A Role of Mineral Oxides on Trace Elements Behavior during Pulverized Coal Combustion

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Abstract: The issues of trace element emissions during coal combustion have been a concern in recent years due to their environmental pollutant. To study the trace element transformation, the thermodynamic calculation (FactSage 7.2) was used. Five kinds of pure mineral oxides (Al2O3, CaO, Fe2O3, K2O, and MgO) and As, B, Cr, F, and Se in fly ash were considered for trace elements. The results confirm that all mineral oxides have a good correlation with arsenic to form Ca3(AsO4)2, FeAsO4, K2AsO4, and Mg3(AsO4)2. Boron has a good relationship with Al, Ca, and Mg to form (Al2O3)B(B2O3)2, Ca3B2O6, and Mg3B2O6. Chromium has a good correlation with K and Ca to form K2CrO4, CaCrO4. Furthermore, FeF3(s), KF(s), and AlF3(s) are predicted from the interaction of fluorine with Fe2O3, K2O, and Al2O3. The effect of mineral oxides on selenium partitioning are not observed. The inhibition order of trace elements by mineral oxides is as follow: As (Al2O3 > MgO > CaO > Fe2O3 > K2O), B (Al2O3, CaO, Fe2O3, K2O, > MgO), Cr (CaO > K2O > Al2O3, MgO, Fe2O3), F (CaO > MgO > Al2O3 > Fe2O3 > K2O). The results will be useful to control the trace element emissions.

Keywords: coal fly ash; trace elements; combustion process; thermodynamic calculation

1. Introduction

According to the International energy agency, coal is still an important position as a world energy source during the next decade due to the perception that coal is the cheapest source and primary position in power generation [1]. In coal-thermal power generation, coal is used as raw material for energy production through the combustion process. The combustion of coal containing even only several parts per million of trace elements (TEs) could result in the release of several tons of pollutants into the environment [2]. The TEs in coal are defined as an element occurring in a very low amount (<100 ppm) [3,4]. The TEs introduced into a combustion system as part of the coal feeds or sorbents can only exit the combustion system through a finite number of pathways [5]. During the combustion process, many TEs such as As, Cd, Hg, Pb, and Se first vaporize and then condense either homogeneously to form submicron ash particles or heterogeneously to adsorb on the surface of fine fly ash particles which are hard to be captured by electrostatic precipitator, baghouse filter, and other air pollution control devices [6,7]. The issues of TEs emissions during coal combustion has been subjected to concern in recent years due to their environmental pollutant and technological problems during coal utilization for energy production. Lots of research has been studied the way to inhibit the release of easily volatilized TEs by the addition of sorbents, as summarized in Table 1.
Table 1. Literature on the ability of sorbents to inhibit the release of volatilized TEs.

| Sorbents                  | Findings                                                                 | Research                                                                 |
|---------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Kaoline                   | Addition of kaolin powders into the sewage sludge combustion contributed to inhibiting Pb and Cd compounds at the temperature of 1223 K due to the reaction of Pb and Cd compounds with the kaolin during combustion. | Yao et al., 2005 [8,9]                                                   |
| Activated carbon          | Activated carbons can capture As and Se by the ash content of the activated carbon and the composition of the atmosphere. | López-Antón et al., (2007) [10]                                           |
| Fly ash                   | Fly ash is an efficient sorbent for inhibiting As, Se, and Zn. Retention capacities of TEs depend on temperature and atmosphere. | Diza-Somoano et al., (2002) [11]                                         |
| Limestone, CaSO₄, bauxite, kaolinite, and CaO | 1. Absorbents can inhibit of TEs emissions. Kaolinite is the best for the sorption of Pb, bauxite for Cd, kaolinite, and bauxite have slight sorption on Cr, lime has no effect on Cr capture.  
2. Combustion temperature influences the capture of TEs. The best temperature on the absorptive capacity was 1473 K.  
3. The retention of As in fly ash is affected by CaO due to their chemical reaction. | Cheng et al., (2001), Gullett and Raghunathan (1994) [12,13] |
| Vanadium (V)              | The correlation analysis between V and As give a coefficient r = 58.7%, Correlation among V and F (r = 31.6%) and B (r = 20.9%) is not significant. | Fiorentino et al., (2007) [14]                                           |
| Titanium (Ti)             | The nanostructured Ti flake surface can inhibit the release of some rare earth elements La, Lu, and Yb. Be recovery percentage was over 90%, while lanthanides have just a satisfactory recovery percentage (about 65% Yb and Lu and 50% La). | Barbulescu et al., 2019 [15]                                            |

