector plates below each set of uniform jets are shown in Table 2.11.

Table 2.11 APPROXIMATE d_{50} VALUES FOR CASCADE IMPACTOR STAGES:

The Particle Diameter Peak Distribution of the Material Depositing at Different Levels of the Cascade Impactor and on the Final Filter (FF) is Shown in this Table

Stage:	1	3	5	7	FF
$d_{50} (\mu\text{m})$:	10	4	1	0.3	<0.3

Figure 2.4 SCHEMATIC OF TWO CONTIGUOUS STAGES OF A MULTISTAGE CASCADE IMPACTOR:

This Schematic Illustrates that the Increasing Gas Velocity through Progressively Smaller Jets Below Each Other, Provides Additional Inertial Energy to the Medium and Smaller Particles, and Results in More Likely Deposition at the Sharper Turns at Lower Levels

2.3.2.2 Analysis of Plates and Filters for Background Correction

The background contaminant concentration levels for the different impact collector plates, the polycarbonate and the cotton (carbon-doped) filters analyzed by NAA, are given in Table 2.12 on a weight-parts-per-million (wppm) basis, and on a total mass in microgram per filter basis. Because the weights of individual carbon-doped filters were not determined prior to use, the analytical values for this filter are approximate. Weighing several duplicate units later revealed the average filter weight to be 1.77 g with a range of 1.69 - 1.86 gram, giving in general an approximate range of $\pm 5\%$ for the data. Br, Na, As, Zn, Fe, and Cr were the only elements detected in greater than 0.5 wppm concentrations in the carbon impregnated final filters. Generally, both NAA and PIXE analysis procedures were used to evaluate trace contaminant content and, even though the two analytical methods are somewhat complementary (i.e., different elements are more sensitively analyzed by one than by the other method), there have been a number of similar values obtained for individual elements with good correlation.

Table 2.12 NEUTRON ACTIVATION ANALYSIS (NAA) OF BLANK PLATES AND FILTERS:
Background Corrections are Shown in wppm, and Between Brackets in $\mu\text{g}/\text{filter}$, to be Used for Correcting all the Neutron Activation Analyses Obtained on Impactor and Filter Samples

Element	Cascade Impactor				Polycarbonate Filter*		Carbon-doped Filter	
	Stage 1		Stage 3, 7					
<u>Majors</u>								
S	-	-	-	-	-	-	-	-
Br	54	(11)	38	(8.9)	2.6	(0.2)	2.1	(3.7)
Na	28	(5.7)	31	(7.4)	-	-	260	(460)
<u>Minors</u>								
As	0.04	(.004)	0.03	(.007)	0	(0)	0.52	(0.93)
Se	-	-	-	-	0	(0)	0.046	(0.08)
Sb	0.01	(.002)	0.01	(.003)	0	(0)	0.037	(0.07)
K	-	-	-	-	-	-	-	-
<u>Trace Metals</u>								
Zn	3	(0.6)	2.5	(0.59)	0.9	(.076)	4.1	(7.3)
Pb	-	-	-	-	-	-	-	-
Cd	<0.01	(<.002)	<0.004	(<.001)	0	(0)	0.012	(0.02)
Hg	0.04	(.008)	0.02	(.007)	0	(0)	0.021	(0.04)
Ni	-	-	-	-	-	-	-	-
Fe	27	(5.6)	29	(6.9)	18	(1.6)	140	(250)
Mn	-	-	-	-	-	-	-	-
Cr	8	(1.7)	8	(1.9)	9	(0.7)	2.5	(4.4)

* manufacturer's reported data

WM9907

In general, it should be realized that when comparisons between the two types of analytical results are made, NAA usually shows somewhat different levels than PIXE because of the lesser or greater homogeneity of element distributions in **bulk** samples. Of course, NAA is a bulk method which analyzes the entire sample while PIXE is a **surface** analytical technique which only analyzes a few square centimeter of the total filter and, hence, an extensive normalization technique had to be employed to obtain comparable wppm data (see Appendix A). On various occasions, data for more than 27 different elements ranging from aluminum to uranium were determined by these two methods, but many elements were present in only minute quantities. This report will generally limit itself to presenting only the concentrations obtained on 15 of the most significant elements. And for simplicity of correlation, these elements will always be presented in the same order throughout this report. Of the 15 important elements, 5 significant trace contaminant species were then selected for further theoretical and experimental study. This was subsequently done in terms of thermodynamic calculations, TGA analyses, and trace capture experiments, as discussed in Sections 2.3.1, 2.3.3 and 2.3.4, respectively.

The background contaminant concentration levels by Proton Induced X-ray Emission (PIXE) analysis for the impactor plates and filters are given in Table 2.13. Only values exceeding the detection limits for particular elements are provided. The measured background concentrations for elements which did not exceed the detection limit, background corrections were not applied (see Table A.1, Appendix A for details). The samples submitted for PIXE analysis when corrected differed slightly from those submitted for NAA. For PIXE, the samples collected from stages 1, 5, 7, and the final filters were usually analyzed, whereas for NAA, samples from stages 1, 3, 7, and the final filter were analyzed. All the data shown with respect to subsequent experiments have been background-corrected using the appropriate blank filter analyses that are provided here.

Table 2.13 PROTON-INDUCED X-RAY EMISSION (PIXE) OF BLANK PLATES AND FILTERS:

Background Concentrations are Shown in wppm, with Dashes Indicating Elements not Analyzed or Below the Detection Limit, to be Used for Correcting all the Proton Induced X-ray Emission Data Obtained on Ash Samples or Filter Matrices

Element	Cascade Impactor, wppm			Polycarbonate Filter, wppm
	Stage 1	Stage 5	Stage 7	
<u>Majors</u>				
S	1220	960	1170	-
Br	0.13	0.093	0.13	320
Na	-	-	-	-
<u>Minors</u>				
As	-	-	-	-
Se	-	-	-	-
Sb	-	-	-	-
K	-	-	-	-
<u>Trace Metals</u>				
Zn	1.8	1.7	1.9	4.3
Pb	-	-	-	-
Cd	-	-	-	-
Hg	-	-	-	-
Ni	0.29	0.24	0.26	0.82
Fe	5.0	4.5	5.6	10
Mn	-	-	-	-
Cr	0.14	0.14	-	4.7

WM9908

2.3.2.3 Initial Screening Experiments

Size-segregated ash samples generated during the first gasification screening experiments with Illinois #6 coal (Table 1.3) and classified by collection on the cascade impactor stages were analyzed for trace element content using PIXE and NAA procedures as previously discussed. Procedures for the PIXE analyses differed slightly from those submitted for NAA. For PIXE analysis, the samples were collected from stages 1, 5, 7, and from the final particle filter, whereas for NAA, the samples were from stages 1, 3, 7, and two final filters. The impactor dust samples have the approximate d_{50} values provided in Table 2.11. With PIXE analysis, the stages 5 and 7 samples (i.e., the smallest particle sizes) were analyzed three times to assess analytical consistency. NAA duplicate samples obtained during successive gasification runs under identical conditions were additionally submitted to assess experimental reproducibility. The background-corrected data for the initial screening experiments analyzed by NAA are reported in Table 2.14.

Table 2.14 NAA-ANALYSIS OF ASH FROM INITIAL GASIFICATION (SCREENING) RUN:

These are Background Corrected Values from the First Experimental Gasification Run Calculated in wppm per Impactor Stage or Filter

Element	Cascade Impactor, wppm			Polycarbonate Filter, wppm
	Stage 1	Stage 3	Stage 7	
<u>Majors</u>				
S	-	-	-	-
Br	120	2	14	1240
Na	2700	4700	0	360
<u>Minors</u>				
As	2	5	11	28
Se	3	6	9	24
Sb	-	1	4	12
K	-	-	-	-
<u>Trace Metals</u>				
Zn	120	450	520	2300
Pb	-	-	-	-
Cd	1	2	1	2
Hg	-	1	1	1
Ni	-	-	-	-
Fe	65,000	61,000	460	920
Mn	-	-	-	-
Cr	430	430	27	52

WM9909

It was noted that the metalloids, As, Se, and Sb, became absorbed (enriched) primarily on the smallest particles (i.e., collected on stage 7 and on the $\sim 0.1 \mu\text{m}$ polycarbonate filter). This behavior is indicative of volatility of the elements during coal gasification because when the temperature is rapidly dropped to the low cascade impactor levels, vapors preferentially condense or absorb on the high surface area, smallest diameter, ash particles. High temperature (tissue quartz) and activated carbon final filters were not used in these first screening experiments. Of the trace halide elements for which concentrations were analyzed, bromine (Br) and chlorine (Cl) demonstrated considerable evidence of volatility and absorption after gasification, which was especially true for the smallest particles retained on the polycarbonate filter.

Also, Zn-concentrations became steadily larger as smaller particles were examined as a result of their greater surface area acting as absorption and condensation sites for Zn-vapor. On the other hand, as expected, Na, Fe, and Cr, concentrations diminished when compared to their concentrations found on Stage 1 and 3. Hence, they are relatively non-volatile or (in the case of Na) remain part of the silica-aluminate fraction of the flyash particulates. Finally, Cd and Hg, although moderate to highly volatile respectively, are present at such low levels as evidenced by their low abundance in Illinois #6 coal (Table 1.5), that their condensation and absorption on colloidal flyash particles and soot will probably allow them to be ignored for the time being.

The samples from the initial screening experiments were also analyzed by Proton Induced X-ray Emission analysis providing a complementary analysis especially for those elements not easily analyzable by NAA such as K, Pb, Ni, and Mn. Samples from the blank kapton impactor stages normally greased with Apiezon type-T grease, were also analyzed to provide the background concentration levels for this analytical method (Table 2.13). As was also mentioned in Section 2.3.2.2, Appendix A describes the details of the technique used to calculate total wppm values for contaminants collected on filters and plates from just the surface area ($\mu\text{g}/\text{cm}^2$) analysis obtainable by PIXE-measurement. The background-corrected PIXE data for the plates and filters obtained in the initial screening experiments are shown in Table 2.15. It was noted that the trace elements Pb and Zn were present in **increasing** concentrations with **decreasing** ash particle sizes. Hence, this is an indication of volatility/nucleation and condensation. Conversely, Ni, Mn, and again Fe, and Cr concentrations **diminished** while particle sizes **decreased** on successive impactor stages, indicating a lack of volatility under the equivalent conditions.

