



Modeling trace element partitioning during coal combustion



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ABSTRACT

A model to predict the partitioning of semi-volatile TEs such as arsenic, antimony and selenium, during coal combustion has been developed. Because the initial mode of occurrence of a trace element (TE) impacts its partitioning after coal combustion, the model uses computer controlled scanning electron microscopy data sets of the target coal's ash analysis to determine the mineral inclusion, mineral exclusion, and organically associated TE content, which are then modeled using a semi-random mineral placement approach. Previously developed mathematical approaches, in conjunction with pyritic mineral transformation mechanisms, exclusion fragmentation and recently determined experimental speciation details, were employed to predict TE partitioning during combustion and TE spatial evolution.

Initial validation of the model was performed using a subbituminous coal. The residence time dependent particle temperature histories resulting from the combustion of this coal in a lab-scale down-fired combustor were generated using computational fluid dynamic simulations which were then used to predict the size-dependent TE evolution. A reasonable agreement with previously published measurements of the fractions of TEs vaporized was obtained. Of the original arsenic, antimony or selenium introduced in the simulated coal environment, 38%, 32% and 94% respectively were predicted to be released from pyritic family mineral inclusions. For excluded particles of similar size and temperature histories, a larger fraction (81%) of the initial selenium contained in pyritic family mineral exclusions was released than the fractions of either arsenic or antimony (33% and 26%, respectively). Fragmentation, which is associated with an increase in surface area, increased the TE release rates by 7–8%.

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1. Introduction

It is anticipated that even though other forms of electric power generation are being developed, the usage of coal will continue to increase over the next few years [1]. However, governmental legislations (including the Utility – Mercury and Air Toxics Standards – Act [2], the endangerment finding provided by the US Environmental Protection Agency [3], as well as the previously enacted Clean Air Act and its related amendments [4]) have put the economic viability of coal use into question. Federal, academic, and industrial energy sector personnel are working collaboratively to find methods to make coal fired power generation technologies economically viable.

Even though greenhouse gas emissions have gained widespread recent attention, they are not the only form of pollution associated with coal. Several of the trace elements (TEs) liberated from the coal matrix during combustion have the potential to impact human health and the environment. Models that accurately simulate aspects of the combustion environment, important to the behavior of these TEs, would facilitate the development of technologies to mitigate their impact. In addition, TEs may interfere with emerging technologies such as oxy-

coal combustion systems. It is therefore important that the behavior of TEs during coal combustion be understood. Such models would also assist in trouble-shooting trace-element-related process issues, such as corrosion and fouling by TE deposition. Specific elements, including arsenic (As), antimony (Sb) and selenium (Se), are of particular interest due to their semi-volatile nature.

TEs have a variety of ways in which they are associated within coal but are generally categorized as belonging to one of three forms of occurrence: organically associated, contained in mineral inclusions, or contained in mineral exclusions [5]. The original form of occurrence influences how TEs partition during combustion and will ultimately influence the fraction of TEs that exit the combustion system in vapor form compared to TEs associated with particulate matter. The forms of occurrence will also impact the TE concentration of the coal's size-distributed fly ash, which in turn, determines the effectiveness of pollution control devices in capturing TEs.

For definition purposes [6], *included TEs* are elements found within inorganic minerals that were encapsulated by the coal carbon matrix during coalification. Because included minerals are surrounded by burning char during combustion, inclusions can experience a highly reducing, high temperature environment.

Organically bound TEs include those elements that are bonded to carbon-based compounds within the coal. This type of element sees

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high temperatures and a reducing atmosphere, and is released from the coal matrix as its carbon bonds break. After volatilization, the species will diffuse out of the surrounding structure and past the burning char's boundary layer to enter the bulk gas phase.

Excluded TEs are elements found within inorganic constituents that may be mixed with the coal after coalification but are not intrinsic parts of the coal. Thus, exclusions tend to encounter lower temperatures and neutral/oxidizing conditions compared to inclusions. These differences in the surrounding environment will lead to changes in the rate and degree of TE vaporization out of the minerals' combustion. Although primarily a function of temperature, the vaporization of TEs bound within the center core of minerals is also limited by diffusion, which contributes to the overall retention of trace materials within them. The diffusion rate is influenced by the physical characteristics of the minerals such as their melting behavior, relative position to other minerals, and mineral transformations such as coalescence, fragmentation, and vaporization.

Many existing TE models are based on bulk gas-phase conditions and empirically derived predictors [7–9] while other models are based on thermodynamic equilibrium [7,10]. The latter approach assumes that vaporization and reaction to gas phase speciation are thermodynamically limited when in fact, these processes are expected to be transport limited at the highly dynamic conditions of char pyrolysis (i.e., fast heating under reducing atmospheric conditions). Therefore, thermodynamic-based models can only provide insights into possible forms of occurrence of gas phase elements at bulk or post-combustion conditions but cannot predict the forms of occurrence present in the microenvironment surrounding the burning char. To the best knowledge of the authors, none of the models reviewed or discussed publicly in the literature accounts for the drastic differences that TEs experience during combustion due to their origination (i.e. organic, inclusion, or exclusion associated).

