Trace Metal Transformations in Gasification

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Objectives

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

Background Information

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

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

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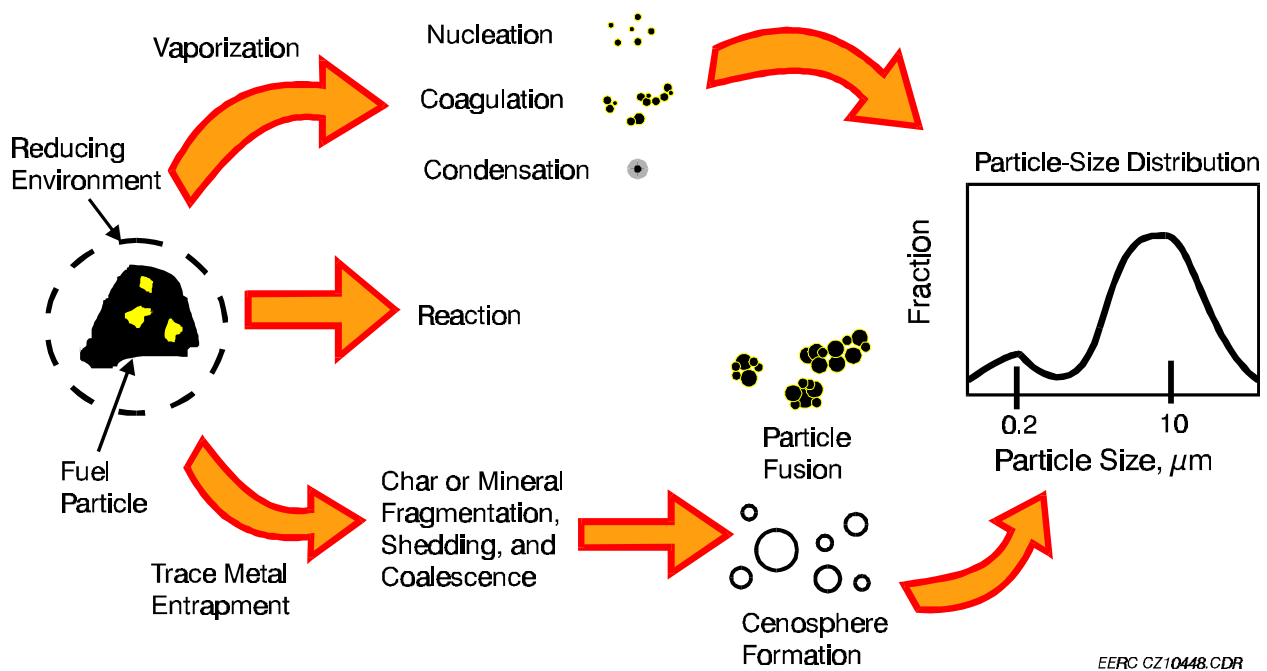

Figure 1. Trace metal transformations and partitioning.

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Project Description

The approach of this project is to identify and model important physical and chemical transformation mechanisms of the trace elements during gasification as a function of coal compositions (trace element abundance and association) and gasification conditions. Identification of the reactions and transformations, coupled with accurate modeling of trace element behavior, is providing essential information for the identification of the form of the inorganic species. Gasification conditions—such as reducing and oxidizing atmospheres, gas-phase composition, pressure, and temperature—influence the partitioning of the air toxics between various gases, liquids, and solid inorganic components as a function of location in the gasifier. This information will be used to identify the most effective control technology by predicting the form of the trace element as a function of operational conditions. The model will be used to predict the initial partitioning of the metals in the gasifier and their form downstream of the gasifier in the gas cleanup systems.

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

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

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

The identification of control technologies will be incorporated into the project after most of the testing and modeling are complete, at which time multiple scenarios can be addressed using the data and models. The model testing and verification will consist of testing the model and assumptions on the transport reactor scaleup facility located at the EERC.

Results

The levels of the metals found in the coals are summarized in Table 1. The associations of the metals with minerals and organic portions of the coal were described in detail at the last conference (Benson and others, 1994). Table 2 summarizes the generalized associations found for the metals.

Partitioning of Trace Metals. The partitioning of trace metals was ascertained by determining the fraction in which the different trace metal species were collected. Metals that are not vaporized during gasification remain in the residual ash and are collected in the size fraction greater than 1 µm. Metals that are vaporized but condense in the system are collected in the submicron fraction. Metals such as Se and Hg, which may not condense in the system but remain in a vapor state, will escape the multicyclone system and will be collected in the impinger train. Several runs were made in the PDTF varying pressure, gas temperature, and O/C ratio.

Comparison of the average percentages of each element in the collection devices shows that a substantial portion, 40% or more, of the total amount of the trace elements is recovered in the coarse ash of the first cyclone (Figures 2 and 3). The trace elements have remained with the larger ash particles, have recondensed, or have been captured on the ash. Cr, Ni (Figure 3) and, surprisingly, Hg (Figure 2) partition with the coarse ash, with an average of more than 65% remaining in the >3-µm fraction of collected sample, with the balance appearing in the

TABLE 1

Abundance of Trace Metals in Coals Tested (µg/g, dry coal basis)