In connection with the large amount of gaseous H_2S being emitted with the exhaust gases from these actual coal experiments, one set of analyses of the particulates and filter fines was also performed with respect to sulfur (S). This has provided clear evidence that this major contaminant element to some extent becomes already absorbed on most sizes of ash particles, but primarily on the very finest aerosol particulates filtered out by the polycarbonate filter, and probably as both sulfide and sulfate condensates.

Table 2.15 PIXE-ANALYSIS OF ASH FROM INITIAL GASIFICATION (SCREENING) RUN:

These are Background Corrected Values from the First Experimental Gasification Run Correlated and Calculated in wppm

Element	Cascade Impactor, wppm			Polycarbonate Filter, wppm
	Stage 1	Stage 5	Stage 7	
<u>Majors</u>				
S	1900	-	1900	37,000
Br	-	11	20	-
Na	-	-	-	-
<u>Minors</u>				
As	-	-	-	-
Se	-	-	-	79
Sb	-	-	-	-
K	7500	1500	66	1600
<u>Trace Metals</u>				
Zn	140	1300	1050	8900
Pb	-	250	300	2500
Cd	-	-	-	-
Hg	-	-	-	-
Ni	590	140	95	140
Fe	77,400	19,000	690	1500
Mn	350	100	4.4	-
Cr	1100	280	20	-

WM9910

Regarding potassium (K), it is believed, as also shown by the NAA-analyses for sodium (Na), that alkalis are a major constituent of the ash and flyash aluminosilicates. But, it is possible, because of the rather major amounts of sodium and potassium oxides in Illinois #6 coal (i.e., ~30,000 wppm in the non-volatile ash fraction as shown in Table 1.3), that a fair amount of this alkali may also escape as alkali vapors with the product gas. Finally, in connection with beryllium, the cascade impactor samples from stages 1 and 7, as well as the greased impactor blanks, were examined at a commercial laboratory using Inductively Coupled Plasma (ICP) Emission Spectroscopy for beryllium concentrations. The levels of Be reported both in the blank and in the collected ash samples were all less than this analytical method's detection limit which is somewhat less than 1 ppm.

In conclusion, it is seen by comparison of background-corrected PIXE and NAA results for many elements that a good correlation exists between concentrations measured by either method. For example, even though results for chromium reveal some differences in absolute concentrations, the trends were identical, as shown in Table 2.16.

**Table 2.16 COMPARISON OF CHROMIUM CONCENTRATIONS
BY TWO ANALYTICAL METHODS:**

Reasonably Comparable Results were Obtained in the Trends of wppm
Analyses of Equivalent Cascade Impactor and Filter Stages

Impactor Stage	NAA	PIXE
1	430	1100
3	430	-
5	-	280*
7	27	20*
FF	52	-

* average of three analyses per sample

WM9928

To test the overall mass balance in gasification experiments, the concentration of elements in the parent coal can also be calculated from the experimentally measured concentrations in the ash and the cascade impactor's overall mass distribution and the fractional conversion of hydrocarbon matter in the coal. To do this, define $C_{j, \text{coal}}$ as the concentration of element j in coal measured in wppm. The concentration of that element in the products of gasification, defined here as ash because they are primarily inorganic, is therefore:

$$C_{j, \text{ash}} = C_{j, \text{coal}} / A_{\text{pg}} \quad (1)$$

where A_{pg} is the fractional amount of coal plus ash remaining after gasification. This can be written as:

$$A_{\text{pg}} = f_a + (1-f_a)(1-f_{\text{conv}}) \quad (2)$$

where f_a is the fractional ash content of the coal and f_{conv} is the fractional conversion of non-ash matter to gaseous products.

The average concentration of element j in the ash product can then be determined from cascade impactor data:

$$C_{j, \text{ash}} = \sum_i m_i C_{ij, \text{ash}} / \sum_i m_i \quad (3)$$

where m_i is the total mass collected on stage i of the cascade impactor and $C_{ij, \text{ash}}$ is the concentration of element j in the ash on impactor stage i . These equations can be combined to yield a relationship for directly calculating the mass of an element in the coal:

$$C_{j,coal} = \left\{ \sum_i m_i C_{i,j,ash} / \sum_i m_i \right\} \{f_a + (1-f_a)(1-f_{conv})\} \quad (4)$$

Because concentration data for all seven stages of the cascade impactor were not collected, some interpolation is required. Nevertheless, calculation of the concentration in the coal and comparison with reported data provides an approximate check of mass balance closure.

The mass distribution of gasification products on the various stages of the cascade impactor was determined in all experiments that used greased collectors to minimize particle bounce. The results for these screening measurements are reported in Table 2.17 below. Five of the seven measurements yielded consistent results. But two data sets obtained on different days indicated considerably less material in the smaller particle sizes. The second of these runs on 6/26/93 was of very short duration (1 minute) for the purpose of generating lightly loaded stages for PIXE analysis, and was, therefore, not included in the average distribution calculation shown at the end of the table. Also for the other short duration run of 6/25/93, it was assumed that steady state was not achieved. Average distributions were not weighted to account for the mass collected in any given experiment; rather, the distributions as reported for individual runs were used directly to determine the average values as shown in the last column of Table 2.17.

Table 2.17 CASCADE IMPACTOR MASS DISTRIBUTION AVERAGES:
The Result of Seven Experimental Runs Were Averaged to be Used later for Overall
Material Balance Calculations Relative to Individual Impactor Stages and Filters

Date:	6/4/93	6/5/93	6/4/93	6/5/93	6/25/93	6/26/93	10/28/93	
Mass Col- lected (mg)	703	302	461	196	186	34	353	
Percent C* conversion	96	91	96	91	87	94	89	
Impactor Stage	% of Mass Collected on Each Stage							Average of Individual Runs
1	34	32	31	33	66	87	23	37
2	26	37	14	26	12	8	22	23
3	10	8	13	10	7	0	13	10
4	4	1	6	1	2	0	6	3
5	3	1	4	0	1	0	4	2
6	7	2	9	3	2	0	8	5
7	5	6	7	7	3	0	8	6
FF	11	13	16	20	7	5	16	14

* measured on side arm of total filter and defined as non-ash mass loss

Using the cascade impactor data in Table 2.17 and equation (4), mass balances were calculated for several of the trace elements studied in this program. Linear interpolation was used to estimate elemental concentrations for impactor stages that were not analyzed. Other methods of data interpolation could, of course, have been used if a mechanism of transformation is assumed for each element. For example, for volatile elements that **condense** heterogeneously on existing ash particles, a $1/d^2$ dependence is expected, and for volatile elements that **react** with ash particle surfaces, a $1/d$ dependence is expected. For non-volatile elements, a d^n dependence may occur with n greater than or equal to 0. Because these interpolation methods presume some knowledge of fundamental behavior, and since the goal of this study was the actual determination of that behavior, it was felt that simple linear interpolation was the only justifiable method. Clearly, measurement of the concentration of each element on each impactor stage would have been the best approach, but this amount of detail was beyond the scope and time allotted for this program.

Results of these mass balance calculations for individual elements are reported in Table 2.18 and are compared with the coal trace element concentration data provided to this program by UND-EERC. In instances where trace element concentration data were not available for this particular coal, the geometric mean concentration for U.S. coals as reported by Finkelman⁵ (1992) was used. Neutron activation data compare favorably with measured and average coal concentrations, and are generally within a factor of 2 to 5 of the measured trace element concentrations in Illinois #6 coal. The higher discrepancies in PIXE data result in part from the lack of data at particle sizes between 1 and 10 μm (i.e., Stage 3) which lending more uncertainty to the data interpolation. These data also reflects some uncertainty in the definition of active filter area for aerosol samples, as discussed in Appendix A.

From the overall screening data, the following conclusions were drawn for entrained-flow gasification of Illinois #6 coal:

1. Trace Elements Showing Enrichment on the Smallest Particle Sizes and Filters (i.e., volatile elements):
As, Se, Sb, Zn, and Pb
2. Elements Only Present as Minimal Traces having No Size Dependence (Cd could be volatile but non-reactive with aluminosilicates; Hg is clearly volatile and may be absorbed if activated carbon is present):
Cd, Hg
3. Elements Showing Diminishing Concentrations with Decreasing Particle Sizes (i.e., definitely non-volatile):
Ni, Fe, Mn, Cr
4. Air Toxic Element That Could be Present but only in Very Small Trace Amounts with Behavior Still Uncertain:
Be

**Table 2.18 INDIVIDUAL TRACE ELEMENT MASS BALANCE
CALCULATIONS RELATIVE TO THEIR COAL CONTENT:**

Equivalent Species Concentrations wppm Calculated from Gasifier Ash Data for Filter and Impactor Stage Distribution Averages (as Shown in Table 2.17) are Compared to Illinois #6 Solid Coal Analyses in wppm (Table 1.5)

Element	NAA	PIXE	Illinois #6
<u>Majors</u>			
Cl	-	76	470
Br	36	0.6	-
Na	390	-	820
<u>Minors</u>			
As	1.1	-	1.7
Se	1.1	1.8	1.5
Sb	0.37	-	<1
K	-	810	2200
<u>Trace Metals</u>			
Zn	85	270	65
Pb	-	69	3.2 to 6
Cd	0.21	-	0.14
Hg	0.079	-	0.032
Ni	-	66	8.8 to 24
Fe	7300	8100	23,000
Mn	-	37	19 [†]
Cr	51	110	19 to 34

† estimated by Finkelman⁵

WM9915

2.3.2.4 Additional High Temperature Sampling Experiments

During the first of the supplemental experiments with high sampling temperature, Illinois #6 coal was again gasified under the same conditions as the prior screening experiments. Namely, 3.7 g/min coal feed rate was used with 15% oxygen in nitrogen gas and 2 ml/min water addition under entrained flow conditions at 1500°C. The mass distributions obtained on the different filters and impactor stages for these runs are presented in Table 2.19. A tissue-Quartz filter, which was previously described with respect to this high temperature contaminant removal effort, was used to eliminate most of the non-volatile mass at high temperature, thus, enabling us to better examine condensed volatile trace species in the smallest particle diameter ranges from the final filters.

