

TRACE ELEMENT BEHAVIOR IN GASIFICATION SYSTEMS

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ABSTRACT

Research has been initiated to determine the behavior of trace elements in integrated gasification combined cycle (IGCC) and integrated gasification fuel cell (IGFC) systems. The goal is to identify and model the important physical and chemical transformation mechanisms of seven trace elements (arsenic, chromium, cadmium, mercury, nickel, selenium, and lead) during gasification as a function of coal composition (trace element abundance and association) and gasification conditions. Identification of the reactions and transformations of trace elements is being conducted in laboratory-scale coal gasification systems. This experimental work is coupled with the development of a computer model to predict the state of trace elements in gasification systems and to identify effective control technologies.

INTRODUCTION

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.

Gasification conditions, such as reducing and oxidizing atmospheres, gas phase composition, pressure, and temperature, influence the partitioning of trace elements between various gases, liquids, and solid inorganic components as a function of location in the gasifier. 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. 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.

EXPERIMENTAL APPROACH

The predicting of inorganic transformations (major and minor components) during coal combustion has long been the focus of many research programs.¹⁻³ In the program described in this paper, the predictive techniques that have been applied to combustion are being modified to predict inorganic transformations under gasification conditions. Many of the current trace element predictive techniques are based on the assumption of equilibrium conditions and not on actual kinetically constrained transformations that occur during coal utilization. The approach used in the program is to combine inorganic transformation algorithms and the thermochemical equilibrium calculations.^{4,5} These techniques will be developed to predict the particle-size and composition distribution of the resulting coal ash particulate, along with the state of the vapor species at selected conditions for major, minor, and trace constituents.

The predictive techniques being applied to the modeling of trace elements during gasification require state-of-the-art analytical and experimental data. The modeling of trace elements requires particle-size and composition distributions of the trace constituents in relation to the major and minor species in the coal. To provide the necessary data, computer-controlled scanning electron microscopy (CCSEM) is being adapted to include trace element analysis through the use of wavelength dispersive x-ray spectrometers. Although the automated adaptations to the CCSEM technique will require significant development, generalized distributions of the trace elements can be made manually in conjunction with the CCSEM analysis. To generate the essential experimental data, a pressurized drop-tube furnace (PDTF) is being used to simulate coal gasification. Ash and vapor samples produced from the PDTF are characterized by CCSEM with wavelength adaptations for determining trace elements, wavelength and energy dispersive x-ray fluorescence, inductively coupled argon plasma spectroscopy (ICAP), and atomic adsorption (AA). The following sections discuss the three major developments taking place to produce a predictive methodology for trace element emissions during gasification: transformation modeling, microscopic sample characterization, and laboratory-scale coal gasification.

TRANSFORMATION MODELING

A computer model to predict the evolution of major, minor, and trace elements during the gasification of coal is being created based on the algorithm shown in Figure 1. The shaded boxes in Figure 1 represent the inputs required, while the boxes with a drop shadow are the outputs generated from the model.

The first task of the model is to determine the associations of the major, minor, and trace elements in the coal prior to utilization. The association of the elements prior to utilization will affect their phase, size, 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). The mineral associations are elements which comprise discrete minerals in the coal (such as clays, carbonates, and sulfides).

Due to the complexity of interaction of the 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 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 . This will result in a greater potential for mineral fragmentation, depending on the system conditions. Clays which contain high levels of moisture may fragment initially due to the release of H_2O from their porous structure. 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 are rarely free from 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 the liberated minerals. The liberated particles will also experience a slightly different gas environment during coal gasification since they are not intimately in 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 gasification process. These calculations will be performed with the use of a thermochemical equilibrium program, PHOEBE,^{4,5} created at the Energy and Environmental Research Center (EERC). This code is currently being upgraded to include the appropriate trace element phases. With the exclusion of the vaporized species, the remaining constituents will be processed through algorithms for mineral fragmentation, coalescence of both minerals and organically associated species, and shedding of resulting particles.

The fragmentation, coalescence and shedding algorithms will be developed with the aid of data generated in the pressurized drop-tube furnace (PDTF). These algorithms are designed on various frequency distributions for each of the minerals and physical processes. The organically associated species which 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 due to their lack of intimate contact with the coal.