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

TABLE 2

Trace Metal Associations

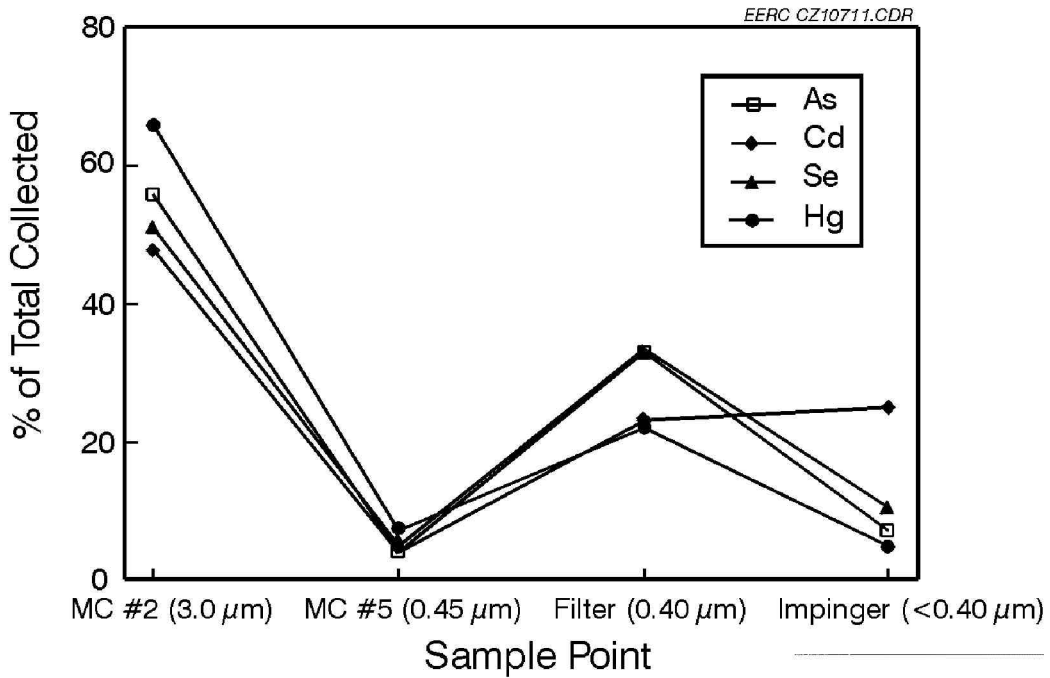| Element	Associations
As	Pyrite, other sulfides, arsenates
Cd	Sulfides, clays
Cr	Clays, organic compounds
Hg	Pyrite, other sulfides
Ni	Pyrite, clays, organic compounds
Pb	Pyrite, other sulfides, clays
Se	Pyrite, other sulfides, organic compounds, sulfate

Figure 2.   Average percentages of As, Cd, Se, and Hg collected in size fractions of the sampling train.
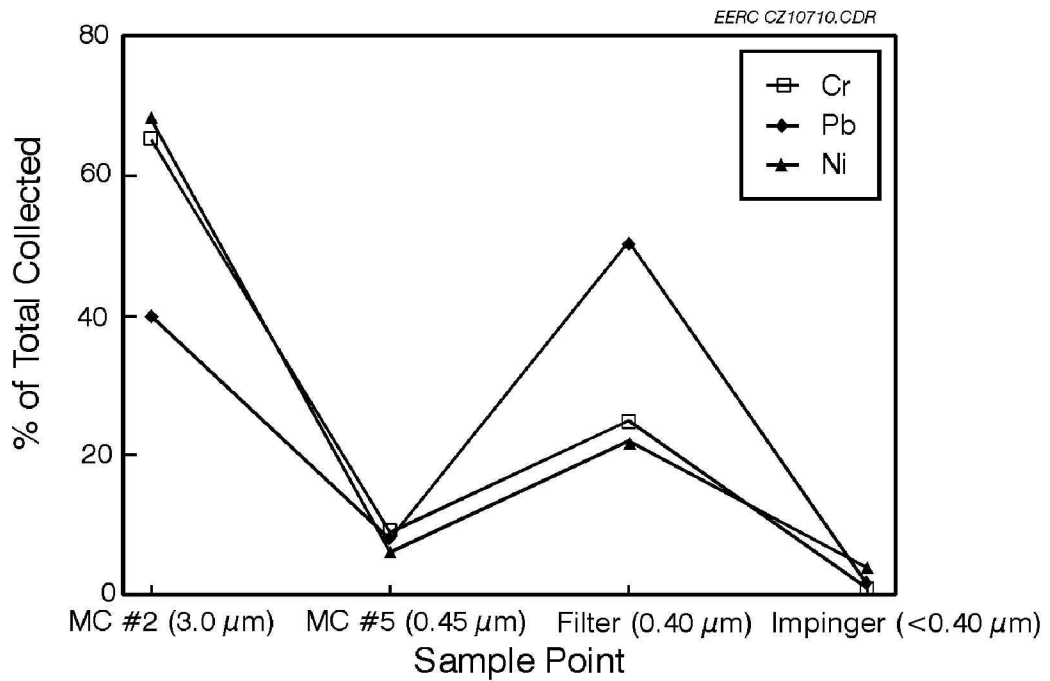
Figure 3.   Average percentages of Ni, Cr, and Pb collected in size fractions of the sampling train.

1–3-µm fraction or the <0.4-µm filter fraction. Very little Cr and Ni pass through the filter into the impingers (Figure 3), which is probably an indication that they are nonvolatile species, such as refractory oxides. The behavior of Hg is more complex. Although much of the Hg is collected in the cyclones and filter, under certain test conditions up to 30% of the Hg is in a volatile form passing through the filter into the impingers. Pb partitions primarily in the 1–3-µm ash fraction and the <0.4-µm filter, probably as a very fine oxide fume (Figure 3). Generally, little Pb passes through the filter into the impingers. Along with Hg, the trace elements As, Cd, and Se showed appreciable quantities in the impingers. Cd in particular appears to be exceptionally volatile or in the form of a very fine fume, with approximately 25% of that recovered present in the impingers (Figure 2).