It is necessary to understand TEs behavior during the coal combustion and gasification processes. Using the computation method of the thermodynamic equilibrium, lots of research has been studied TEs behavior and transformation during combustion and/or gasification process [16–23]. Liu et al. [21] investigated the effects of sewage sludge (SS) co-combustion conditions and interactions with Al₂O₃, CaO, Fe₂O₃, and SiO₂. Their results show that in the SS co-combustion system with the multiple oxides of Al₂O₃, CaO, and SiO₂, As reacted with Al₂O₃ and CaO to form AlAsO₄(s) and Ca₃(AsO₄)₂(s) which in turn inhibited As volatilization. SiO₂ prevented As from reacting with CaO, thus decreasing Ca₃(AsO₄)₂(s). Shuqin Liu et al. [22] reported that the effect of mineral elements, the presence of K makes As less volatile due to the formation of K₃AsO₄ and Se is not affected. Based on the results of lots of researches both in the experimental and thermodynamic study, it is clear that the emission of TEs during coal combustion is frequently controlled by the use of sorbents such as Al₂O₃, CaO, and K₂O.

Mineral oxides are major elements present in fly ash, so understanding how TEs vapor interacts with these elements could lead the way to evaluate their use. Previous research narrowly focuses on calcium-based or carbon-based sorbents [10,11,24]. This paper presents the results of TEs vapor inhibition using five different kinds of mineral oxides. The experiments were carried out using the computation method of thermodynamic equilibrium (FactSage 7.2, Environmental and Renewable Energy Laboratory, Gifu University, Gifu, Japan). The effects of combustion temperature, mineral oxide type, and inhibition mechanism are tentatively determined. Applying these mineral oxides in the combustion process is a promising method to prevent trace element compounds into the environment and inhibit the release of the easily volatilized TEs.

2. Materials and Methods

2.1. Coal Fly Ash (CFA)

CFA was obtained from coal-fired power plants in Japan. The chemical properties of the CFA sample were determined based on X-ray fluorescence (XRF) analysis results (WDXRF S8 Tiger, Bruker AXS, Gifu, Japan), as shown in Table 2. In the sample, Al₂O₃ is the higher mineral oxide contain (20.45%), followed by Fe₂O₃ (15.65%), CaO (11.3%), K₂O (1.06%), and MgO (0.61%). 12.53, 160, 7.7, 10, 3.87 mg/kg of As, B, Cr, F, and Se exist in the CFA sample, respectively.
Table 2. Chemical composition of CFA.

| Main Oxides | Proportion (%) |
|-------------|----------------|
| SiO\(_2\)   | 59.38          |
| Al\(_2\)O\(_3\) | 20.45         |
| TiO\(_2\)   | 0.62           |
| Fe\(_2\)O\(_3\) | 15.65         |
| CaO         | 1.13           |
| MgO         | 0.61           |
| Na\(_2\)O   | 0.47           |
| K\(_2\)O    | 1.06           |
| P\(_2\)O\(_5\) | 0.08          |
| MnO         | 0.07           |
| V\(_2\)O\(_5\) | 0.01          |
| SO\(_3\)    | 0.49           |
| Total       | 100            |

Trace elements (mg/kg)

|          |     |
|----------|-----|
| As       | 12.53 |
| B        | 160.00 |
| Cr       | 7.70  |
| F        | 10.00 |
| Se       | 3.87  |

