



Full Length Article

Molecular scale studies that inform trace element sulfide evaporation and atomization behavior during coal combustion

Anastasia A. Artemyeva^a, Wayne S. Seames^b, David T. Pierce^a, Evgenii I. Kozliak^{a,*}^aUniversity of North Dakota, SUNRISE Group, Department of Chemistry, 151 Cornell St. Stop 9024, Grand Forks, ND 58202, USA^bUniversity of North Dakota, SUNRISE Group, Department of Chemical Engineering, 241 Centennial Dr. Stop 7101, Grand Forks, ND 58202, USA

HIGHLIGHTS

- GFAAS provides insights into trace element (TE) sulfides speciation during coal combustion.
- TGA-DSC was used under varied N₂ flow rates to study microaerobic regimes of TE evolution.
- Antimony trisulfide demonstrated strong binding affinity to the carbon surface.
- Selenium disulfide tends to form molecular clusters prior to vaporization.
- TE sulfide evaporation is the rate limiting step.

ARTICLE INFO

Article history:

Received 22 June 2016

Received in revised form 10 September 2016

Accepted 2 October 2016

Available online 18 October 2016

Keywords:

Trace element partitioning

Sulfide/pyrite fraction

Mineral inclusions

Excluded minerals

Coal combustion

Graphite furnace atomic absorption spectrometry

ABSTRACT

Understanding the chemical mechanisms of trace element (TE) evolution is essential for accurate modeling of coal combustion. A novel graphite furnace atomic absorption spectrometry (GFAAS) method was used to simulate the evaporation and atomization behavior of TE sulfides (arsenic, antimony and selenium) in the two distinct microenvironments that mineral inclusions and exclusions experience during the onset of coal combustion. Additional insights were obtained using thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). Potassium polysulfide was used as an additive to water to facilitate the dissolution of all three TE sulfides. TE sulfides in inclusions were studied by adding the test mixture to a graphite tube in a reducing (anaerobic) micro-environment whereas the TE evolution in excluded sulfide minerals was studied by blocking the graphite tube surface with an inert ZrO₂ or WO₃ coating. Arsenic sulfide, As₂S₃, exhibits a lower Arrhenius activation energy of atomization, E_a, than that of the corresponding oxide in both mineral inclusions and exclusions, apparently because of the availability of a specific facile path to atomization. A higher E_a was observed for antimony sulfide, Sb₂S₃, than that of the corresponding oxide from inclusions and is most likely due to its strong binding affinity to the carbon tube surface. The low GFAAS signal of selenium sulfide suggests the formation of molecular clusters, e.g., Se₂, Se₈ or similar mixed clusters with sulfur atoms prior to vaporization, an effect not observed for selenium oxide evaporation. For all three TE sulfides, either elemental species or unstable sulfides with low sulfur content appear to be predominant in the gas phase associated with both mineral inclusions and exclusions, with TE sulfide evaporation being the rate limiting step. Comparing the GFAAS activation energy values obtained with and without the coating showed that in a reducing micro-environment (anaerobic conditions) characteristic during the initial period of combustion for mineral inclusions, carbon merely adsorbs TE sulfides without chemical reactions. Yet TGA-DSC data showed that powdered graphite may react with TE sulfides in an oxidizing micro-environment (microaerobic conditions), such as those experienced during the later period of combustion for inclusions and during the entire combustion period for exclusions thus accelerating TE evolution without making qualitative changes in the vapor composition.

© 2016 Elsevier Ltd. All rights reserved.

Abbreviations: TEs, trace elements; CAAAs, Clean Air Act Amendments; GFAAS, graphite furnace atomic absorption spectrometer; TGA, thermogravimetry; DSC, differential scanning calorimetry.

* Corresponding author.

E-mail address: evgenii.kozliak@und.edu (E.I. Kozliak).

1. Introduction

An important environmental issue associated with coal combustion is the release of trace elements (TEs) into the atmosphere. The U.S. Clean Air Act Amendments (CAAAAs) classify these TE

species as toxic air pollutants [1]. Both the form of TE occurrence and the coal type determine the TE solid/gas phase partitioning within the combustion system which ultimately affects their environmental fate and the toxic effects that may ensue. Understanding the mechanisms of TE partitioning during coal combustion is an essential step towards minimizing the environmental impact caused by the emission of TEs from the substantial installed capacity of coal-fired power generation systems throughout the world.

TEs occur in coal in three different forms: organically associated, mineral inclusions and excluded minerals, characterized by a decreasing access to carbon and decreasing peak localized temperature within this series. The organically associated TEs exhibit strong interactions with the coal carbon matrix whereas TEs within mineral inclusions are too remote from the carbon for significant interaction. TEs in mineral inclusions are surrounded by the carbon matrix, which may interact with the TEs as included minerals begin to melt [2,3]. The distance from the combusting coal matrix also affects the localized temperature, which could vary as much as 100–1000 K, as well as the presence or absence of available oxygen in the microenvironment the TE will experience.

A pronounced difference in both localized temperature and oxygen availability is expected to significantly affect partitioning and speciation as TEs transition into the gas phase. This difference in TE partitioning and speciation may also be amplified by more subtle yet no less significant specific effects of the chemical microenvironment surrounding the TE atoms such as the TE's chemical speciation in the solid phase and the interactions of TE-containing molecules with the adjacent inorganic matrix. While temperature changes and oxygen depletion can be taken into account by modeling, the presumed impacts of chemical microenvironments can neither be modeled using the currently employed methods [4–7] nor studied *in situ* with real coal particles. This consideration warrants conducting experimental studies using simulated environments.