In general, it can be summarized that Hg, As, Cd, and Se appear to be the most volatile, simply because a greater portion of the mass of these elements is in what would be considered condensed volatile size fractions. Here we are assuming that the trace metals in these fractions, since they are associated with particulate that is essentially less than 0.45 µm, were in a vapor phase until capture. In contrast, Ni and Cr, along with Pb to a certain degree, concentrate primarily with the larger-sized particulate and are classified more as nonvolatile or vaporized species, with Pb showing consistently more mass in the 1–3-µm range than Ni and Cr. Caution must be taken in making these types of assumptions, because some of these trace metal species may be condensing onto the particulate already trapped in the multicyclones or on the filter. For example, elemental Hg and mercury chloride are known to be captured on activated carbon, coal char, and fly ash. Of special concern in these results is the amount of unburned carbon present in the ash samples. Because the PDTF tests were all run under reducing conditions, unburned carbon was found to varying degrees in nearly every size fraction of product ash collected. It is possible that some of the trace metals have not been released from their original coal host minerals or particles. Several ash grains from the largest cyclone were analyzed using wavelength-dispersive spectrometry (WDS) and yielded only Ni and Hg in iron–sulfur-rich particles and Cr in aluminosilicate particles. When this information is compared with Table 2, it could be inferred that trace metal-bearing pyrite and clay mineral aluminosilicates may not have yielded the trace metals contained within them to a vapor or fine aerosol form before they were quenched in the multicyclone. Ideally, the PDTF test runs should have 100% carbon conversion, which would ensure a minimum of carbon carryover and would maximize the release of trace metals into true postflame forms.

The effects of pressure were not clear from the data collected; however, some trends were noted for O/C and temperature effects. Figures 4 and 5 illustrate the effect of O/C ratio on the abundance of As, Cd, Se, and Hg in the assumed vapor phase at 1500° and 1000°C initial gasification temperatures, respectively. The results indicate a general decrease in As, Cd, and Hg with increasing O/C ratio and a slight increase in Se with increasing O/C ratio. A possible explanation for these results is that more oxidized forms of As, Cd, and Hg are less volatile, whereas the oxidized form or species of Se is more volatile. The lower volatility of reduced Se relative to the oxide form has been discussed by Dismukes (1994).

The effect of initial gasification temperature on the abundance of trace metals in the gas phase is depicted in Figure 6. At a constant pressure of 50 psi and an O/C ratio of 2.0, increasing the gas
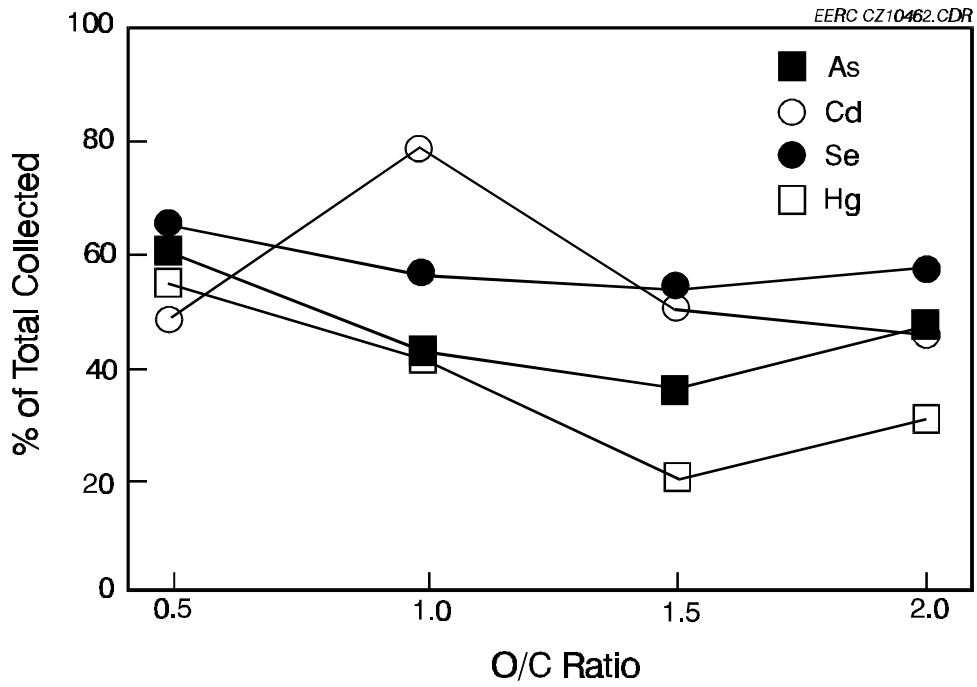
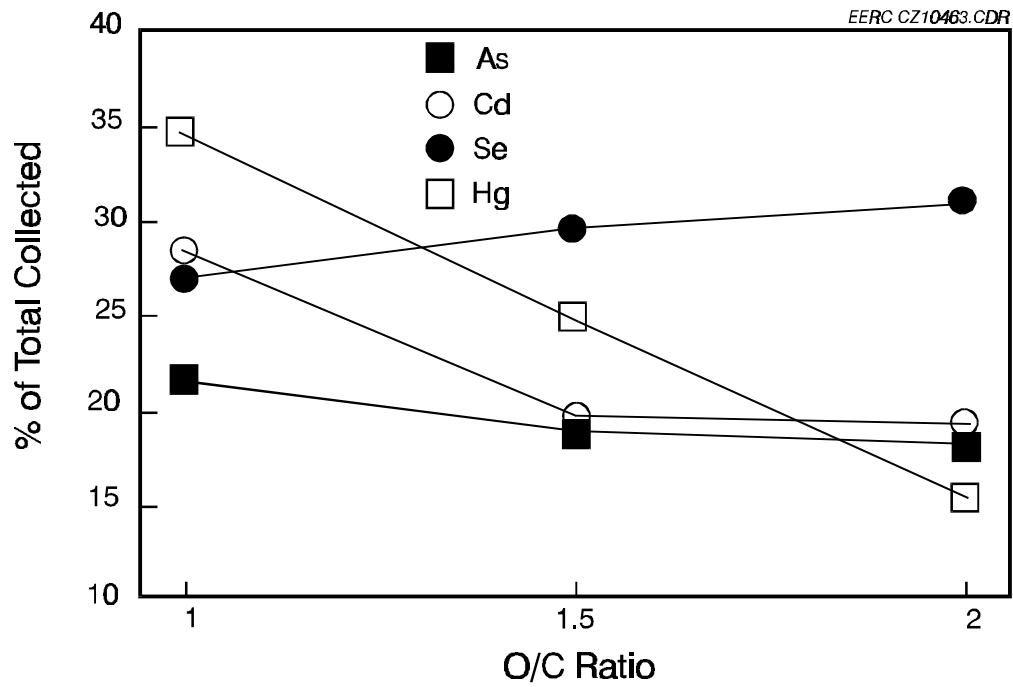Figure 4.   Trace metal distribution vs. O/C ratio for Illinois No. 6.