2.2. FactSage: Thermodynamic Calculation

A thermodynamic calculation model used in this study was FactSage 7.2 software to make the thermodynamic calculation based on minimization of the Gibbs free energy. FactSage covers a compound database of all CFA components. Fiona et al. [25] reported that combining the mineral components (three major minerals: Al, Ca, and Fe) in samples (Victorian brown coal and Xin Jiang coal), Cr displayed excellent correlation with Al, while As has a good correlation with Ca. Following those results, in this study, five kinds of pure mineral oxides (Al\(_2\)O\(_3\), CaO, Fe\(_2\)O\(_3\), K\(_2\)O, and MgO) and the major elements such as Al\(_2\)O\(_3\), CaO, Fe\(_2\)O\(_3\), SiO\(_2\), etc. in coal were considered for trace elements (As, B, Cr, F, and Se) in combustion process simulation. This calculation was used to predict the possible TEs-bearing compounds in CFA, their distribution, and the dominant interaction between minerals to each trace element. The data search used in this analysis includes FactPS and FToxid. The temperature selected for the simulation process range from 100 °C to 1600 °C and is performed in the combustion atmosphere condition. For calculations, 100 g of CFA was used to calculate the input data under pure oxygen combustion conditions. Firstly, equilibrium composition was determined for trace elements individually, with 3% addition of each mineral oxides (Al\(_2\)O\(_3\), CaO, Fe\(_2\)O\(_3\), and K\(_2\)O and, MgO), then the calculation was determined for each trace element, with the major components present in the original CFA. All the input reactant temperature was 25 °C at atmospheric conditions. During simulation analysis, gases and solid species are chosen as output.

3. Results

3.1. Trace Elements Interaction with Mineral Oxide

The thermodynamic equilibrium calculations were conducted to predict the possible interactions between TEs and mineral oxides. The TEs distribution by the effect of adding mineral oxides during combustion at temperature range 100–1600 °C were shown in Figures 1–5 and Table 3, respectively. As shown in Figure 1a–e, As and mineral oxides (Al, Ca, Fe, K, and Mg) interact to form new species including AlAsO\(_4\), Ca\(_3\)(AsO\(_4\))\(_2\), FeAsO\(_4\), K\(_3\)AsO\(_4\), and Mg\(_3\)(AsO\(_4\))\(_2\) with a small contribution of gaseous species such as AsO and As\(_4\)O\(_6\). Many studies have confirmed that As was associated with both organic matter and inorganic minerals (clay minerals, sulfides). Figure 1a–e, indicates that all mineral oxides can minimize the release of emission.
Ca, Fe, K, and Mg) interact to form new species including AlAsO$_4$, Ca$_3$(AsO$_4$)$_2$, FeAsO$_4$, K$_3$AsO$_4$, and Mg$_3$(AsO$_4$)$_2$ with a small contribution of gaseous species such as AsO and As$_4$O$_6$. Many studies have confirmed that As was associated with both organic matter and inorganic minerals (clay minerals, sulfides). Figure 1a–e indicates that all mineral oxides can minimize the release of emission.

During coal combustion, B has a good relationship with Al, Ca, and Mg, which are important for the reaction with B to form (Al$_2$O$_3$)$_9$(B$_2$O$_3$)$_2$, Ca$_3$B$_2$O$_6$, and Mg$_3$B$_2$O$_6$ in the temperature in the range 100–1400 °C and transform into BO$_2$ and B$_2$O$_3$ in gaseous species with temperature increases (except the interaction with Ca).

The effect of mineral oxides on Cr, the presence of Ca and K make Cr less volatile due to the formation of CaCr$_2$O$_4$ and K$_2$CrO$_4$, and the effect of Al$_2$O$_3$, Fe$_2$O$_3$, MgO is not affected on Cr as shown in Figure 3a–e. The interaction of Al$_2$O$_3$, Fe$_2$O$_3$, MgO were introduced on Cr. At T > 1100 °C, CrO$_3$(g) was formed and became the main gaseous species with a small contribution of CrO$_2$(g). At T < 1200 °C, Cr$_2$O$_3$, and CrO$_2$ were formed in the solid phase. Cr becomes volatile only at high combustion temperatures, and gaseous species leave the combustion zone and cooling condition [20,22].

Figure 1. Equilibrium composition of As-Mineral oxides interactions during combustion: (a) As-O$_2$-Al$_2$O$_3$; (b) As-O$_2$-CaO; (c) As-O$_2$-Fe$_2$O$_3$; (d) As-O$_2$-K$_2$O; (e) As-O$_2$-MgO.