Table 2.19 FILTERS AND IMPACTOR STAGE MASS DISTRIBUTIONS FOR HIGH TEMPERATURE SAMPLING EXPERIMENTS:

A Very Different Mass Distribution of the Collected Ash Appears to Result when the Sampling is Done at High Temperature Compared to the Lower (Quenched) Temperatures of the Original Screening Runs (Table 2.17)

Filters and Impactor Stage Numbers	Percent of Total Mass Collected
Tissue-Quartz	90
1	2
2	2
3	1
4	0
5	0
6	0
7	3
Polycarbonate Filter	3
Carbon-doped Filter	0

WM9911

In the originally screening experiments, many trace species and elements were found on all successive stages and filters. However, in the high temperature ash removal runs illustrated above, no detectable mass was collected on the three cascade stages above the very last one, and almost none on the carbon-doped filter. To assess the volatility of trace elements under these conditions, the tissue quartz, polycarbonate, and carbon impregnated filter samples were all analyzed by neutron activation analysis. Duplicate runs were also conducted and the samples from each run analyzed to provide a measure of experimental reproducibility. Background concentrations for the polycarbonate filters were assumed equal to those reported earlier.

Thus, the background-corrected trace element data for the high temperature experiments are presented in Table 2.20 and illustrate elements detected in the polycarbonate and carbon filter samples that are still volatile at sampling conditions of 800°C. The elements As, Se, Sb, Zn, and Hg are prominent in this group, suggesting that the downstream enrichment relative to the concentrations found on the initial ash particles collected at high temperature (i.e., on the tissue Quartz filter), is due to gas phase volatility. Only Hg and Zn were also detected in significant concentrations on the activated-carbon filter placed downstream of the polycarbonate unit which had only 3 wt.% of the total weight of ash collected on it. This suggests that together with the seventh impactor stage, a maximum of 3 to 6% of the ash is volatile under these gasification and sampling conditions. Comparing these data with those obtained during the initial (screening) runs, it is apparent that this high temperature sampling effort arrived at essentially the same conclusions as were originally obtained. An interesting observation was made, however, with regard to mercury (Hg). In the first screening runs, no carbon-doped final filter was employed and presumably whatever gaseous mercury evolved was not retained to any significant extent by the alumina-silicate flyash particles that were collected on the final polycarbonate filter (originally ~14 wt.% of total ash).

Table 2.20 NAA-ANALYSIS OF ASH FROM HIGH TEMPERATURE RUNS:

Considering the Very Different Distribution of the Masses Collected
at Low and High Temperature, the wppm Values Calculated are
not that Different from those Provided in Table 2.14

Element	Tissue-Quartz Filter	Polycarbo- nate Filter	Carbon-doped Final Filter
<u>Majors</u>			
Br	0.78	110	0
Na	6100	490	0
<u>Minors</u>			
As	6.1	9.0	0
Se	5.3	6.1	0
Sb	0.82	2.6	0
K	-	-	-
<u>Trace Metals</u>			
Zn	28	100	17,000
Pb	-	-	-
Cd	-	-	-
Hg	0.1	1.5	2000
Ni	-	-	-
Fe	106,000	51	0
Mn	-	-	-
Cr	430	0	0

WM9912

However, during these present high temperature sampling runs which terminated with a **carbon-doped** final filter which, although it did not retain a significant amount of ash, did show a great deal of Hg absorption (2000 wppm was detected on a very light filter). The significance of this will be further discussed in Section 2.3.5, in connection with possible control strategies.

2.3.2.5 Final High Oxygen Experiment

Because the volatility of some trace elements usually observed under **combustion** conditions differed from that presently reported under **gasification** conditions, two additional experiments were conducted to determine the effects of this difference and of the particle temperature on trace element volatility. The baseline experiments were, therefore, repeated at an oxygen concentration of 40% oxygen in nitrogen, corresponding to a stoichiometric ratio (SR) of approximately 1.0 (i.e., approaching complete combustion conditions). Again, the quenched, particle-containing, gas streams were sampled in the cascade impactor, with alternate stages greased with Apiezon Type-T hydrocarbon grease to prevent particle reentrainment. For these experiments, an activated carbon trap was also used downstream of the cascade impactor and polycarbonate filter.

For run consistency, two sets of samples were analyzed by NAA for all size cuts except for impactor Stage 3, where one sample was analyzed. Additionally, individual samples were analyzed via the PIXE method, with each sample analyzed three times for analytical reproducibility. The data being reported here represent the averages of the two run samples obtained by NAA, and in the case of the PIXE analyses, for each available sample which was then analyzed three times. The neutron activation data of these 40% oxygen experiments corrected for background trace element concentrations are reported in Table 2.21. Similar to the baseline screening data reported earlier, Cd, Hg, and Zn exhibited clear evidence of volatility. As, Se, and Sb, also demonstrated the usual increase in concentration with decreasing particle size, suggesting similar volatility under the more highly oxidizing conditions. Surprisingly, however, Cr was detected in the carbon filter samples along with Hg. Because only one blank carbon filter sample was analyzed, it is difficult to determine whether this result is significant or an artifact.

Table 2.21 NAA-ANALYSIS OF ASH FROM FINAL HIGH-OXYGEN RUNS:

Considering the Difference in Oxidizing Activity, the wppm Values Calculated in this Table are not that Different from Those Provided in Table 2.14, Except for Hg and Cr Collected on the Additional C-doped Filter

Element	Cascade Impactor, wppm			Polycarbonate Filter, wppm	Carbon-doped Filter, wppm
	Stage 1	Stage 3	Stage 7		
<u>Majors</u>					
Br	8.2	24	0	710	-
Na	4600	7100	0	280	-
<u>Minors</u>					
As	4.3	14	8.3	18	-
Se	5.5	14	7.5	14	-
Sb	1.1	3.6	4.1	13	-
K	-	-	-	-	-
<u>Trace Metals</u>					
Zn	240	1170	620	1900	-
Pb	-	-	-	-	-
Cd	0.53	2	0.31	2.8	-
Hg	0.26	1.2	0.32	0.61	13,000
Ni	-	-	-	-	-
Fe	76,100	81,300	700	1100	-
Mn	-	-	-	-	-
Cr	970	460	0	43	310,000

WM9927

All previous indications were that Cr is non-volatile, but this may not be realistic under the virtually complete oxidation conditions when total combustion occurs which could generate highly volatile Cr-VI as CrO_3 , CrO_2Cl_2 , or $\text{Cr}(\text{CO})_6$. For the time being, however, it will be assumed that this non-typical result is an artifact resulting from an insufficient number of background filter analyses. Samples from the final high oxygen run were also analyzed by proton induced X-ray analysis as described in previous sections. Background-corrected data, calculated by using the background concentrations reported previously, are given in Table 2.22.

Table 2.22 PIXE-ANALYSIS OF ASH FROM FINAL HIGH-OXYGEN RUNS:
Showing Values Calculated in wppm with Background Correction Included to Supplement Table 2.21. No PIXE Analyses was Obtained on the Carbon-doped Filter

Element	Cascade Impactor, wppm				Polycarbonate Filter, wppm
	Stage 1	Stage 3	Stage 5	Stage 7	
<u>Majors</u>					
S	15,000	51,000	152,000	37,000	18,000
Cl	-	-	-	-	1800
Na	-	-	-	-	-
<u>Minors</u>					
As	-	-	-	-	-
Se	-	-	-	-	35
Sb	-	-	-	-	-
K	13,000	4500	2000	340	300
<u>Trace Metals</u>					
Zn	310	380	800	380	3200
Pb	-	-	-	-	300
Cd	-	-	-	-	-
Hg	-	-	-	-	-
Ni	180	64	30	16	49
Fe	117,000	40,000	58,000	14,000	1000
Mn	430	190	295	77	-
Cr	440	115	-	-	39

WM9926

Table 2.23 FILTER AND IMPACTOR MASS DISTRIBUTIONS FOR HIGH-O₂ RUNS:
Mass Distributions Collected in These High-O₂ Experiments without Quartz Filter are more in Line with Those Obtained in Table 2.17

Impactor Stage Numbers and Final Filter	Percent of Total Mass Collected
1	62
2	18
3	3
4	1
5	1
6	3
7	3
FF	9

The cascade impactor average of the mass distribution data for the high-O₂ experiments is illustrated above in Table 2.23. As done before, these data can be used to calculate the vaporization tendency for the key elements. However, for the Stage 1 cascade-impactor samples, the outer ring was analyzed this time. This is in contrast to earlier PIXE analysis of Stage 1 samples where the inner spot contained an estimated 80% of the mass that was analyzed. To convert the PIXE $\mu\text{g}/\text{cm}^2$ concentrations to ppmw, it was assumed that 20% of the mass was uniformly deposited over the outer annular ring of Stage 1. The size of the annulus was computed by subtracting the measured central area of mass deposition as shown in Figure 2.5.

Figure 2.5 SKETCH OF FIRST IMPACTOR STAGE ACTIVE SAMPLE AREA EMPLOYED FOR REDUCTION OF PIXE DATA (See Appendix A):
A Slightly Different Sample Mass Treatment was Used Providing

2.3.2.6 Comparison and Summary

Thus, when the overall results are calculated in terms of fractional vaporization data as shown in Table 2.24 and compared with those generated during the initial or baseline screening experiments, it appears that higher oxygen partial pressures have somewhat reduced the fraction of each element vaporized, with the exception of chromium, suggesting possibly more interaction of volatile trace elements with the ash sorbents retained on the initial cascade impactor stages.

Table 2.24 FRACTIONAL VAPORIZATION (f) OF TRACE ELEMENTS COMPARED BY ANALYTICAL METHOD AND TYPE OF EXPERIMENT:

A Relatively Good Correlation is Shown of the Trends and Fractions of Trace Elements Vaporized in this Table. A Few Available Cobalt Data were also Added.

Elements	Initial Screening Experiments		High Oxygen Experiments	
	f (NAA)	f (PIXE)	f (NAA)	f (PIXE)
<u>Majors</u>				
Br	0.74	-	0.88	-
Na	0.02	-	0.006	-
<u>Minors</u>				
As	0.53	-	0.23	-
Se	0.45	0.85 - 1.0	0.18	>0.13
Sb	0.70	-	0.43	-
K	-	0.04	-	0.003
<u>Trace Metals</u>				
Zn	0.58	0.76	0.32	0.48
Pb	-	0.84	-	0.29
Cd	0.20	-	0.28	-
Hg*	0.27	-	0.17	-
Ni	-	0.05	-	0.03
Co	0.03	-	0.01	-
Fe	0.003	0.004	0.002	0.001
Mn	-	0 - 0.005	-	0 - 0.007
Cr	0.02	0 - 0.005	0.006	0.01

WM9924

* Since 100% Hg-vaporization is likely, reported values <100% are indicative of Hg-adsorption probably on residual carbon associated with particles >1 μ m

A final mass balance summary of back-calculated concentrations for each element in two types of experiments was also computed using the same approach outlined in Section 2.3.2.3 (Table 2.18). Thus, correlation of all the results with the original concentrations in Illinois #6 coal are shown in Table 2.25, illustrating essential agreement with prior results.