Figure 5.   Trace metal distribution vs. O/C ratio at 1500°C.
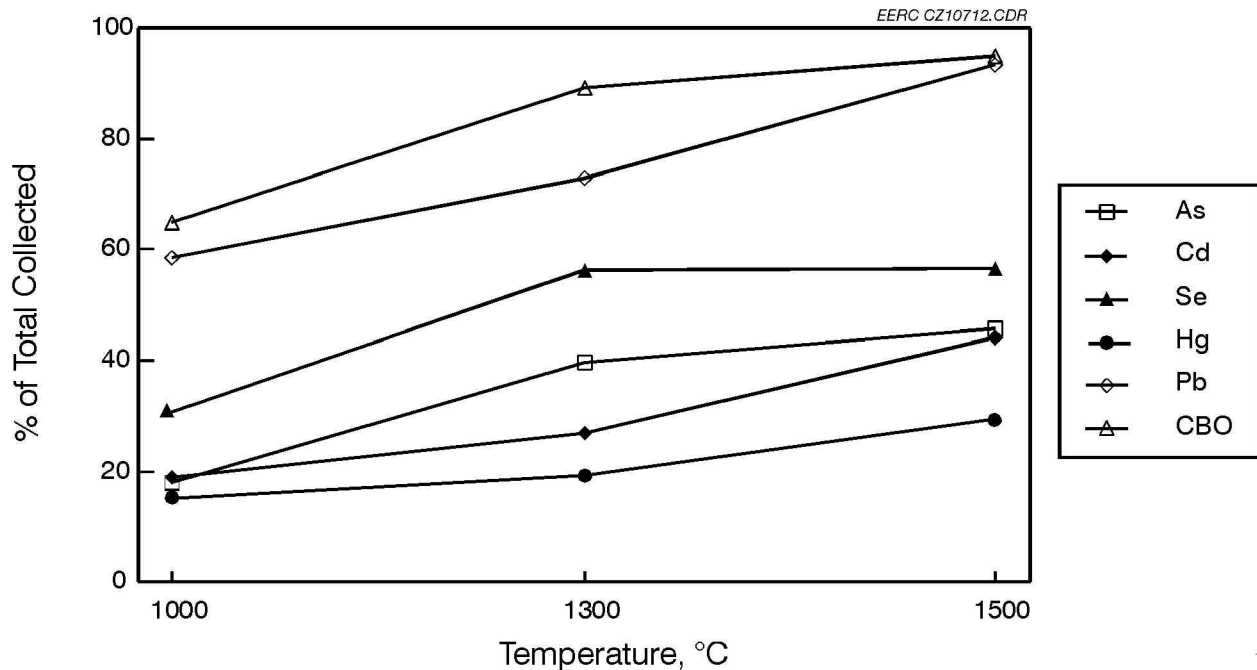
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Figure 6.   Trace metal distribution vs. O/C ratio at 1000°C.

temperature causes the abundance of As, Cd, Se, Hg, and Pb to increase. The effects of carbon burnout, which also tends toward greater values with increasing temperature, may be over-shadowing the temperature effect somewhat. Figure 7 illustrates a temperature effect by showing that the concentrations in the vapor phase of two of the more volatile elements, Hg and Se, increase with increasing temperature at constant carbon burnout.

Predicting Trace Metals Behavior

Model Design. A computer model, TraceTran, to predict the evolution of major, minor, and trace elements during coal combustion and gasification has been created (Erickson and Benson, 1993), based on the algorithm shown in Figure 8.