Figure 2. Equilibrium composition of B-Mineral oxides interactions during combustion: (a) B-O$_2$-Al$_2$O$_3$; (b) B-O$_2$-CaO; (c) B-O$_2$-Fe$_2$O$_3$; (d) B-O$_2$-K$_2$O, and (e) B-O$_2$-MgO.

Figure 3. Equilibrium composition of Cr-Mineral oxides interactions during combustion: (a) Cr-O$_2$-Al$_2$O$_3$; (b) Cr-O$_2$-CaO; (c) Cr-O$_2$-Fe$_2$O$_3$; (d) Cr-O$_2$-K$_2$O, and (e) Cr-O$_2$-MgO.
Figure 2. Equilibrium composition of B-Mineral oxides interactions during combustion: (a) B-O2-Al2O3; (b) B-O2-CaO; (c) B-O2-Fe2O3; (d) B-O2-K2O, and (e) B-O2-MgO.

Figure 3. Equilibrium composition of Cr-Mineral oxides interactions during combustion: (a) Cr-O2-Al2O3; (b) Cr-O2-CaO; (c) Cr-O2-Fe2O3; (d) Cr-O2-K2O, and (e) Cr-O2-MgO.

Figure 4. Equilibrium composition of F-Mineral oxides interactions during combustion: (a) F-O2-Al2O3; (b) F-O2-CaO; (c) F-O2-Fe2O3; (d) F-O2-K2O, and (e) F-O2-MgO.

Figure 5. Equilibrium composition of Se-Mineral oxides interactions during combustion: (a) Se-O2-Al2O3; (b) Se-O2-CaO; (c) Se-O2-Fe2O3; (d) Se-O2-K2O, and (e) Se-O2-MgO.
Figure 4. Equilibrium composition of F-Mineral oxides interactions during combustion: (a) F-O2-Al2O3; (b) F-O2-CaO; (c) F-O2-Fe2O3; (d) F-O2-K2O, and (e) F-O2-MgO.

Figure 5. Equilibrium composition of Se-Mineral oxides interactions during combustion: (a) Se-O2-Al2O3; (b) Se-O2-CaO; (c) Se-O2-Fe2O3; (d) Se-O2-K2O, and (e) Se-O2-MgO.

Table 3. Prediction of the main species during the interaction of trace elements with mineral oxide during the combustion process.

| Component Interactions | Formed Species                  |
|-------------------------|---------------------------------|
| TEs-O2-K                | K2AsO4(s)  KBO2(s)  K2CrO4(s)  KF(s)  SeO2(s) |
| TEs-O2-Ca               | Ca3(AsO4)2(s)  Ca3B2O6(s)  CaCr2O4(s)  CaF2(s)  SeO2(s) |
| TEs-O2-Al               | AlAsO4(s)  (Al2O3)+6(B2O3)+2(s)  CrO2(s)  AlF3(s)  SeO2(s) |
| TEs-O2-Fe               | FeAsO4(s)  B2O3(s)  CrO2(s)  FeF3(s)  SeO2(s) |
| TEs-O2-Mg               | Mg3(AsO4)2(s)  Mg3B2O6(s)  CrO2(s)  MgF2(s)  MgSeO3(s) |

During coal combustion, B has a good relationship with Al, Ca, and Mg, which are important for the reaction with B to form (Al2O3)(B2O3)2, Ca3B2O6, and Mg3B2O6 in the temperature in the range 100–1400 °C and transform into BO2 and B2O3 in gaseous species with temperature increases (except the interaction with Ca).

The effect of mineral oxides on Cr, the presence of Ca and K make Cr less volatile due to the formation of CaCr2O4 and K2CrO4, and the effect of Al2O3, Fe2O3, MgO is not affected on Cr as shown in Figure 3a–e. The interaction of Al2O3, Fe2O3, MgO were introduced on Cr. At T > 1100 °C, CrO3(g) was formed and became the main gaseous species with a small contribution of CrO2(g). At T < 1200 °C, Cr2O3, and CrO2 were formed in the solid phase. Cr becomes volatile only at high combustion temperatures, and gaseous species leave the combustion zone and cooling condition [20,22].