Table 2.25 CONCENTRATION OF TRACE ELEMENTS MEASURED IN SOLID COAL CORRELATED WITH SEVERAL GASIFICATION EXPERIMENTS:

Essential Agreement of Back-calculated Ash Concentrations of Trace Elements (wppm) in Two Types of Experiments is Shown when Correlated with the Content in Solid Coal

Elements	Measured in Illinois #6 Coal	Screening Experiments		High-O ₂ Experiments	
		NAA	PIXE	NAA	PIXE
<u>Majors</u>					
Cl	470	-	76	-	27
Br	-	36	0.6	12.2	-
Na	820	390	-	720	-
<u>Minors</u>					
As	1.7	1.1	-	1.2	-
Se	1.5	1.1	1.8	1.3	0.5
Sb	<1	0.37	-	0.4	-
K	2200	-	810	-	1700
<u>Trace Metals</u>					
Zn	65	85	270	90	99
Pb	3.4 to 6	-	69	-	4.5
Cd	0.14	0.21	-	0.16	-
Hg	0.032	0.079	-	0.075	-
Ni	8.8 to 24	-	66	-	24
Fe	23,000	7300	8100	10,900	15,200
Mn	(19)	-	37	-	57
Cr	19 to 34	51	110	130	56

() estimated by Finkelman⁵

WM9923

2.3.3 THERMOGRAVIMETRIC EXPERIMENTS

The thermogravimetric method discussed here has assisted us greatly in gaining an understanding of the interactions and operative decay mechanisms that occur in fuel cells during testing in the presence of trace contaminants. In recent years, numerous thermogravimetric (TGA) experiments have been performed at ERC to closely examine trace species volatilities both in humid and dry fuel gas. Other experiments have also been done to observe contaminant interactions occurring when trace species vapors are exposed to different sorbents, or when reactions occur among the different trace species, the fuel cell components, and the fuel cell's depleted exit gas inside the anode plenum. These types of TGA experiments have all been done in the facility illustrated in Figure 1.3. This facility is capable of testing, simultaneously, five low level vapor concentrations generated from the solid elements and two or more gaseous compounds that can be blended in cylinders. To do this, a multicomponent fuel gas blending system was included with the TGA apparatus so as to supply the various preheated gas flows to the sample chamber to simulate reducing (or inert), as well as dry or humidified, contaminated, fuel compositions. A walk-in fume hood and filtering system sufficiently sized to prevent toxic gases from escaping also became an integral part of this TGA facility.

2.3.3.1 Experimental Facility

Most of our past experiments have been performed under the isothermal (650°C) and atmospheric pressure conditions characteristic of carbonate fuel cell operation. However, volatility and sorption experiments at lower temperatures were also performed which resulted in only small weight changes of solid contaminant sources which were used to generate low level trace species concentrations in coal gas. Many of these measurements were initially done to provide basic background data for designing the contaminant addition apparatus shown to the left of the Cahn-TGA apparatus in Figure 1.3. Thus, the facility shown in this figure is a unique ERC development for the rapid simulation of trace contaminants in gases from which to obtain reaction measurements indicative of contaminated fuel gas (or oxidant gas) under equilibrium 1 atm. conditions.

Since most of the above mentioned experiments have required fairly large sorbent samples and the apparatus had to be capable of also containing relatively large-sized fuel cell components a large thermal analysis chamber was needed. Hence, a Cahn-TG131 model thermogravimetric analysis system was specified, modified, and expanded to include the aforementioned system for blending and humidification of ppm- (or even -ppb) levels of homogeneously mixed contaminants in simulated fuel gas. A data acquisition system and dedicated computer/plotter interface to provide complete instrument control over all the various functions was also installed. In some cases special parts were designed and manufactured, for example the photograph in Figure 2.6 illustrates a quartz weighing susceptor for large surface exposure of samples; this is an ERC design to provide maximum sorbent exposure area for the contaminants blended in the gas stream as they slowly flow past this device. The weight of this susceptor + 6 grams of sample is generally continuously monitored to 10 μ g accuracy. It is of interest to note on this photograph that a ZT-4 sample, which remained in the 5-level pan after being exposed for some time to humidified fuel at high temperature, has become dark grey, probably indicating that some surface ZT-4 was reduced to metallic zinc; this is further illustrated by a reaction equation later on.

Figure 2.6 QUARTZ SUSCEPTOR FOR 5-LEVEL SAMPLE EXPOSURE IN TGA EXPERIMENTS:

High Surface Exposure can be Achieved with Susceptor Holding ~1.2g of Sample Per Pan

2.3.3.2 Sorbent Stability

Because earlier TGA experiments at ERC had already indicated that zinc ferrite was not entirely stable as a sorbent material between 550° to 650° C in reducing atmosphere, the first tests done in this current project utilizing the new sorbent material previously mentioned, have involved primarily stability testing. Thus, technique was developed to test ZT-4 (the zinc titanate composition patented by Research Triangle Institute) by scanning the weight changes occurring with respect to roughly 6 gram samples of sorbent while maintaining the material at five consecutive temperature plateaux, each for about 12 hour duration, and doing this in different gas environments.

Figure 2.7 shows in one combined illustration assembled from the computer plotted curves, the weight change data for a number of stability experiments derived directly from the recorded runs. The dwell temperatures (same for every run) are also shown with respect to the axis on the right. This initial stability investigation has been obtained with three gas environments at five temperatures, all in the absence of any contaminants. The figure illustrates that as the $H_2/H_2O/CO-CO_2$ levels of the gas atmospheres differ, the correlated equilibrium weight change response of the sorbent (i.e., its stability as temperature increases) changes. As is shown in the figure, the stability of ZT-4 desulfurizer sorbent cannot be maintained above 450° C in high H_2 -concentration fuels. But only in humidified coal-gas with a much lower H_2 -concentration is

there sufficient thermodynamic stability to maintain constant sorbent weight at temperatures as high as 500°C. At this temperature it is, therefore, possible to employ ZT-4 for contaminant absorption purposes without its own weight changes interfering with the measurements of contaminant sorption. At higher temperatures (near 550°C), it is clear that ZT-4 continuously loses its mass in typical coal-gas environment.

Figure 2.7 STABILITY OF ZT-4 ILLUSTRATED BY THREE TGA EXPERIMENTS:

Results Only Show Complete Sorbent Stability at 500°C and Atmospheric Pressure for Coal Gas Containing 42% H₂, 10% H₂O, 23% CO, 25% CO₂ (top curve)

The above measured effects are the result of a fundamental equilibrium that governs the vapor formation from any zinc compound or complex such as ZnO, ZnO•Fe₂O₃, etc. in hydrogen atmosphere. This reduction reaction has already been measured a number of times in the past relative to different temperatures and various H₂ and H₂O activities in fuel gas atmosphere⁶, and for ZT-4 can be written:

The metallic zinc that is formed already becomes quite volatile at a temperature of 300° C. Thus, the equations clearly illustrate that depending on the ratio of H₂ to H₂O in the atmosphere, the equilibrium will move either to the right or to the left. This reduction + volatilization that has been observed in the case of ZT-4 and a number of other Zn-compounds is a thermodynamically controlled zinc-reaction which appears generic to practically all zinc complexes. Therefore, this puts a definite limit on the stable sorbent temperatures at which Zn-compositions can be used. However, the equation also shows that the solution for higher temperature operation may lie in pressurization which drives the reaction to the left for greater sorbent stability.

2.3.3.3 Trace Element Sorbency

The next investigation in task 330 concerned behavior during the desulfurization process. Elimination of the five volatile trace elements together with the absorption of sulfur from hot coal gas during desulfurization appeared a distinct possibility and, hence, was of great interest. Subsequent to observing that ZT-4 could provide a stable equilibrium response in the TGA apparatus when using coal gas at 500° C and atmospheric pressure, trace elements were added in the vapor phase to the gas. Arsenic (As @ 3.2 ppmv), selenium (Se @ 4.6 ppmv), cadmium (Cd @ 6.9 ppmv), and antimony (Sb @ 2.2 ppmv) were the first low level contaminant species studied for their possible chemisorption by zinc titanate at these indicated concentrations. The trace element cadmium was chosen here instead of lead (Pb) because it is equally high in toxicity and has greater volatility. Figure 2.8 shows the poor equilibrium sorption of As and Se on ZT-4 for a period of at least 70 hours at 1 atm isobaric, 500° C isothermal conditions. The figure illustrates that even at these low levels (but still higher than occurs typically in coal gas), these elements are not absorbed during desulfurization when ZT-4 is used. However, Cd and Sb at levels of 6.9 and 2.2 ppmv vapor in the gas stream (i.e., also at levels somewhat higher than their probable concentration in coal gas), do become absorbed respectively to the extent of about 50% and 100%. This is shown by examining the contaminant absorption (weight change records) over long periods of contact; the offset dotted and dashed lines below and above each element signify 0% and 100% theoretical absorption.

2.3.3.4 Sulfur Absorption

Since zinc as one of the five contaminants is also involved in the zinc titanate equilibrium already tested earlier as part of the ZT-4 stability experiments, this trace species was not considered for further testing. On the other hand, the lowest level of the major contaminant, H₂S, that can still be absorbed under equilibrium conditions on zinc titanate at 500° C is of great interest. Thus, the final contaminant studied at low concentration levels was sulfur (H₂S @ 10 and 15 ppmv). Although the presence of sulfur at these concentrations still implies a rather high level for the carbonate fuel cell (as earlier indicated) Figure 2.9 shows that at ~10 ppmv sulfur level, the absorption on ZT-4 becomes negligible. And only at ~15 ppmv does H₂S(g) begin to show some minor sorption under equilibrium conditions. Hence, it can be inferred that at 10 ppmv the reaction probably has arrived at its equilibrium end-point, with ZnS solid vaporizing as fast as it is formed, as illustrated by the equation:

Figure 2.8 ABSORPTION ACTIVITY OF ZT-4 FOR As, Se, Cd, and Sb:
Arsenic and Selenium are not Chemisorbed by the ZT-4 Desulfurizer Sorbent, but Cadmium and Antimony Appear More Readily Removable at 500°C and Atmospheric Pressure

Figure 2.9 ABSORPTION ACTIVITY OF ZT-4 FOR SULFUR IN COAL GAS:
No Sorption is Evident at 9.3 ppmv and Only Very Slight Absorption Occurs at 14.3 ppmv

Finally, considering that the equilibrium sorption reaction of sulfur may also be affected by temperature variations, this was tested with the TGA apparatus using a set of lower temperature plateaux as shown in Figure 2.10. This figure illustrates that there is no increased sorption effect at lower temperatures for ~10 ppm H_2S and, hence, it may be concluded that ZT-4 is not sufficiently active as an ultimate sulfur polishing sorbent.