This point is worth emphasizing. It is not possible with current techniques to study the distinctly different microenvironments of mineral inclusions and exclusions using real coal particles. The best that can currently be accomplished is the study of the surrounding micro-environment or of the overall behavior of TEs from coal particles, irrespective of originating domain (e.g. inclusion, exclusion, or organically associated). Yet it is the highly dynamic, very short lived initial stages of combustion that influence TE partitioning the greatest. Accurate modeling of TE behavior requires greater insight into the mechanisms of TE partitioning than can be achieved with current coal study methods. As such, simulated environments must be employed.

In our previous work, a method was developed that simulates and evaluates the partitioning of organically associated TEs. The original method allows for the measurement of the kinetic parameters associated with TE vaporization/atomization in an environment that corresponds to the behavior expected from TEs in the organic fraction of a coal particle. It is based on the use of a modified graphite furnace atomic absorption spectrometer (GFAAS) as both an *in situ* measurement platform and carbon source [8]. The method was then extended to study TE partitioning from coal mineral inclusions by introducing homogeneously mixed TE/inorganic matrix solutions into the graphite furnace tube [9] and to simulate TE partitioning from excluded minerals by introducing TEs, with or without matrices, into a metal oxide-coated graphite furnace tube [10] (i.e., in an environment where the TEs are not directly exposed to the carbon matrix).

However, the previous studies were only conducted with TE oxides. Completely absent were studies of the other equally important form for TEs in coal, namely TE sulfides. These TE sulfides are often associated with other sulfides in coal, e.g., pyrite, marcasite, galena, sphalerite, etc. [11] with pyrite association generally being

the most common form. Thus, the goal of the current study was to apply the previously developed method to evaluate the release of TE sulfides from the pyrite fraction of coal inclusions and exclusions.

The main challenge in this work was developing a method to introduce representative samples of TE sulfide, with and without matrices, into the GFAAS as homogeneous mixtures, i.e., solutions. While As(III), Sb(III), and Se(IV) oxides are soluble in water, the corresponding TE sulfides are not. However, we were able to dissolve all three TE sulfides in water upon the addition of sulfide and polysulfide ions, which are essential components of all sulfide mineral inclusions and exclusions in coal. This finding laid the foundation for this study allowing the trends in TE sulfide atomization with and without accessible carbon to be investigated.

It should be noted that coal contains numerous other entities, such as volatile matter and metal oxides, that may impact TE partitioning behavior. The impacts of these other entities is outside of the scope of the present study but will be investigated in future work. Furthermore, untreated coal-derived flue gas is known to be a complex mixture containing numerous species such as particulates, nitrogen, carbon dioxide, moisture, oxygen, sulfur dioxide, sulfur trioxide, nitrogen oxides and hydrogen chloride [12–15]. These gas-phase species may also impact TE partitioning behavior as well as post-volatilization secondary reactions. The impacts from these species was also outside of the scope of the current study.

Just as for TE oxides [8], a complementary method based on thermogravimetry (TGA) coupled with differential scanning calorimetry (DSC) was used to decouple the TE vaporization and atomization phenomena. The flow of nitrogen was varied between 400 and 50 mL/min during TGA experiments to allow simulation of both near-anaerobic (reducing micro-environment) and microaerobic conditions (oxidizing micro-environment).

These two conditions, near-anaerobic and microaerobic, are important for accurate modeling of trace element partitioning. Included material is completely surrounded by a coal matrix. During the initial stages of combustion, oxidation of the coal leads to a highly reducing environment for the inclusions. As combustion progresses, carbon oxidation slows and the microenvironment surrounding the inclusion goes to neutral and then finally to an oxidizing condition. These rapidly changing conditions can only be studied using model systems such as those devised here.

Similarly, the microenvironment surrounding mineral exclusions will be at a lower oxygen content than the surrounding bulk flue gas, but is likely to never reach reducing conditions. Thus an oxidizing micro-environment is likely to replicate that of exclusions during the initial stages of combustion [16]. In this work, we postulated that the use of TGA-DSC under varied flow rates may provide a bridge to GFAAS data obtained under strictly anaerobic (reducing) conditions. As a result, the obtained data, though qualitative and indirect, provided novel and somewhat unexpected information on the influence of traces of oxygen on TE sulfide evolution in the presence of elemental carbon.

2. Experimental section

2.1. Materials and reagents

Potassium polysulfide (Acros Organics, New Jersey, USA) was used to prepare 11 mg/mL matrix solutions. As₂S₃ (diarsenic trisulfide henceforth called arsenic sulfide, Strem Chemicals, Newburyport, MA, USA), Sb₂S₃ (diantimony trisulfide henceforth called antimony sulfide, Strem Chemicals, Newburyport, MA, USA) and SeS₂ (selenium disulfide henceforth called selenium sulfide, Alfa Aesar, Ward Hill, MA, USA) were used to prepare 100 ppm aqueous

Download English Version:

<https://daneshyari.com/en/article/6475865>

Download Persian Version:

<https://daneshyari.com/article/6475865>

[Daneshyari.com](https://daneshyari.com)