The FeF3(s) KF(s), and AlF3(s) are predicted in equilibrium calculations from the interaction of F and Al2O3 Fe2O3, and K2O in low-temperature combustion (<700 °C) as shown in Figure 4a,c,d and then transforms into AlF3(g), FeF3(g), and KF(g) with the temperature increase. The presence of Ca and Mg make F less volatile due to the formation of CaF2 and MgF2 events in high-temperature combustions (T = 1100–1200 °C). Wang et al. [26]
reported that mainly F compound in coal is insoluble fluoride such as AlF$_3$, CaF$_2$, FeF$_3$, and MgF. These fluorides are the main occurrence state after the coal combustion process and are difficult to break down even at high temperatures.

The effect of mineral oxides on Se are different from other TEs. Figure 5a–e, Se forms in the gas phase almost over the whole range of temperatures (i.e., SeO and SeO$_2$). The Se can be endured in the gas phase even at temperatures lower than 200 °C. The effect of Al, Ca, Fe, and K on Se partitioning are not observed. On the other hand, the interaction of Se with MgO promotes the formation of MgSeO$_3$ at temperatures 100–300 °C as shown in Figure 5e. As reported, almost all of the Se was presented as the vaporized SeO and SeO$_2$.

3.2. Trace Element Interactions with Coal Fly Ash Components

Arsenic-CFA interaction favors the formation of arsenates such as AlAsO$_4$, Ca$_3$(AsO$_4$)$_2$, K$_3$AsO$_4$, and gaseous arsenate such as AsO, As$_2$O$_3$, As$_4$O$_6$, etc. All the main CFA components (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Ti, and V) interaction have been introduced in the input calculation to study which are the dominant interaction with As, and it can be seen from Figure 6a. In that case, As is predicted to form AlAsO$_4$. When the temperature is higher than 1400 °C, a small amount of AsO$_2$(g) appears and the formation of AlAsO$_4$(s) is decreased to the final temperature of the combustion process, indicating that AlAsO$_4$(s) is the arsenate species form during the combustion process. The mechanism process can be explained according to the following Equation (1).

$$\text{Al}_2\text{O}_3 + \text{As}_2\text{O}_3 + \text{O}_2 \rightarrow 2\text{AlAsO}_4.$$  (1)

Although Si as SiO$_2$ is the highest percentage component in CFA ash samples, the presence of Al as Al$_2$O$_3$ inhibits the effect of the other components on the formation of TEs-bearing species during the combustion process. This result is in line with Liu et al. [21] Al$_2$O$_3$ reacted more easily than CaO, Fe$_2$O$_3$, and SiO$_2$ and related to the reactivity of the oxides, the order of the reactivity of the oxides with As was thus: Al$_2$O$_3$ > CaO > Fe$_2$O$_3$ > SiO$_2$. Roy et al. [23] reported that the equilibrium distribution of As during oxy-fuel combustion of three Victorian brown coals at different temperatures, almost all the As was found to present as As$_2$O$_3$(s), Ca$_3$(AsO$_4$)$_2$(s), and As$_4$O$_6$(g).

Boron-CFA ash interaction, ($\text{Al}_2\text{O}_3$)$_9$(B$_2$O$_3$)$_2$ is predicted as the most probable species forming resulting from B-main CFA components interaction at a temperature below 1400 °C with a small contribution of gaseous boron such as BO, BO$_2$, B$_2$O$_3$, NaBO$_2$, and KBO$_2$. The mechanism process can be explained according to the following Equation (2).

$$4\text{BO} + 9\text{Al}_2\text{O}_3 + \text{O}_2 \rightarrow (\text{Al}_2\text{O}_3)_9(\text{B}_2\text{O}_3)_2.$$  (2)

In the case of Cr, the main coal and Cr interaction, the Cr compounds preferentially formed are, CrO$_3$(g) (T > 1200 °C), Cr$_2$O$_3$(s) (T = 200–1100 °C), CrO$_2$(g) (T > 1400 °C) and CrO$_2$(s) (T < 200 °C). CrO$_2$ in the solid phase is predicted to be chromate species consistent in the CFA. The mechanism process can be explained according to the following Equation (3).