Figure 2.10 ZT-4 ABSORPTION ACTIVITY FOR H_2S AT DIFFERENT TEMPERATURES AND AMBIENT PRESSURE:

The Lowest Achievable Level of Sulfur Absorption on ZT-4 Lies at Approximately 10 ppmv

2.3.4 TRACE ELEMENT CAPTURE EXPERIMENTS

The objective of this task was to develop an understanding of the distribution and fate primarily of volatile trace metals (and some metalloid species) that are difficult to remove from hot coal gas. This task began to identify the type of control technologies that had to be developed to completely protect downstream components of power generating systems and, of course, protect the environment as well against the five toxic and decay producing contaminants selected for this study. Clearly, there are still gaps concerning vaporization and sorption of contaminants under gasification conditions and how to prevent the effects of minor or trace amounts of those elements on the various system components. During partial coal combustion or gasification there are still many inorganic elements generally present in coal which will partially vaporize and the more volatile elements such as Zn, As, Sb, Se, Pb, Cd and Hg, as well as alkali metals, may (except for Hg) condense in the cooler regions of the downstream equipment, often as fine powders or adhering deposits on surfaces.

Because it was shown that the very fine flyash generated during gasification constitutes a large amount of available high surface area material, it appears to be an excellent sorbent on which metal and contaminant compound vapors can condense and then be captured by particulate collection devices. Building on this insight, the concept developed that it is more desirable and appropriate to capture as many and as much of the trace contaminants as early as possible when they are still under pressure and in fairly concentrated gaseous form in reducing coal gas

environment. Thus, in a **gasification** system, contaminants will be most easily removed from the gas stream by absorption or condensation on the very fine particulates that are simultaneously generated at high temperature; this will both conserve heat energy and, at high pressure, reduce volume. Therefore, a large percentage of metal vapors and trace compounds may be removable from the gas phase by absorption followed by high temperature filter devices as early in the cleanup cycle as possible. Due to the reducing conditions found during coal gasification, the speciation of the various trace elements may be very different from what happens immediately if coal is completely combusted and species becoming fully oxidized. This could affect the ability of control technologies which come too late in the process to capture the same elements.

For this trace element capture task it was proposed to test (on a bench-scale system) certain sorbents that have already been successfully used in recent studies for the control of toxic trace metals released after complete combustion of various fuels and wastes. Such sorbents may also be employable in gasification systems by injecting them ahead of the high temperature filters where capture occurs in flight and/or within the filter cake. Based on an assessment of the NAA and PIXE analytical results obtained in the previous coal gasification experiments, three test elements were initially chosen for evaluation of sorbents in our trace metal capture experiments: namely, As, Se, and Zn. Arsenic and selenium were chosen for their relatively high volatility and greater capture difficulty on sorbents, as was shown by their enrichment on the smallest size particle fractions trapped on the last cascade impactor stages. They were also selected for relative ease of experimentation because the appropriate reduced forms (AsH_3 and H_2Se) can be injected into the experimental system as a room temperature gas phase. This way of introducing the elements into the fuel is more desirable than vaporization of a solid, affording greater control of the trace concentrations in the gas stream. Zinc was chosen as an important species because of its decay effects on fuel cell performance and its similar characteristics compared to metals such as Pb and Cd. Selection of these three test elements also allowed simultaneous injection of three contaminants to better simulate field conditions.

2.3.4.1 The Trace Element Capture Facility

An original configuration of the trace element capture facility, as shown in Figure 1.4, evolved when taking into account data from previous tasks to better adapt the apparatus to pressurized testing in a reducing atmosphere. Hence, since mostly gases and one metallic vapor species were initially to be investigated, a single fixed bed, pressurizable, capture reactor was designed and is shown (together with the other facility details) in Figure 2.11. The fixed bed reactor is constructed of Inconel (1.9" O.D. and 1.68" I.D.), and is 18" in length. The gasification product gases (1 l/min) were simulated by mixing six individual gas streams allowing independent control of each of the major compounds.

Zinc was introduced into the system by passing pure nitrogen through a small heated chamber containing a crucible of ZnCl_2 . The temperature of the chamber was adjusted so that the concentration of zinc in the reactor was approximately 1.3% by weight. All gas flows were monitored by mass flow meters and, in addition to manual metering valves, were controlled by an electrically operated system of solenoid valves that permitted immediate shut off and purging of all lines if necessary. Table 2.26 illustrates the flow and composition of the coal gas used for trace capture simulation. Gases leaving the reactor were quenched and diluted with a cold, liquid- N_2 , flow to reduce the gas temperature to approximately 50°C, low enough for the plastic

filter housing containing a polycarbonate membrane filter. This quench flow of N_2 was roughly seven times the product gas flow. This reduction of temperature also promoted the condensation of metal vapors and provided for safety by diluting the levels of toxicity and flammability of the exiting gases.

WM9989

Figure 2.11 MODIFICATIONS TO THE TRACE ELEMENT CAPTURE FACILITY:

This Simplified Facility for Generating and Absorbing Three Test Contaminant Species on Different Sorbents Under Pressurized Conditions Supersedes the Figure 1.4 Drawing

Following the filter, a set of high-pressure impingers containing aqueous 5% HNO_3 /10% H_2O_2 absorbing solution, were included to capture the trace metals not retained by the fixed bed. This solution is recommended for use in the impinger train of EPA's draft method 29 for sampling multiple metals (including As, Se, and Zn) in oxidized flue gas from various combustion processes. The method's calculated detection limits at the flow rates used in this system using graphite furnace atomic absorption (GFAAS) as the analytical technique are: 4 $\mu g/m^3$ for As, 8 $\mu g/m^3$ for Se, and 21 $\mu g/m^3$ for Zn. There is currently no other approved method available for sampling metal species in flue gas, although the solutions may not be exactly applicable to the fuel gas streams produced under reducing conditions. The final component in the system was the back-pressure valve which allowed control and adjustment of the system pressure from 1 to 10 atmospheres.

Table 2.26 BLEND OF THE GASES, NOMINAL FLOW, AND CONSTITUENT CONTENT TO SIMULATE COAL GAS DURING THE EXPERIMENTS:
 A Versatile Method for Providing Many Different Gas Compositions and Contaminant Additions was Established

Gas Cylinder Contents	Nominal Flow Rate (cc/min)	Concentration in Reactor
59% CO, 35.9% H ₂ , 5.1% CO ₂	460	27.1% CO, 16.5% H ₂ , 2.5% CO ₂
1% HCl in N ₂	50	500 ppmv HCl
23.7% H ₂ S	50	1.2% H ₂ S
87 ppm H ₂ Se in N ₂	25	2.2 ppmv H ₂ Se
885 ppm AsH ₃ in N ₂	25	22.1 ppm AsH ₃
N ₂ + H ₂ O + Zn(v) added	290* + 100 + ~5	42.8% N ₂ † + 10% H ₂ O + ~5000 ppmv Zn

* N₂ flow without the 100 ml water vapor added for humidification

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† N₂ concentration includes N₂ from other cylinders used as contaminant carrier gas

Due to the type of Hazardous Air Pollutants (HAPs) associated with our coal gas streams, several safety precautions were taken both in the design of the system and in the development of operational procedures. Each component of the system, while being assembled, was pressure tested using nitrogen. Larger pieces such as the reactor and the water vaporizer were hydrostatically tested. As much of the system as possible, including the smaller gas cylinders, were placed under a continuously operating fume hood, and before operation each day, the entire system was leak-tested. A safety system consisting of several electrically operated solenoid valves with manual overrides was incorporated. This system (with the activation of one switch) is capable of simultaneously shutting off the flow of all hazardous gases, venting the system into the hood, and purging all gas lines with nitrogen as well as shutting down all electrical components in the experiment. Proper respiratory equipment is provided for protection of personnel during normal operation and for emergency exiting.

2.3.4.2 Selection of Sorbents and Experiments

The sorbents selected for our initial tests were Celatom and calcium oxide. Celatom is a granular, calcined, diatomaceous earth prepared by Eagle-Picher and represents a low cost, high temperature sorbent often used for a variety of applications requiring high stability and sorbency. It is an alumino-silicate material which PSI has used with some success for the capture of toxic trace metals at atmospheric pressure under oxidizing conditions. In those cases, it has demonstrated high efficiency in capturing Pb, Cd, Ni, Ba, and Zn. Under these same oxidizing conditions, pulverized CaO was also found to be the next best sorbent, especially for the capture of arsenic. This was confirmed in both fixed bed and entrained flow testing with these sorbents. The main advantage for using these types of once-through sorbents is that the leachability of the captured metals and metalloids on diatomaceous earth appears to remain below the regulatory limits determined by EPA Method 1311 and, therefore, the spent sorbent can be safely disposed of in landfill.

Thus, it appeared that these very useful sorbents should also be tested under reducing gas conditions such as would be encountered in an integrated gasifier system after the initial hot-gas desulfurization step (i.e., at Node c). A reactor test temperature of 650°C was used, consistent with normal carbonate fuel cell operating temperature. This temperature, however, can be lowered somewhat if improved absorption is needed since the primary desulfurization step, when using zinc compounds before trace element polishing, does not seem to operate well at fuel cell temperatures. The test matrix for the first trace metal capture experiments done under this task is shown in Table 2.27.