The state of the volatile species at the resultant conditions will then be determined using the PHOEBE code again. The quantity of species that will condense prior to the resultant conditions are calculated from the PHOEBE data. The condensing species will then be homogeneously and heterogeneously condensed. The heterogeneous condensation will be based on the surface area of the particles. The resultant particulate and vapor species will be compiled and manipulated into various composition and size distributions as to 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, little attention is being given at this time to the effects of size and composition of inorganic ash components on control technologies. Once this model has been tested and verified, the next logical step will be to investigate the control technologies as a function of particulate and vapor properties.

MICROSCOPIC SAMPLE CHARACTERIZATION

Many of the computer models recently developed to predict the evolution of major and minor elements during coal gasification were made possible by the development on a highly quantitative analytical technique for coal analysis, CCSEM.⁶ CCSEM provides a particle-size and composition distribution for the mineral contents of a particular coal for twelve major and minor elements. These raw CCSEM data are the primary input to the newest computer models ash formation. The CCSEM data are used in conjunction with a bulk ash determination (x-ray fluorescence or atomic absorption) to determine the content of nonmineral species by mass balance. The goal for trace element modeling is to provide particle-size and composition distributions for the trace elements and a bulk composition containing trace elements similar to the current data produced for major and minor species. The bulk trace element composition has long been attainable by ICAP or AA, and the size and composition distributions are nearly obtainable by combining the current CCSEM technique with wavelength dispersive x-ray analysis capabilities for trace elements.

The standard CCSEM technique uses an energy dispersive spectrometer (EDS) which allows for the simultaneous determination of major and minor species in the minerals. However, the EDS detector is not sufficiently sensitive to trace elements. A wavelength dispersive spectrometer is much more sensitive for trace elements, but can only characterize one element at a time, thus making it impractical for the time-consuming rigors of the CCSEM technique. By combining both detectors during a single analysis, trace, minor, and major elements can be recorded. This procedure is currently being developed, but is not expected to be fully operational until the second quarter of 1993.

In an initial effort to determine the generalized associations of trace elements with minerals, the standard CCSEM procedure is run on a coal. At the completion of each frame of analysis, the operator can locate the specific minerals and reanalyze them with the wavelength dispersive instrumentation.

The wavelength data analysis can then be manually compared to the standard CCSEM data to correlate the presence of trace elements with specific mineral species. A generalized trace element profile can then be created for a number of coals to be used for data correlations in the model until the more rigorous technique is completed. In addition, the chemical fractionation technique is being used to support the CCSEM by providing data on the general association of the seven trace metals.

LABORATORY-SCALE COAL GASIFICATION

The fate and distribution of trace elements under the effects of temperature, pressure, and gas composition in IGCC systems are important to the emerging technologies. Laboratory-scale experiments performed in the EERC PDTF are being used to study the partitioning of important trace elements and to enable the prediction of trace element emissions for IGCC and IGFC systems.

The PDTF furnace assembly, Figure 2, consists of a 2.875-inch ID alumina tube (55 inches long) with a slightly reduced end, used to support a flow accelerator in a fixed position, nested on top of a tube of the same dimensions (25 inches long). These tubes are concentrically surrounded by a tube of slightly larger dimensions. The tubes are heated externally by high-temperature tube furnaces equipped with Kanthal Super 33 elements. The entire reactor and the heating elements are housed in a water-jacketed pressure vessel. Coal is introduced into the reactor with a carrier gas through a traversing, water-cooled injector located in the center of the tube. Optional, secondary air enters the reactor at the top of the tube and flows through the tube around the injector assembly. The coal residue and process gases travel down the tube in a laminar flow regime and pass through the accelerator where they are collected by a water-cooled, nitrogen-quenching ash collection probe. Various collection devices can be attached to the collection probe to collect the solids. Size segregation of the ash is obtained using a multicyclone or impactor in conjunction with a final filter. A bulk filter is used to collect ash for bulk chemistry. A water-cooled deposition probe can also be inserted, in place of the ash collection probe, to simulate the deposition conditions in a utility boiler. The product gases are monitored on-line by O₂, CO, and CO₂ gas analyzers or are intermittently sampled for a gas chromatograph (GC).

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

In this initial modeling effort, three coals will be run under multiple temperatures, pressures, gas compositions and residence times. The resultant samples will be collected in a three-stage multicyclone and characterized using scanning electron microscopy, wavelength dispersive x-ray fluorescence, inductively coupled plasma spectrometry, and atomic absorption. The data generated from the PDTF will support the development of the physical interaction algorithms in the model.

CONCLUSIONS

A computer model to predict the transformations of trace, minor, and major elements during coal gasification is expected to be completed by late 1993. This model will generate the particle-size and composition distribution of the inorganic constituents as a function of the original coal content and system conditions. Advances in both analytical and experimental technologies are currently being made to provide added insight into the modeling of these inorganics during coal utilization.