$$\text{CrO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CrO}_2.$$  (3)
In the case of Cr, the main coal and Cr interaction, the Cr compounds preferentially formed are, CrO3(g) (T > 1200 °C), Cr2O3(s) (T = 200–1100 °C), CrO2(g) (T > 1400 °C) and CrO2(s) (T < 200 °C). CrO2 in the solid phase is predicted to be chromate species consistent in the CFA. The mechanism process can be explained according to the following Equation (3).

\[
\text{CrO} + \mathrm{O}^\cdot \rightarrow \text{CrO}^\cdot, \tag{3}
\]

During the combustion process, F is predicted to form mostly gaseous oxide and fluoride. Figure 6c, at the highest temperature, SiF4(g) FeF3(g) and NaF(g) in the gaseous phase were the dominant species forming during interaction of F and fly ash components and SiAl2F2O4(s) was formed at temperature <700 °C. The mechanism process can be explained according to the following Equation (4).

\[
\text{SiO}_2 + 2\text{Al}_2\text{O}_3 + \text{SiF}_4 \rightarrow 2\text{SiAl}_2\text{F}_4, \tag{4}
\]

**Figure 6.** Equilibrium composition of TEs-Coal fly ash components interaction: (a) arsenic; (b) chromium; (c) fluorine; (d) boron, and (e) selenium.
Selenium compounds are present during the combustion process in the gas phases (SeO and SeO₂) at the highest temperature. As shown in Figure 6e and Table 3, Se is predicted to form gaseous oxide and selenite. SeO₂ is predicted to be the dominant species over the entire temperature range studied with a small contribution of SeO. At temperatures below 300 °C, MgSeO₃ in solid-phase starts to form, which results in a small drop in the SeO and SeO₂ compound, and MgSeO₃ is the selenite species contained in coal. The mechanism process can be explained according to the following Equation (5).

\[
\text{SeO} + \text{MgO} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgSeO}_3
\]  

(5)

4. Discussion

4.1. The Migration of Trace Elements during Combustion Process

According to the above results, the interactions of trace elements with CFA components and/or mineral oxides may reduce the emission of gaseous TEs due to the formation of thermally stable TEs such as ash arsenates as shown in Equations (1)–(5). During the combustion process, mineral oxides make the TEs less volatile due to the formation of a complex compound of TEs and releasing the TEs emissions as tabulated in Table 4. The releasing of As emission formed at higher temperature (T > 1400 °C), B emission at T > 1100 °C, Cr emission at T > 1000 °C, F emission at T > 600 °C, and the most volatile are Se at T > 200 °C.

| Interaction   | Species of Trace Elements Produced | Gaseous                                                                 | Solid                                           |
|---------------|-----------------------------------|------------------------------------------------------------------------|------------------------------------------------|
| Arsenic (As)  | As, As₂, As₃, As₄, AsN, AsO, As₂O₃, As₄O₆, AsS, As₄S₄ | AlAsO₄, K₃AsO₄, Ca₃(AsO₄)₂                                           |
| Boron (B)     | B⁺, B⁻, B²⁺, B⁻², BN, BO, B₂O, BO₂⁻, BO₂⁻, (BO)₂⁻, B₂O₃, NaBO₂, AlBO₂, BS, B₂S₂, B₂S₄, KBO₂ | (Al₂O₃)₄(B₂O₃)₂, Mg₂B₂O₅, (CaO)₂(Al₂O₃)(B₂O₃), Mg₃B₂O₆, Ca₁₁B₂Si₄O₂₂ |
| Chromium (Cr) | Cr, Cr⁺, Cr²⁺, CrN, CrO, CrO₂, CrO₂⁻, CrS | Cr₂O₃, Cr₂O₇, K₂Cr₂O₇, Ca₃Cr₂S₁₇O₁₂ |
| Fluorine (F)  | F⁺, F⁻, O₂F⁻, ONF, NaF, (NaF)₂, MgF, MgF₂, AlF, AlF₃, AlF₄⁻, OAlF₂⁻, NaAlF₄, SiF₄, OSiF₂⁻, KF, (KF)₂, KAlF₄, CaF₂, TiF₅, OTiF, OTiF₂, FeF, FeF₂, FeF₃ | SiAl₂F₂O₄, Mg₃SiF₂O₄, Mg₅Si₂F₂O₆, CaF₂, Ca₆Si₂F₁₇O₂₇, Ca₆Si₂F₁₇O₃₂, Ca₅Si₂F₂O₇ |
| Selenium (Se) | Se, Se₂, Se₃, Se₄, Se₅, Se₆, Se₇, Se₈, SeO₂, Se₂O₂, NSe, AlSe, Al₂Se, SiSe, SiSe₂, SeS₂TISE | MgSeO₃ |