The first task of the model is to determine the associations of the major, minor, and trace elements in the coal prior to utilization. The association of the elements prior to utilization will affect their phase, size, and composition distribution in the residual ash and gas streams. The three primary inorganic associations are water, organic, and mineral. Water-associated constituents are generally in the form of sulfates or chlorides present in the moisture of a coal particle. The organically associated constituents are generally found as the salts of carboxylic acid groups attached to the carbon matrix and as oxygen replacement (such as organic sulfur).
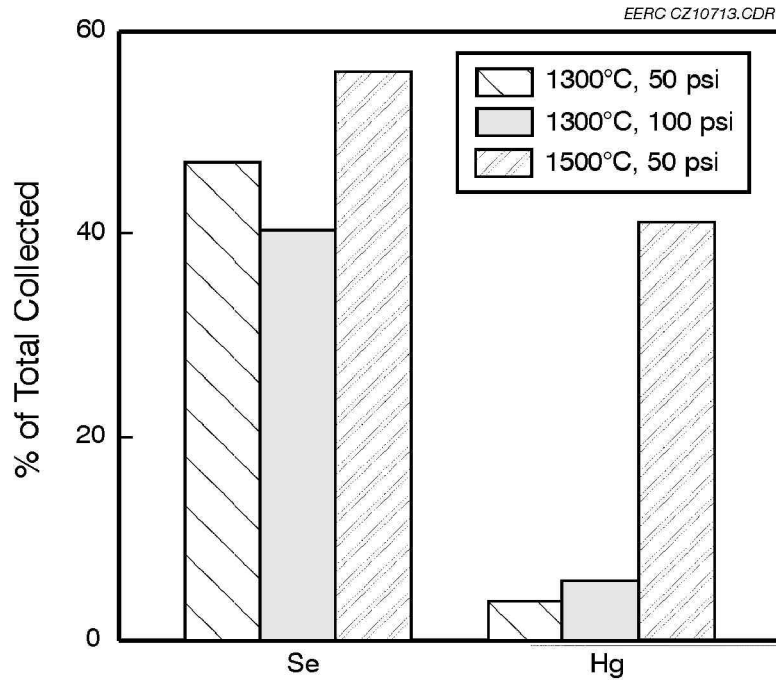
Figure 7.   Concentrations in the vapor phase of Hg and Se with increasing temperature at constant pressure and carbon burnout.
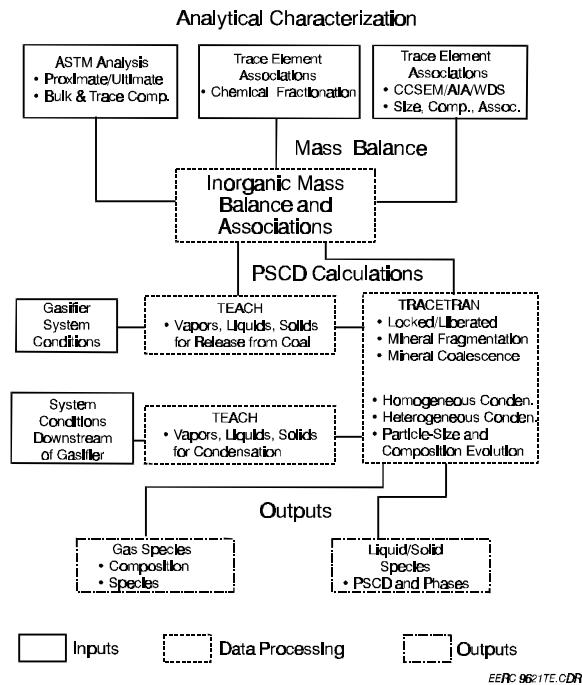

Figure 8.   Model algorithm for trace element emissions.

The mineral associations are elements that comprise discrete minerals in the coal (such as clays, carbonates, and sulfides).

Because of the complexity of the interaction of inorganics during coal gasification, the mineral associations are further divided into mineral type, trace, minor, and major element content, size, and juxtaposition. Juxtaposition refers to the association of the minerals with the coal matrix and with other minerals. A locked mineral is intimately associated in the coal particle, while a liberated mineral is external to the carbon matrix. The detailed mineral classification is very important because different minerals behave differently. For instance, carbonates will commonly release CO_2, resulting in a greater potential for mineral fragmentation, depending on the system conditions. Clays that contain high levels of moisture may fragment initially because of the release of H_2O from their porous structures. Silicates are much less prone to fragmentation because they lack any of the previously discussed components.

Many of the mineral particles encountered in coal utilization contain trace and minor components. To predict the transformations of the trace and minor elements effectively, their distribution among the minerals is required. Whether a mineral is locked within the coal matrix or external to the coal can also have a large impact on its transformations. Locked minerals will be much more likely to coalesce with other minerals and organically associated constituents than are the liberated minerals. The liberated particles will also experience a slightly different gas environment during coal gasification, since they are not in intimate contact with the highly reducing, exothermic reaction of the carbon matrix.

Once a mass balance is performed around the coal input data, it is necessary to determine which of the inorganic components will be vaporized during the initial conversion process. These calculations are performed with the use of a thermochemical equilibrium program created at the EERC. This code has been upgraded to include some of the appropriate trace element phases, and the ability to include more phases is being considered through the use of additional thermochemical equilibrium programs. With the exclusion of the vaporized species, the remaining constituents are processed through algorithms for mineral fragmentation, coalescence of both minerals and organically associated species, and the shedding of resulting particles. Examples of data obtained from the thermochemical equilibrium portion of the code are illustrated in Figures 9–11.