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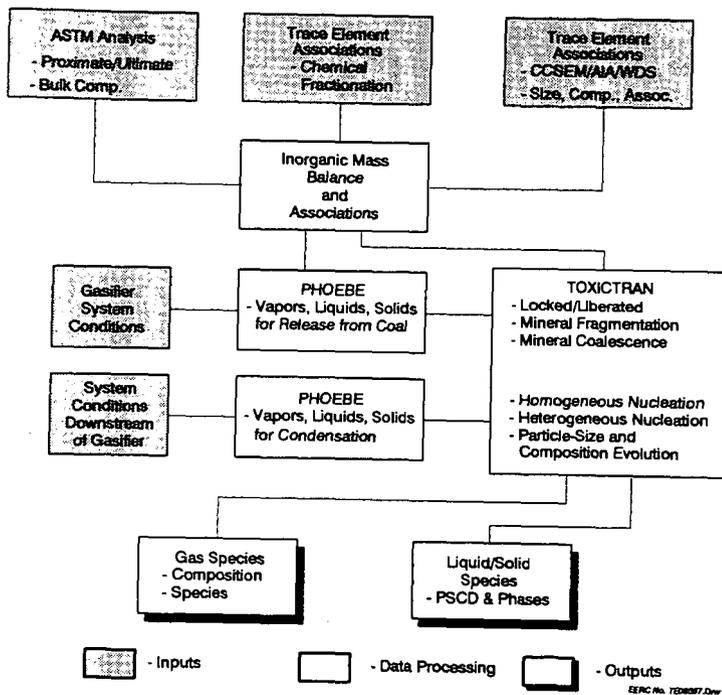


Figure 1. Trace element emissions model algorithm.

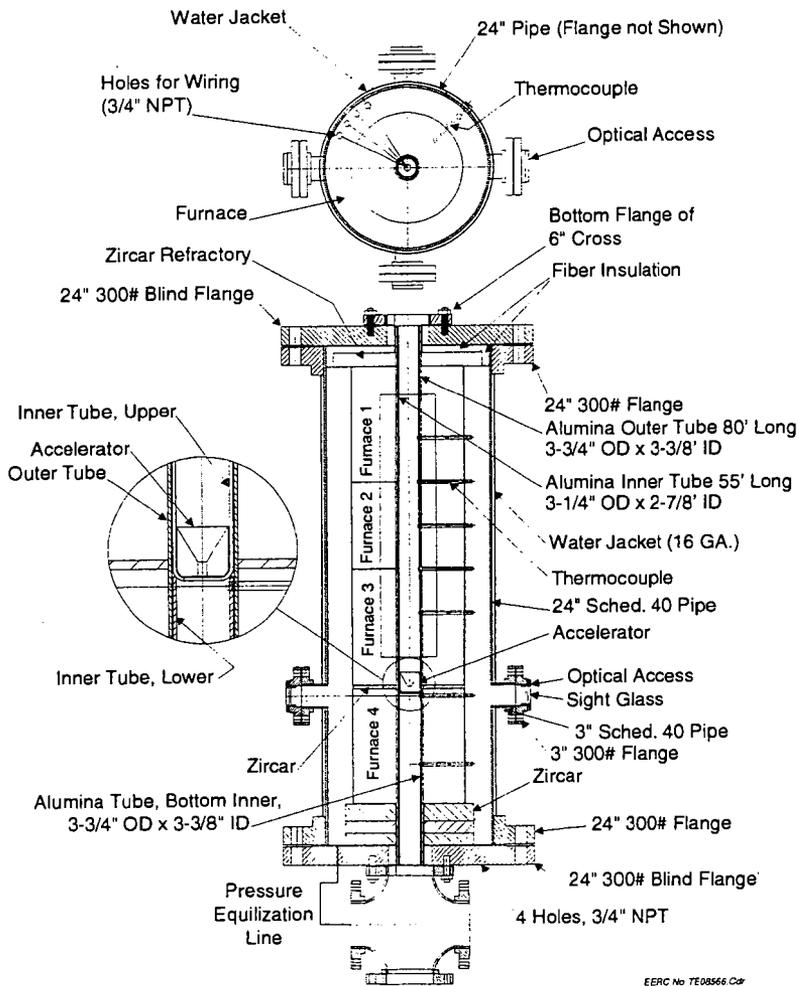


Figure 2. Pressurized drop-tube furnace assembly.