4.2. Trace Element Inhibition Characteristic during Combustion Process

Some of the researchers have confirmed that the migration of TEs is influenced by the combustion parameter, concentration, flue gas component, occurrence state in coal, volatility of trace element compounds, etc. [28,29]. Combustion temperature as a combustion parameter affected the inhibition of TEs. Figure 7 shows the trace element inhibition function of adding different mineral oxides (CaO, MgO, K₂O, Al₂O₃, and Fe₂O₃) under combustion temperature at 400, 800, and 1200 °C atmospheric conditions. From Figure 7a, the arsenic inhibition ratio was observed at 400 °C as a function of adding mineral oxides was 100% for each kind of mineral oxides. In the temperature studied 400, 800, and 1200 °C, the inhibition of arsenic by CaO, MgO, K₂O, Al₂O₃, and Fe₂O₃ decreased from 100 to 42.64 to 42.64%, 100 to 59.34% to 59.34%, 100 to 25.39 to 25.38%, 100 to 70.37 to 70.37%, and 100 to 44.93 to 0%, respectively. As temperature increases, the inhibition of arsenic was decrease as follow: T = 800 °C Al₂O₃ > MgO > Fe₂O₃ > CaO > K₂O, T = 1200 °C Al₂O₃ > MgO > CaO > K₂O > Fe₂O₃. The results showed that the inhibition ratio of Al₂O₃ was higher than other mineral oxides in each temperature range. Comparing the effect of combustion temperatures, the best condition given by at T = 800 °C. As reported by Chen et al. [30] the inhibition of As was affected by the adsorption temperatures. The inhibition of As was enhanced with temperature increasing (T = from 573 to 723 K). However, less As was captured by CaO at a lower temperature (T = 573 K) and higher temperatures (T = 1173 K
and 1323 K). Han et al. [31] also reported, CaO inhibited the As releasing more effectively than Fe$_2$O$_3$ at 723 K. However, when it reached higher temperatures (T > 973 K), CaO did not show more excellent inhibitory effects than Fe$_2$O$_3$ due to sulfur dioxide formed and competes with As$_2$O$_3$ to react with CaO which would obstruct the inhibition of As$_2$O$_3$ by CaO. Zhang et al. [32] suggest that Ca and Fe provide reactive sites and act as a catalyst and reactant in the inhibition processes. Physisorption may be the main As inhibition mechanism for Al$_2$O$_3$ due to the great surface area, which suggests that the great surface area may provide more active sites for gaseous arsenic [32,33]. Comparing the surface area of Al$_2$O$_3$, CaO, Fe$_2$O$_3$, and MgO the surface area of MgO (~90 m$^2$/g), Al$_2$O$_3$ (87.19 m$^2$/g) was higher than Fe$_2$O$_3$ (12.19 m$^2$/g) and CaO (8.91 m$^2$/g) [32,34]. Mineral oxides on the surface of activated carbon can act as a catalyst in the inhibition process, indicating that Al provides a large number of reactive sites per unit mass relative to Ca and Fe.

The inhibition ratio of B at temperature 400–800 °C by Al$_2$O$_3$, CaO, Fe$_2$O$_3$, K$_2$O, and MgO were 100% (except for K$_2$O at T = 800 °C, the inhibition ratio was 0%) when the combustion temperature is further increased to 1200 °C, the inhibition ratio was 0% as shown in Figure 7b. The inhibition ratio of Cr shows almost the same behavior as B at temperature 400–800 °C for all mineral oxides. When the temperature reaches 1200 °C, only CaO and K$_2$O can inhibit Cr release during combustion as shown in Figure 7c.