To accurately model TE partitioning behavior, a model must incorporate (1) combustion system design characteristics, such as furnace design configuration, furnace size, burner arrangement, and combustion system thermal behavior, as well as (2) fuel properties, such as total ash content of the coal, ash constituents and properties, trace species' thermodynamic properties, trace species' modes of occurrence, distribution of mineral matter, and the distribution of trace species [11]. TE partitioning behavior depends upon the state of the originating material in the coal feedstock, and whether the TE originates in a mineral inclusion, in a mineral exclusion or as an organically bound species [12]. Within the combustion zone, environmental properties vary as a function of time and space due to inherent temperature dependencies as well as the presence of both oxidative and reducing environments that are within and surrounding a particle. Quantitative determination of partitioning during pulverized coal combustion processes requires modeling of detailed heat transfer, mass transfer, and kinetic relationships within individual coal particles. Analytical solutions have been limited due to the mathematical complexity of the process as well the persistent kinetic rate, elemental speciation, and mass transfer data information gaps that are needed to describe the behavior of TE species.

At the present time, there is no practical way to experimentally study mode of occurrence-dependent combustion zone partitioning, so an evaluation can best be accomplished through modeling. This manuscript describes the TE Partitioning during Coal Combustion (TEPCC) mathematical model, to predict TE partitioning. The TEPCC model employs inputs from *computational fluid dynamic* (CFD) simulations to determine TE liberation from the coal matrix during the combustion zone based on the form of the TE in the coal feed to the combustor. The TEPCC model incorporates aspects found in various mathematical models previously developed by other researchers [12], yet is distinctive in that it includes a semi-random placement of mineral particles based on *computer-controlled scanning electron microscopy* (CCSEM) data [13] to determine a unique mineral distribution within the coal particles. The semi-random method is used to generate statistically plausible coal

particles with individualized composition. This methodology should provide better estimates of mineral particle surface area, which ultimately affects the flux of TEs from a coal particle during combustion. Recent kinetic speciation data provided through the research of Raeva and colleagues [14,15] is also incorporated. These kinetic data are distinguishing in that they sought to determine plausible mode of occurrence speciation as well as kinetic parameters during specific idealized combustion environments that simulate the three regimes of occurrence (inclusions, exclusions, organically bound) using a novel experimental method.

Finally, predictions from the TEPCC model as they relate to the release of arsenic, antimony, and selenium from pyritic family mineral inclusions, and exclusions as well as organically bound TEs of a Southern Powder River Basin (PRB) subbituminous coal in a 19 kW down-fired furnace are presented as model verification and a demonstration of its capabilities. Most of the TE content in coal has been shown to be associated with three major mineral groups: pyrite, kaolinite, and illite [16, 17]. Pyritic family minerals are the focus of the present study due to their known association relationships with arsenic, antimony, and selenium. In addition, pyritic minerals (exclusions in particular) can undergo fragmentation that can increase the surface area and impact the TE release rates [18].

2. Experimental method

2.1. TEPCC: a model for TE liberation during pulverized coal combustion

2.1.1. Model overview

The TEPCC model takes data from several sources: (1) the ASTM proximate and ultimate analyses of the parent coal, (2) elemental associations ascertained from computer controlled scanning electron microscopy (CCSEM) data (which includes the size, the composition, and the association of the element), and (3) particle temperature–residence time histories from computational fluid dynamics (CFD) simulations. The model uses these data to predict the spatial TE evolution in pulverized coal combustion systems. A logic flow diagram for the TEPCC model is shown in Fig. 1.

2.1.2. Semi-random mineral placement

Several options are available to determine the mineral matter composition, amount, and distribution within coal. A thorough review of the subject is given by Vassilev [19]. One of the primary methods used to determine the associations of inorganic components in coals is CCSEM, which provides quantitative means to determine the abundance, shape and size of mineral grains, chemical form of minerals, and mode of occurrence of inorganic components of coal [20–22].

Mineral grain CCSEM data were divided between included and excluded mineral grains using a Monte Carlo method to “semi-randomly” redistribute mineral grains among simulated coal particles [13]. It is hoped that the semi-random mineral composition would more accurately simulate mineral compositions than the uniform distributions that have been employed in prior-modeling approaches [12] since coal is not uniformly distributed and particles are more realistically modeled when they have unique compositions based on the CCSEM analysis rather than a uniform overall composition based on the proximate and ultimate analyses.

For the purpose of the TEPCC model, included and excluded mineral grain data were preprocessed into six discrete size bins as follows: 1.0–2.2 μm , 2.2–4.6 μm , 4.6–10.0 μm , 10.0–22.0 μm , 22.0–46.0 μm , and 46.0–400.0 μm . These bins provide the basis for separation of the mineral grains within the raw coal particles. Details of the mineral group concentrations (in wt.%) of a few select mineral groups and their relative sizes can be found in Appendix A. The total mineral mass is 6.4 wt.% of the total coal mass. Not all mineral groups are found in every mineral size bin. Furthermore, the mineral groups will not necessarily have the same relative abundances.

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