The fragmentation, coalescence, and shedding algorithms have been developed with the aid of data from full-scale systems and data generated in pilot- and laboratory-scale facilities. These algorithms are designed using data on various frequency distributions for each of the minerals and physical processes. The organically associated species that do not readily volatilize will also undergo coalescence with mineral particles as a function of the surface area of the minerals during coalescence. A portion of the organically associated species also homogeneously coalesces. The liberated minerals undergo fragmentation, but do not appreciably coalesce with other minerals because of their lack of intimate contact with the coal.

The state of the volatile species at the desired downstream conditions will then be determined. The quantity of species that will condense prior to the given conditions is calculated from the
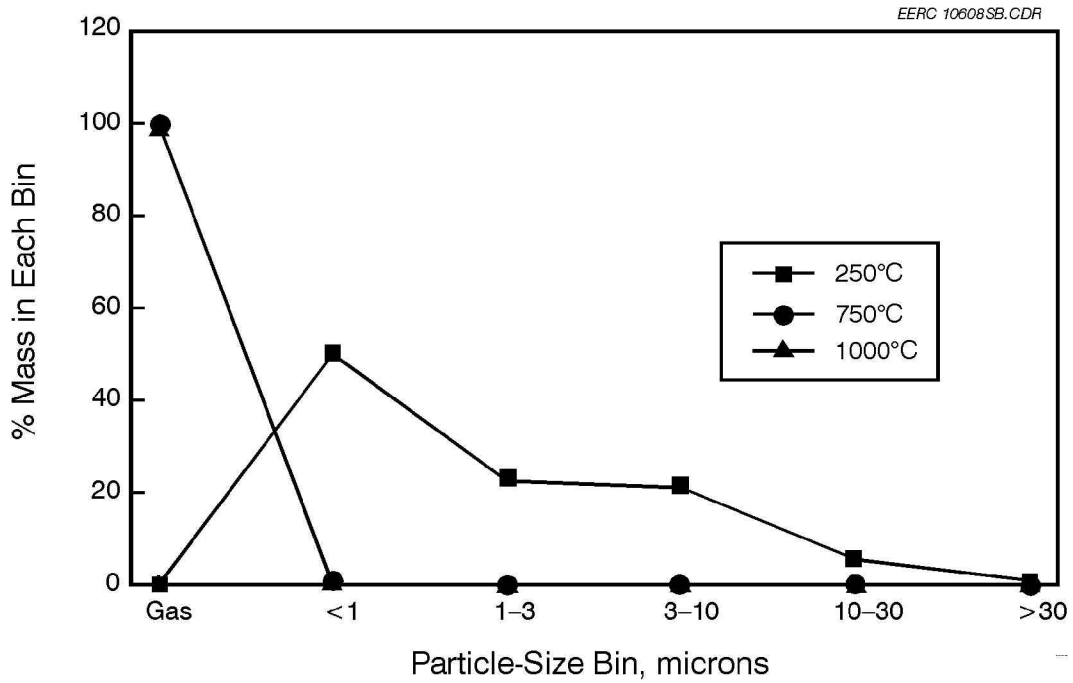
Figure 9.   Illinois No. 6: TraceTran predictions – arsenic particle-size distribution.
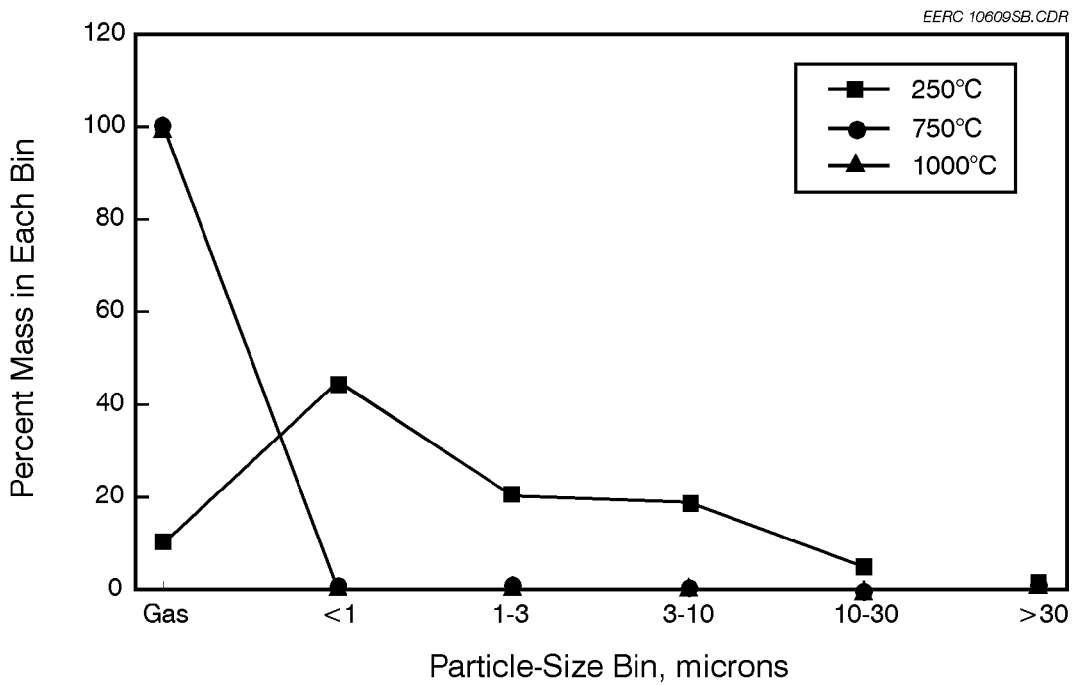
Figure 10.   Illinois No. 6: TraceTran predictions – cadmium particle-size distribution.
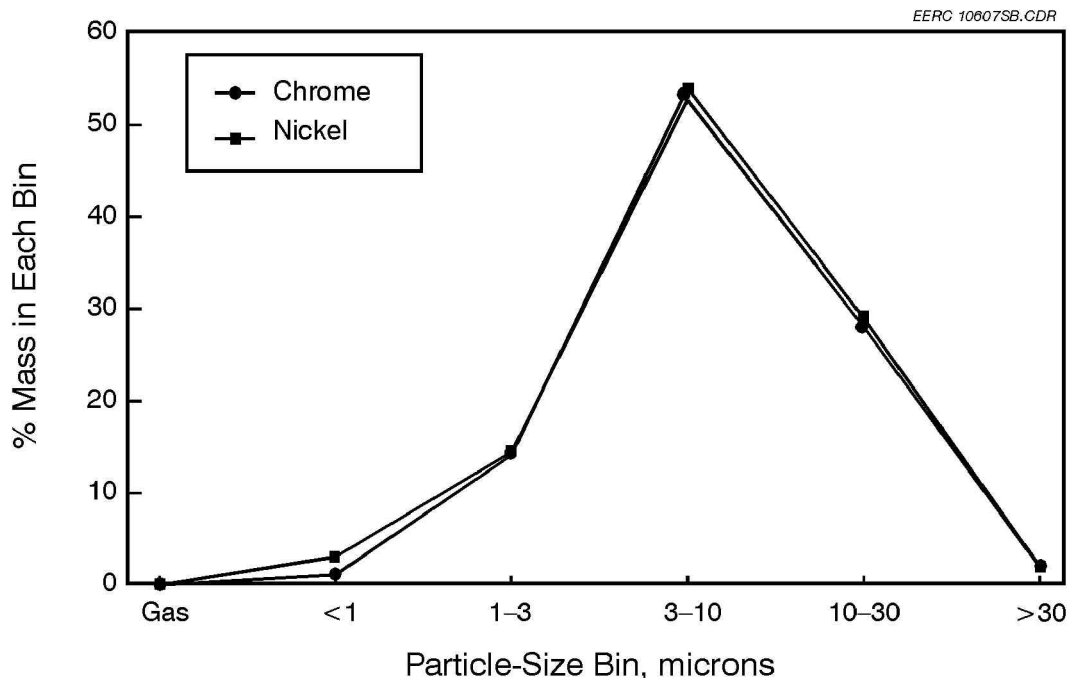
Figure 11.   Illinois No. 6 TraceTran predictions – particle-size distribution, 750°C.