For fluorine, the inhibition ratio at temperature 400 °C, again Al$_2$O$_3$ shows more effectively than other mineral oxides. The fluorine inhibition by Al$_2$O$_3$, CaO, Fe$_2$O$_3$, K$_2$O, and MgO accounts for 40.66%, 56.57%, 24.20, 67.08%, and 39.70%, respectively. When the temperature reaches 800 °C, only CaO and MgO can inhibit F release with the inhibition rate were 40.66% and 56.57% and at temperature increase to 1200 °C, only CaO can inhibit F release during the combustion as shown in Figure 7d (inhibition ratio decreases to 26.31%).

Figure 7. Impact of addition of mineral oxides on trace elements (TEs) inhibition during combustion at T = 400 °C, 800 °C, and 1200 °C; (a) arsenic; (b) boron; (c) chromium, and (d) fluorine.
On the other hand, different results pattern was investigated for Se. All the mineral oxides at all temperatures studied did not show inhibitory effects to Se during the combustion process. As mentioned before, almost all of the Se was presented as the vaporized SeO and SeO2 during coal combustion conditions.

The inhibition order of TEs during combustion is as follow: As (Al2O3 > MgO > CaO > Fe2O3 > K2O), B (Al2O3, CaO, Fe2O3, K2O, > MgO), Cr (CaO > K2O > Al2O3, MgO, Fe2O3), and F (CaO > MgO > Al2O3, > Fe2O3 > K2O). Based on the discussion above, mineral oxides and temperature have an important role in the migration of TEs during the combustion process. This condition is because mineral oxides have a negative charge and a high surface-to-volume ratio. Otherwise, trace elements have a positive charge, adsorbed on their surface [35]. In coal combustion and gasification processes, ash deposits are formed on the heat-absorbing surfaces of the exposed process equipment. Ash fusion temperatures (AFTs) are the important characteristics of the coal ashes and signify the temperature range over which the ash deposits are formed on the heat absorbing surfaces of the process equipment [36].

5. Conclusions

The distribution and transformation mechanism of As, B, Cr, F, and Se in CFA during the combustion process based on thermodynamic calculation was investigated. During coal combustion, all mineral oxides correlate with As to form Ca3(AsO4)2, FeAsO4, K3AsO4, and Mg3(AsO4)2 with a small contribution of gaseous species such as AsO and As2O3. B has a good relationship with Al, Ca, and Mg to form (Al2O3)x(B2O3)y, Ca3B2O6, and Mg3B2O6 in the temperature in range 100–1400 °C. The effect of mineral oxides on Cr, the presence of Ca and K make Cr less volatile due to the formation of CaCr2O4 and K2CrO4, the effect of Al2O3, Fe2O3, MgO is not affected on Cr. The AlF3(g), FeF3(g), and KF(g) are predicted in equilibrium calculations from the interaction of F with Al2O3, Fe2O3, and K2O in low-temperature combustion (<700 °C) and then transforms into AlF3(l), FeF3(l), and KF(l) with the temperature increase. The effect of Al, Ca, Fe, and K on Se partitioning are not observed, almost all of the Se was presented as the vaporized SeO and SeO2. The interaction of Se with MgO promotes the formation of MgSeO3 at temperature 100–300 °C. The results confirm that the interaction between mineral oxides and gaseous trace elements promotes the formation of stable TEs such as arsenate, fluoride, etc. This is because mineral oxides have a negative charge, a high surface-to-volume ratio, otherwise, trace elements are usually with a positive charge, adsorbed on its surface. The inhibition order of trace elements by mineral oxides during combustion is as follow: As (Al2O3 > MgO > CaO > Fe2O3 > K2O), B (Al2O3, CaO, Fe2O3, K2O, > MgO), Cr (CaO > K2O > Al2O3, MgO, Fe2O3), and F (CaO > MgO > Al2O3, > Fe2O3 > K2O). As and B have a good correlation with Al2O3, while Cr and F with CaO.

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