Table 2.27 MATRIX OF EXPERIMENTAL CAPTURE RUNS:

Three Trace Elements Were Tested at the Same Time Using
Four Runs with Two Different Sorbent Compositions at 650°C and
Utilizing Two Pressure Levels in the Trace Capture Facility

Run #	Down Flow Sorbent Bed where the gas first contacts:	Pressure, atm	Temperature, °C
1	1" mix of 50% Celatom, 50% CaO with a 0.5" Celatom base below it	1	650
2	1" mix of 50% Celatom, 50% CaO with a 0.5" Celatom base below it	5	650
3	1" pure Celatom layer with a 0.5" Celatom base below it	1	650
4	1" pure Celatom layer with a 0.5" Celatom base below it	5	650

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The fixed bed material was placed on a 60 mesh Inconel screen which was supported on a 0.125 in. thick perforated Inconel plate. In order to prevent the pulverized CaO from being drawn through the bed support, a 0.5 in. bed of pure Celatom was always first placed on the screen. The equal volumes mixed of Celatom and CaO was then placed on top of this Celatom base. In all cases, the bed depth for each run was the same at 1.5 in.. Once the bed was inserted into the reactor, the system was checked for leaks by pressurizing to 100 psig with nitrogen. After leak testing, the system was depressurized and the final impingers were each filled with 200 ml of analyte-sorbent solution to capture any metal escaping from the bed and filter. The reactor was then turned on and a flow of nitrogen was initiated to purge the system of oxygen while the reactor was heating up to operating temperature. Once the operating temperature was reached, the back-pressure valve was set for the desired reactor pressure and all of the gas flows were adjusted to the values shown in Table 2.26. During each two hour run, the reactor pressure was monitored and, if necessary, adjustments made using back-pressure regulation.

At the end of the run, the gas flows were stopped and the system purged with nitrogen to remove any toxic and/or explosive gases before opening the reactor. Each impinger was emptied and rinsed, and the liquid sample set aside for later analysis. The filter was removed and placed in a petri dish to be sent to the analytical laboratory. The inside of the quench tube and lines were checked for particulate deposition; none was found in any of the runs. The zinc crucible was removed from the heated chamber and weighed to determine the amount of zinc chloride vaporized. Finally, the fixed bed was removed from the reactor, weighed, and placed in a glass sample jar.

2.3.4.3 Sample Analysis and Results

The fixed bed samples were analyzed and the results compared as shown in Table 2.28. Sample preparation was achieved using a microwave hydrofluoric acid digestion process. This was done because of our past experience with the incompleteness of normal nitric acid digestion to entirely remove the target analyte from the alumino-silicate matrix which resulted in metal concentration values that are lower than actually absorbed. The metal analysis of the resulting analyte solutions, because of the presence of fluorides, was accomplished using the Graphite Furnace Atomic Absorption technique, but the impinger liquids and dissolved filter samples were analyzed using standard acid digestion and an ICP spectrometer using argon gas.

Table 2.28 SAMPLE ANALYSES ON THE RUNS SHOWN IN TABLE 2.27:
Considering the Shallow Bed and Short Contact Times Used, Relatively Good
Absorption of Arsenic, Zinc, and Selenium was Accomplished in that Order

Trace Metal Capture (Wt. % of element collected on total of bed, filter, and sorbent samples)					
Run #	Metal Analyzed	Fixed Bed	Filter	Impinger	Overall Mass Balance, %
1 (1 atm)	Arsenic	99.7	0	0.3	32.3
	Selenium	95.0	1.4	3.6	13.4
	Zinc	80.9	3.3	15.8	13.3
2 (5 atm)	Arsenic	99.5	0.5	0	31.3
	Selenium	100	0	0	8.1
	Zinc	60.2	28.7	11.1	17.7
3 (1 atm)	Arsenic	99.8	0.2	0	40.0
	Selenium	100	0	0	12.5
	Zinc	92.2	4.7	3.1	7.0
4 (5 atm)	Arsenic	99.4	0.7	0	40.3
	Selenium	100	0	0	12.5
	Zinc	98.2	1.3	0.5	29.5

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In examining the column of Mass Balances, it can be seen that closure was not achieved in any of these initial cases of trace element capture on the selected sorbents; namely 30 to 40% of the total calculated arsenic input, 8 to 13% of the selenium, and 7 to 30% of the zinc were recovered on the sorbent bed. In the case of selenium, it may be that it remained in the gas phase as H_2Se upon leaving the reactor, and that the $\text{HNO}_3/\text{H}_2\text{O}_2$ absorbing solution was not appropriate, but rather an alkaline-peroxide solution should have given more complete sorption results. Only in the first run could a small amount of selenium be detected in the impinger solutions. Based on these initial fixed bed capture results, it would appear from Run #1 and 2 that the combined use of Celatom plus CaO is not the best sorbent, especially for selenium at these temperatures. Overall, no large effects of pressure or sorbent ratio on capture efficiency were observed with the other elements. So it does not seem likely that capture of selenium by condensation of the hydride form at lower temperature will succeed since it was only detected once on one filter at 30°C . Investigation of sorbents for eliminating Se even at high temperature with the use of more active **alkaline** sorbent admixtures, however, should not be discounted.

Somewhat surprisingly, arsenic at 32 to 40% sorption exhibited the highest collection rate of the three elements. In examining the differences between runs 1 and 2, and those between Runs 3 and 4, it can be seen that there is no effect of higher pressure on the arsenic capture efficiency of the sorbents used. However, when comparing runs at equivalent pressures, there is a 25% increase in arsenic capture when the fixed bed contains only pure Celatom. This result was unexpected since the admixed CaO has generally performed very well as a sorbent for arsenic under **oxidizing** conditions, albeit at lower temperatures. The reasons for incomplete mass balance closure for arsenic may be somewhat similar to those of selenium hydride; if AsH_3 is still present leaving the reactor, then the impinger solutions that were used may also have been inadequate to absorb this acid-type compound. In contrast to oxidizing conditions, equilibrium calculation under reducing conditions show that there is primarily arsine present at 650°C in the gas stream.

There is also a possibility in all of these tests that some of the calcium may have reacted with the Celatom to form calcium-alumino-silicates preventing the reaction of calcium oxide with arsenic and lowering the active sites on Celatom particles. Further investigation into these interactions could help to clarify this. It is also of interest, that pure silica at quite high temperatures has been used successfully as an arsenic sorbent in bench-scale tests. Hence, future investigation of the use of neat silica as a sorbent may be warranted in these gasification systems, although it may not be as attractive as naturally occurring Celatom from an economic standpoint. Furthermore, it is also possible that arsenic capture efficiency by Celatom may improve at lower temperatures such as found in the system at Node c, after the hot desulfurizer which is not likely to be operable much above 500°C when zinc compounds are used at atmospheric pressure. Finally, leachability tests for arsenic were done, as shown in Table 2.29 with the aid of EPA Method 1311, to investigate the sorption in the samples obtained with the fixed bed experiments from Runs 2, 3, and 4. The arsenic leachability on all post-run materials was well below the regulatory limit of 5 mg/L, indicating that these types of single-use materials in connection with arsenic can be safely landfilled after exposure.

Table 2.29 ARSENIC LEACHABILITY AFTER CAPTURE ON CELATOM:

Levels of Much Less Than the 5 mg/L Regulatory Limit for
As-leachability Were Found for all Runs Tested

Run #	Leachability, mg/L
2	ND
3	0.6
4	0.4

In connection with the most metallic of the three contaminant elements tested, it is noted that zinc exhibited somewhat erratic capture behavior in these experiments. But, the absolute amounts of zinc captured by the fixed beds in Runs 1 and 2 were approximately the same, indicating once again that there seems to be no effect of pressure on capture efficiency. However, the partitioning between filter and impingers was very different for Runs 1 and 2, but this may be due to the fact that some material which deposited in the filter holder and adjacent lines was rinsed out and included with the impinger solutions. No further deposition at this location was noted in subsequent runs. When studying Runs 3 and 4, however, the amount of zinc capture in the fixed bed does not correlate with the increase of the Celatom fraction of the sorbent bed when compared to Runs 1 and 2. Normalized capture decreased by 50% in Run 3 compared to Run 1, but increased by 270% in Run 4 compared to Run 2. This inconsistent behavior has been observed in previous studies with regard to the capture of zinc by sorbents. Lowering the reactor temperature may yield more uniform zinc capture results, but the wide range and generally low values of mass balance closure for zinc may intrinsically be due to the method of introducing zinc into the system.

As solid ZnCl_2 is vaporized in the crucible, there is a possibility that deposition may have occurred in the lines immediately after the addition reactor, even though this area was heated. A deposition rate of only 80 wppm/min would reduce vapor phase zinc levels sufficiently to yield the results shown in Table 2.28. It also appears that the chloride compound of zinc may not have been the optimum compound for addition of zinc to the test system. This is, because, besides solid $\text{ZnCl}_2(\text{c})$ itself vaporizing uninterruptedly, with for example 34 ppm of $\text{ZnCl}_2(\text{v})$ appearing in the gas stream as follows:

there is also the possibility of reduction and/or oxidation reactions occurring with the fuel constituents, such as if H_2 is present:

this would provide an additional 7 ppm $\text{Zn}(\text{v})$ content at about the same temperature, while on the other hand with just the humidity content in N_2 or even in fuel, one could have found:

which provides no volatile zinc at about the same temperature, but suggests that by the formation of a dense ZnO film on the crystal surfaces, complete passivation of the ZnCl₂ crystals may have prevented volatilization from occurring after a short period of time. Analysis by merely sample-weight differences of the ZnCl₂ supply would clearly be affected by these different reactions without an actual correlation with the remaining zinc species instead of just overall weight differences.

2.3.4.4 Conclusions from Preliminary Trace Capture Tests

Several conclusions can be reached after studying the results of these trace metal capture experiments. The use of CaO as a sorbent is clearly not recommended for any of the metals in a reducing gas application at 650°C. No positive effects were observed as a result of the presence of this chemical in the fixed bed of any of the runs. This material has been used very successfully for arsenic capture at lower temperatures under oxidizing conditions, so only if it is determined that arsenic should be removed at a site much further downstream in the system, CaO may again be an appropriate choice. However, Celatom seems to be fairly effective as a sorbent for As, Se, and Zn under the present reducing fuel-gas conditions. For arsenic, it may be that some of the original AsH₃ is converted to As₂ which may be easier captured by the sorbent, while some remaining AsH₃ escapes from the system. Further study of the speciation of arsenic under sorption conditions may help identify more ideal conditions as well as better capture sorbents. The use of pure silica as a high temperature sorbent or the use of some other sorbents at lower temperatures may also improve arsenic capture efficiency.