thermochemical equilibrium predictions. The species will then be both homogeneously and heterogeneously condensed. Heterogeneous condensation is based on the surface area of the existing particles. The resultant particulate and vapor-phase species will be compiled and mani-pulated into various composition and size distributions at the user's discretion. These distributions can be used to determine effective control technologies for a specific coal or to locate a coal compatible to a specific control technology.

Although the emphasis of this model is to aid in the control of trace element emissions, only minor attention has been given at this time to the engineering mechanisms of the control technologies within a system. Once this model has been fully tested and verified, the next logical step will be to incorporate engineering models that mimic the control technologies. Figure 12 shows an example of the overall model applied to a pressurized fluid-bed combustor for selected elements and the measured element distributions from full-scale sampling. A series of "crude" engineering algorithms were used for bed fluidization, cyclone efficiency, and filter performance. As expected, the model predicts well for Hg and Na, which are found largely in the vapor state, but performs only marginally for the mostly particulate lead (primarily because of the lack of robust engineering models).

Similarly, Figure 13 shows the predictions of partitioning for the seven trace elements in an air-blown entrained-flow gasifier at three different locations. In this case, no partitioning was performed to remove some materials in the gasifier slag, ash filter, or gas cleanup device. The

Distribution of Total Hg in System

Distribution of Total Na in System

Distribution of Total Pb in System

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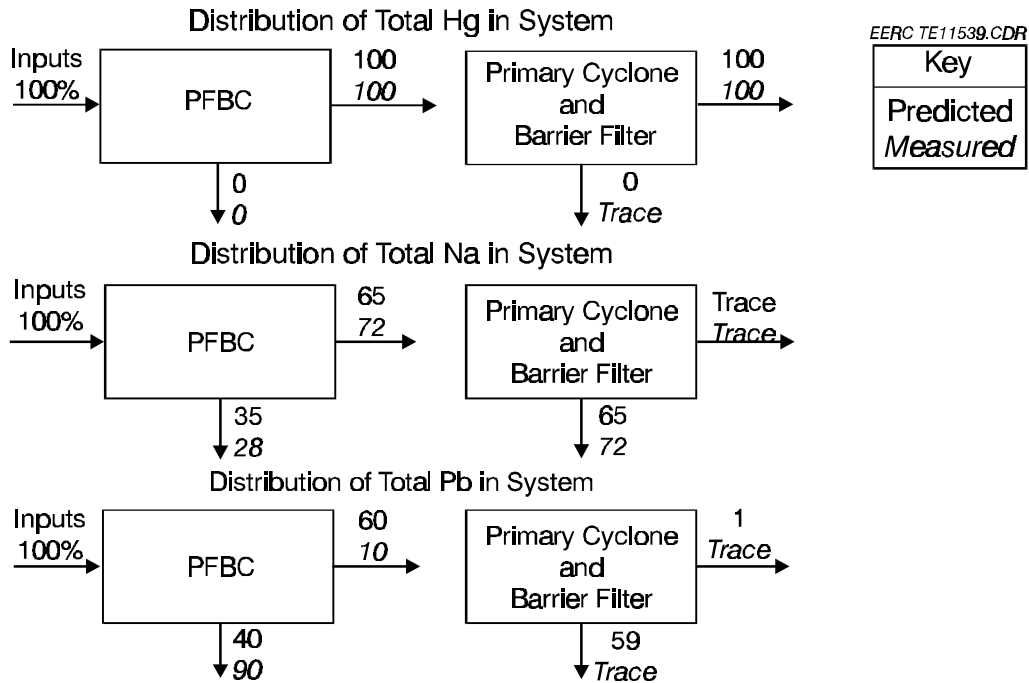**Key**