Selenium, which is stable as H₂Se under these reducing conditions, showed consistent but low capture values in these tests. Lowering the fixed bed temperature may improve capture results, but investigation of alternate sorbents is also indicated in this case. Celatom has been shown to be an appropriate sorbent for zinc in these tests. Since it is likely that all of the zinc did not reach the bed due to deposition on cooler surfaces, it may be safe to say that no zinc escaped the system. If that is the case, the runs utilizing pure Celatom fixed beds show very good capture rates, and these values can probably be improved by reducing the bed temperature to the gas conditions found just prior to a turbine combustor or fuel cell anode plenum, such as in either the IGCC or IGFC systems.

2.3.5 STRATEGIES FOR CONTAMINANT CONTROL

This subtask examines the foregoing work and its conclusions from a control strategies point of view and compares the effort to our originally stated experimental priorities (Subtask 230) of the Work Plan under Task 200. Answers to various questions posed in Section 2.2.3 are presented below.

- A. What is the role of gasified coal as a source of significant Trace Element concentrations which when vaporized under entrained-flow gasification would be of definite concern if emitted into the environment?

It was established during the introductory survey and background for this investigation that there definitely are numerous contaminants and trace elements (both metals and metalloids as well as organic and inorganic compounds) which, over the years, have become of significant concern to various groups in industry and government, resulting in numerous coal combustion and emission studies at home and abroad.¹⁰ A number of elements have been identified in these studies by different government organizations as major and minor contaminants (mostly acid gases such as H_2S , SO_2 , HCl , NO_x , and CO_2) that can become a threat to the environment when emitted in large quantities into the atmosphere. However, small amounts of trace elements of a definitely toxic and sometimes volatile nature are also emitted and classified as Hazardous Air Pollutants (HAP's) now being regarded with increasing concern. Almost every one of these toxic species are, to a great or lesser extent, associated with the combustion, and now also the gasification, of coal.

Generally, although the contaminant quantities from different grades and different sources of coal may vary, it has been shown that the five trace elements on which this study has focused (as enumerated under B) can be readily volatilized by gasification of standard Illinois #6 coal. This coal was selected as a typical, fairly high sulfur composition to represent the most significant trace elements that would be volatilized into coal gas by standard gasification processes. Reactor conditions simulating entrained flow gasification based on the Texaco Coal Gasifier were selected as the process parameters that represent fairly wide usage, and for which there is a well-known background and database.

- B. How do "gasification" conditions, including the production of high temperature ash and fly ash particles, influence the initial volatilization and later recondensation and absorption of important trace contaminants from coal gas?

As to the influence of gasification conditions on the immediate emissions of contaminant species (mostly in reduced form together with alumino-silicate ash particles) which can later recondense and form various ash absorption products, a number of very important insights were gained. It was established under Subtask 320, that the most likely amounts of trace elements to remain volatile after initial slight cooling and hot filtration of the gasified product stream would be: As, Se, Sb, Zn, Pb, and to a somewhat lesser extent also Cd and Hg. The five main trace elements that were selected for further study under the program were thus chosen on the basis

of their volatile behavior under realistic gasification conditions, their abundance in typical coal sources, as well as their toxicity in the environment. Hg remains volatile regardless of reduced or oxidized form, but occurs at much lower concentrations compared to other trace species. Similarly, Cd occurs in much lower abundance and, therefore, did not merit immediate inclusion in this initial effort.

With regard to the fate of the other and heavier elements (e.g., Ni, Fe, Mn, Cr, and certain metallic transition elements) initially carried over with gasified coal-gas in intimate contact with the simultaneously generated ash and fly ash particles, it should be noted that under reducing conditions during the initial cyclone plus gas filtration stages of cleanup (e.g., using high temperature ceramic filters), the gas stream will probably shed most of its heavy metallic content together with the separated ash. The heavier elements either remain part of the alumino-silicate ash particles or become reassociated with them through condensation shortly after gasification. This is probably due to lower temperatures and the lack of transition metal volatility even when in the metallic state.

Although the role of reducing gas in contaminant vaporization during gasification is not yet fully understood, the trace element behavior is quite different compared to direct "combustion" of coal when species are completely oxidized at very high temperature and then can be emitted as gases which contain volatile compounds of chromium, manganese, and possibly nickel, cobalt, and beryllium. All of these are considered toxic and, therefore, are classified as HAPs. Clearly, in a milder process with lower peak particle temperatures such as in the gasification of coal which puts out a reducing gas, there is an advantage over the high temperature direct combustion processes in being better able to eliminate heavy metallic elements from the gas stream as part of the ash that is generated during gasification.

- C. What subsequent fate befalls the unabsorbed, mostly volatile, trace elements and their species in the downstream Cleanup and Power Generation Equipment?

The fate of the selected trace elements that remain volatile in the gas stream and are considered significant in terms of their interactions with other parts of an integrated system when using gasification has been examined by both calculation (Subtask 310) and by near-equilibrium sorption experiments (Subtask 330). Simultaneous elimination of trace elements from coal gas with the sulfur content during hot-gas desulfurization was first considered. Originally, it was proposed that zinc ferrite - at that time the best but mechanically somewhat unstable sorbent option - should be employed under atmospheric, 550°C equilibrium conditions to investigate the possible simultaneous absorption of the five trace species at their nominal coal-gas contaminant levels. However, other materials such as Z-sorb and ZT-4 (both versions of zinc titanate) soon became prominent as better sorbent options. After some delay a sample of (ZT-4) zinc titanate was obtained which proved sufficiently stable at 500°C but at this temperature it was shown that neither As, Se, nor Cd, or sulfur itself, could be absorbed to the required extent to meet fuel cell tolerance levels. Thus, to achieve additional absorption down to fractional ppm-levels of trace species in the exit stream from a desulfurizer (containing zinc compounds) remains difficult.

Hence, it is concluded from our equilibrium TGA experiments in Subtask 330 that the control strategy option for complete cleanup of coal gas down to very low ppm or sub-ppm levels of contamination requires that additional, highly efficient, sorbents must be employed in order to final polish the coal gas stream of its last trace elements and remaining H_2S content. In addition, it appears from thermodynamic calculations (Subtask 310) that desulfurization with zinc compounds should normally take place under as high a pressure as possible to safeguard against zinc loss from the sorbent material. Unfortunately, the ambient pressure TGA apparatus cannot be used to study this behavior experimentally under elevated pressure conditions. However, future work such as this may very well be managed in the trace element capture facility which is discussed under Subtask 340.

- D. Can current, hot-gas cleanup and polishing technologies reduce volatile trace element content to tolerable levels for different power generating systems, and maintain legally acceptable limits for emission into the atmosphere?

The results of our Subtask 340 studies have indicated that there is a definite potential for once-through, almost complete, removal of trace elements from fuel gas streams at elevated temperature and pressure. Although the experimental work has not yet provided for optimization of such a process, the observed removal of As, Zn, and to a lesser extent Se from simulated coal gas at $650^\circ C$ with a new sorbent material, suggests a valid approach. The relatively inexpensive, commercial, alumino-silicate sorbent Celatom was able to capture certain amounts of these trace species under high temperature reducing conditions both at atmospheric pressure and utilizing high pressure fuel gas. The spent Celatom containing absorbed contaminants can likely be safely disposed in landfill since its trace species leachability has been shown to be well below regulatory limits.

- E. If inadequate removal of trace contaminants occurs using current hot-gas cleanup techniques, are there better methods available?
- A packed bed of special sorbent added to the system immediately downstream of the sulfur hot-gas cleanup train could be installed for capture of trace elements at approximately $550^\circ C$ and 10 atm pressure, since zinc desulfurization normally operates at that temperature and is also enhanced by high pressure operation.
 - Separation of ash from the cyclone hopper (removing iron-rich ash particles by density) and alumino-silicate fly ash from the candle-filters could be used as a source of low cost sorbent for final trace contaminant capture, as was demonstrated by the cascade impactor experiments in Subtask 320. This material can be used either inside the hot-gas cleanup reactor or in a separate polishing reactor.
 - Addition of the fly ash or any other once-through trace element capturing sorbent (e.g., Celatom) inside, but directly above the zinc titanate desulfurizer sorbent, could be designed for any regenerable scrubber. This has the advantage of reducing the number of reactors required for gas cleanup, although it will increase the size and/or height of the hot-gas contaminant removal unit.

Building upon the above discussed options, a full scale system for trace element capture can be envisioned as consisting of some or all of these possibilities. Before these concepts can be implemented, however, more trace element capture experiments need to be conducted to define the optimum ash separation method and sorbency, and also to explore the use of recycled ash from different coals for its sorbent properties and to identify the optimum sorption temperature/pressure conditions. Nevertheless, the promising results obtained from this program suggest that systems can be designed to efficiently reduce trace element concentrations at high temperature to levels that are satisfactory for carbonate fuel cell and advanced turbine operation.

Because of the large amounts of sulfur usually involved with coal gas, regenerable desulfurization (probably employing zinc compounds) will continue to be a good method for the major removal of sulfur species. However, such sulfur absorption will always have to be followed by additional cleanup or polishing steps in order to remove any remaining small amounts both of sulfur (which this primary process cannot absorb) and trace amounts of metalloid and metallic contaminant species which can cause equipment decay and also must not be allowed to be emitted into the atmosphere. The PSIT concepts of once-through sorbent use that meets EPA leachability standards regarding landfill safety is one method. ERC is currently also working on a polishing method which utilizes a high temperature 'regenerable' liquid that may be satisfactory for final removal of most of the metallic contaminants from coal gas.

In this connection, it should also be pointed out that the fate of the major and minor (not trace) contaminants such as alkali metal vapors, HCl , and ammonia, are still of concern to advanced power conversion systems (IGCC and IGFC). Slight attention has been paid to these contaminants which may not be as easy to remove as generally thought but because of their large concentrations compared to trace species will present a significant problem. After fly ash absorption and final Celatom polishing, sodium and probably potassium vapors and HCl may be sufficiently removable. Volatile alkali species, of course, remain of concern to turbine operation while HCl can cause major fuel cell decay as has been indicated by the tolerance levels illustrated in Table 1.6.

2.4 CONCLUSIONS AND RECOMMENDATIONS

To sum up the investigation of the fate of contaminants at the various sites that are of concern to evolving integrated power systems, the five most significant trace elements generated by coal gasification have been identified. Also, a pattern for their control and removal at high temperature is now evolving. Figure 3.1 shows approximate contaminant levels of major and trace contaminants as they move through the gasification/cleanup system shown in Figure 2.1. Initial concentrations at gasifier exit are shown as well as carbonate fuel cell anode tolerance levels are indicated by approximate bands. As can be seen, most contaminants are reduced by flyash sorption at node b. As are removed in hot-gas cleanup system at node c, along with H_2S . Further polishing by physical capture (node d) may be desirable to bring the levels of H_2S , HCl , Zn and As to acceptable anode side tolerance levels shown in the figure.

Figure 3.1 APPROXIMATE CONTAMINANT REDUCTIONS DURING COAL-GAS CLEANUP:

Levels of Key Trace and Major Contaminants are Shown at Different Node Points

Because only limited theoretical calculations were done within the scope of the current program and additional experimental confirmations are also needed, there are still a number of areas where future work is recommended. For example, the following general classes of studies should be considered.

- Thermochemical Calculations

The power of computer research techniques has become well established and together with additional modeling would further advance our general ability to quickly predict trace element behavior and effects on IGCC and IGFC systems. Three specific areas requiring further development are:

- 1) *The Gasifier*: Formation and interaction of complex aluminosilicates with the five trace elements to be correlated with experimental partitioning data and also to be explored as a function of different existing gasification conditions.
- 2) *Hot-Gas Cleanup*: Interaction of trace elements with sorbents other than the current zinc titanate desulfurization sorbent should be considered. Modeling of contaminant interactions with zinc titanate sorbents using equilibrium thermochemistry has had considerable success.
- 3) *NiO-cathode on O₂-rich side of Matrix*: Interactions of trace elements in this oxidant part of the carbonate fuel cell after the anode exit-gas is recycled and oxidized (i.e., for CO₂ recovery) are quite likely because at this point trace species become re-exposed to the molten carbonate electrolyte under different (oxidizing) conditions. Such interactions, therefore, need to be addressed probably initially in terms of thermodynamic calculations and further on in terms of small scale fuel cell testing.

- Gasification Experiments

In our current program, the concentration of trace elements as a function of absorption on various ash particle sizes was measured primarily to understand general volatility behavior. Only limited experiments were conducted to start assessing the effects of gasification conditions (and temperature) on changes in ash formation and trace element volatilization. Results indicate that trace element vaporization is dependent on the gasifier's stoichiometric conditions, where the amount of an element that vaporizes decreases with increasing partial pressure of oxygen in the system and the simultaneously increasing temperature of the ash particles. To explore these interactions 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 parameters should be considered.

- Thermogravimetric Experiments

Initial equilibrium experiments of weight loss or gain in a thermogravimetric apparatus (TGA) should usually be considered as a preliminary test in determining new developmental sorbent stability and the affinity for removing low level gaseous trace species. This will also serve to confirm whatever the equilibrium thermochemical calculations may have indicated. Such TGA-runs can be very simply and rapidly performed, and can also be used to establish the regenerability of the new sorbent materials in different gas atmospheres. Such runs have been performed at ERC during the current project and also in connection with a new liquid sorbent with which to scrub high temperature coal-gas for final trace element polishing.

- Trace Element Capture Experiments

In-line experiments, which can closely simulate high temperature and pressure contaminant sorption conditions, can elucidate the kinetics of immediate (post-gasification) trace element capture using a variety of coarse ash, fly-ash and other types of materials. But, also investigations of activated sorbents, such as Celatom as described by PSI, employed for final removal of significant trace elements (the 5 previously mentioned elements as well as Cd and Hg) should continue to be studied by this trace capture methodology. It is further recommended to also expand the sorption test matrix to include studies of the capture of additional major contaminant elements such as chlorine and alkali species. And a further area would be to combine activated sorbents with zinc-based, hot-gas desulfurization (in a single or dual bed reactor immediately after the desulfurizer) and evaluate the combined effect of simultaneously removing major and trace elements in one unit together with any remaining sulfur contamination. In this connection the use of recycled, reconstituted, alumino-silicate gasifier ash as a low cost final trace metal sorbent should definitely be explored.

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List of Acronyms

AAS	Atomic Absorption Spectrometry
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
ERC	Energy Research Corporation
HAP	Hazardous Air Pollutant
HRSG	Heat Recovery Steam Generator
ICP	Inductively Coupled Plasma (Spectrometry)
IGCC	Integrated Gasification Combined Cycle
IGFC	Integrated Gasification Fuel Cell
METC	Morgantown Energy Technology Center
NAA	Neutron Activation Analysis
NEPA	National Environmental Policy Act
PIXE	Proton Induced X-Ray Emission
PSI	Physical Sciences, Inc.
PSIT	PSI-Technology Company (see PSI)
SOLGASMIX	Solid/Gas/Mixture (Software for Thermochemical Calculation)
TAPP	Thermochemical and Physical Properties
TGA	Thermo Gravimetric Analysis
UND-EERC	Univ. of North Dakota, Energy & Environmental Research Center

APPENDIX A

TREATMENT OF PROTON-INDUCED X-RAY EMISSION (PIXE) DATA

Because the PIXE procedure determines the absolute mass of an element *i* within the incident beam, the raw background concentration data presented in Table A.1, are reported on a ($\mu\text{g}/\text{cm}^2$) basis. These concentrations were converted to absolute mass of element *i* in the filter by multiplying them by filter area, yielding the data shown in Table A.2. In Tables A.1 and A.2, < indicates that the element was present in concentrations lower than the detection limit for the element in the sample. The final conversion to wppm is shown in Table 2.13 in the text, summarizing background trace concentrations on a $\mu\text{g}/\text{g}$ basis for only those elements present in measurable concentrations. As these appendix tables indicate, the major contaminants in the sample blanks were sulfur at a level of $10 \mu\text{g}/\text{cm}^2$ on the impactor stage blanks (most likely contributed by the grease), and bromine at a level of $0.3 \mu\text{g}/\text{cm}^2$ in the blank of the final filter.

**Table A.1 PROTON-INDUCED X-RAY EMISSION OF
BLANK PLATES AND FILTERS:**

When Values are Shown After < this is the Detection Limit of the Method per cm^2 , and Implies that NO Background Correction is Needed

Element	Cascade Impactor, $\mu\text{g}/\text{cm}^2$			Polycarbonate Filter $\mu\text{g}/\text{cm}^2$
	Stage 1	Stage 5	Stage 7	
<u>Majors</u>				
S	11	8.6	10	<0.029
Br	0.0012	0.00083	0.0012	0.29
Na	-	-	-	-
<u>Minors</u>				
As	-	-	-	-
Se	<0.00084	<0.00082	<0.00069	<0.0011
Sb	-	-	-	-
K	<0.032	<0.030	<0.034	<0.022
<u>Trace Metals</u>				
Zn	0.016	0.015	0.017	0.0038
Pb	<0.0024	<0.0023	<0.0019	<0.0031
Cd	-	-	-	-
Hg	-	-	-	-
Ni	0.0026	0.0021	0.0023	0.0073
Fe	0.044	0.041	0.049	0.0093
Mn	<0.0015	0.0014	<0.0013	<0.0013
Cr	0.0013	0.0012	<0.0019	0.0042

**Table A.2 PROTON-INDUCED X-RAY EMISSION OF
BLANK PLATES AND FILTERS:**

When Values are Shown After < this is the Detection Limit of the Method per cm², and Implies that NO Background Correction is Needed

Element	Cascade Impactor, $\mu\text{g}/\text{filter}$			Polycarbonate Filter $\mu\text{g}/\text{filter}$
	Stage 1	Stage 2	Stage 3	
<u>Majors</u>				
S	170	180	210	<2.8
Br	0.018	0.017	0.024	21
Na	-	-	-	-
<u>Minors</u>				
As	-	-	-	-
Se	<0.013	<0.017	<0.014	<0.10
Sb	-	-	-	-
K	<0.51	<0.62	<0.70	<2.1
<u>Trace Metals</u>				
Zn	0.26	0.31	0.35	0.28
Pb	<0.038	<0.047	<0.039	<0.29
Cd	-	-	-	-
Hg	-	-	-	-
Ni	0.042	0.044	0.047	0.054
Fe	0.77	0.84	1.0	0.69
Mn	<0.024	0.029	<0.027	<0.12
Cr	0.02	0.025	<0.039	0.31

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PIXE trace element data were corrected for background concentrations as follows. Blank (greased) samples were analyzed, and trace element concentrations Xb_i reported, where Xb_i represents μg of element i per cm² of filter (Table A.1). Gasification ash samples were then analyzed, yielding trace element concentration data Xa_i for each element i . In each case, the concentration X_i represents the mass of element i within the analyzed area A_{spot} . Now,

$$Xb_i = xb_i / Ab_{\text{spot}} \quad (1)$$

and

$$Xa_i = (xa_i + xb_i) / Aa_{\text{spot}} \quad (2)$$

where xa_i is the mass of element i in the ash within the analyzed area, and xb_i is the mass of element i in the greased filter within an equivalent analyzed area. Ab_{spot} is the area analyzed in the background measurement, and Aa_{spot} is the area analyzed in the ash sample measurement.

For our samples, $Aa_{\text{spot}} = Ab_{\text{spot}} = A$. Combining the two equations above and solving for xa_i yields:

$$xa_i = A (Xa_i - Xb_i). \quad (3)$$

To determine the mass concentration of each element i , ca_i , the total sample mass within spot area A is, therefore, needed. This is simply the mass collected on the filter, m_{ash} , normalized by the fractional area of the spot (A/A_{filter}). The mass concentration of element i can be expressed as

$$ca_i = xa_i / \{m_{\text{ash}}(A/A_{\text{filter}})\} = A(Xa_i - Xb_i) / \{m_{\text{ash}}(A/A_{\text{filter}})\} \quad (4)$$

or

$$ca_i = (Xa_i - Xb_i)(A_{\text{filter}} / m_{\text{ash}}). \quad (5)$$

For each stage analyzed, the area A_{filter} should represent the active area of the substrate or filter, i.e., the area over which the ash sample is uniformly deposited. Stage 1 samples were non-uniform, with the central region of the impaction substrate containing most of the sample mass. For the Stage 1 sample, it was estimated that 80% of the ash mass was deposited in this central spot. The area A_{filter} was, therefore, the area of the central deposition zone, and the mass was 0.80 of the total mass collected. For Stages 5 and 7, a deposition pattern consisting of a series of small sample piles was observed. During PIXE analysis, the proton beam was focused in a 1.267 cm² spot (1.27 cm diameter) encompassing several of these piles. The area used in data reduction for Stage 5 and 7 samples was modified to eliminate the non-deposit parts of the plates. For the final filter, the sample was uniformly deposited across the central 97 mm of the 110 mm diameter filter; the central 97 mm region was used to determine area A_{filter} for data reduction.