Predicted
Measured

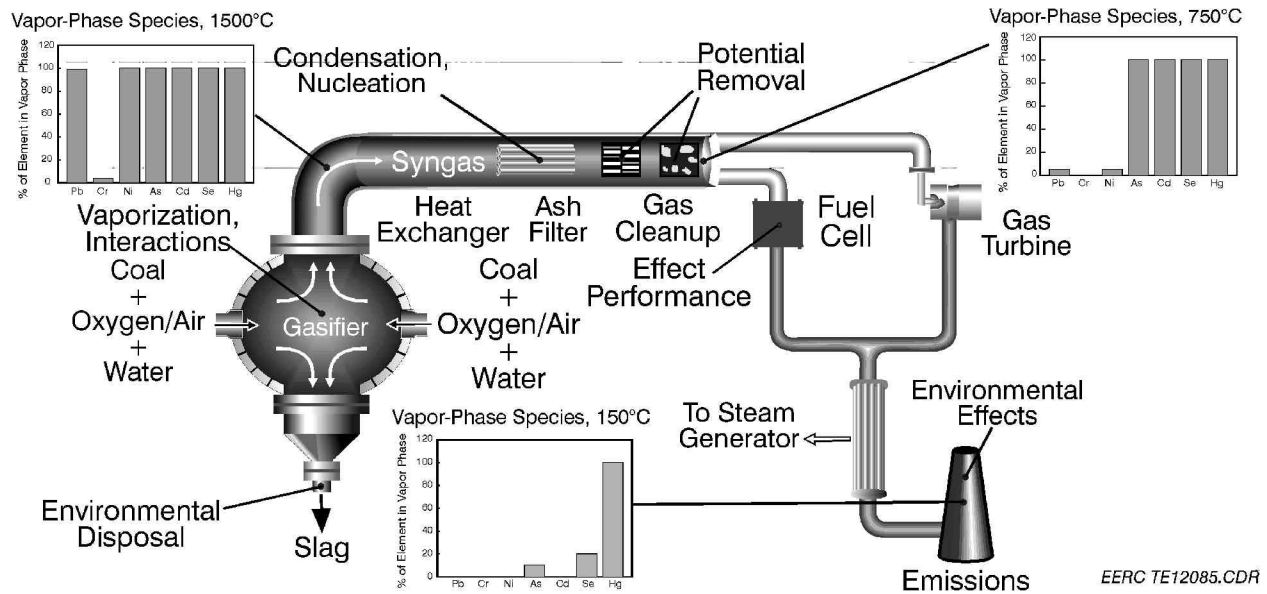Figure 12. Trace metal distributions predicted and measured for a pressurized fluid-bed combustor.

Figure 13. Trace metal vapor-phase distributions in an air-blown gasification system at various locations. No partitioning of the solids has been performed.

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calculations were performed assuming all of the inorganics passed throughout the entire system. This is shown as an example of how the different conditions affect the overall vapor-phase distributions. In actual application, only the vapor phase and a limited amount of the very fine particulate would pass throughout the system.

Model Verification and Scaleup

To ensure the overall model is applicable to larger systems, a verification task is under way. The transport reactor demonstration unit (TRDU) was sampled, and the results will be compared to model predictions. Gas samples were pulled from the TRDU before and after the hot-gas filter; solid samples were also collected from the filter vessel and from the coal. The trace element concentrations from the two gas samples (collected in duplicate) are shown in Table 3. Upon full integration of the model, the predicted concentrations of trace elements will be compared to those that were measured.

TABLE 3

TRDU Trace Element Sampling at Hot-Gas Filtration Unit Runs

	Run No. 5	Run No. 6	Run No. 7	Run No.8
Date	4/17/96	4/19/96	4/19/96	4/19/96
Time	11:14	08:39	12:09	15:46
Port	Inlet	Inlet	Outlet	Outlet
Conc.	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
As	_*	_*	_*	_*
Cd	_*	_*	_*	_*
Cr	10.37	13.22	8.16	4.76
Pb	2.01	–	–	–
Ni	50.53	46.87	31.48	9.05
Se	43.83	36.62	31.37	29.28
Hg	3.30	4.99	4.78	4.79

* Denotes below detection limit.

Future Work

Future work will involve the following:

- Completing the integration of the TraceTran computer code. The thermochemical equilibrium data set will be interfaced into the remainder of the code using a series of look-up tables. In addition, the code will be interfaced with a graphical user interface developed under separate funding.

- Verifying the predictive capability of TraceTran using data obtained from larger-scale systems. Data manipulation from the TRDU sampling will be completed and compared with model predictions. In addition, future TRDU testing in the fall of 1996 is planned. Similar samples will be collected and the results compared.

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