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Prevention of bed agglomeration with iron oxide during fluidized bed incineration of refuse-derived fuels

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Abstract−The present study was performed to evaluate the effect of iron oxide addition on the prevention of bed agglomeration during the fluidized bed incineration of refuse-derived fuels (RDFs) having different alkali contents. To investigate the extent of bed agglomeration as a function of the $Fe_2O_3/(K_2O+Na_2O)$ molar ratio, a simulation was performed by using a thermodynamic equilibrium model. Based on this simulation, potassium (K) component exhibited a much higher affinity for iron (Fe) component than for silicon (Si) component, and the extent of agglomeration was remarkably reduced. Therefore, a small amount of iron oxide added to the bed effectively reduced the extent of bed agglomeration in the fluidized bed incineration process. Furthermore, the extent of agglomeration decreased as the molar ratio of $Fe_2O_3/(K_2O+Na_2O)$ increased until unity was attained. In excess Fe_2O_3, no potassium silicate melts existed in the products, while the amount of sodium silicate melts remained constant.

Key words: Fluidized Bed Incineration, Bed Agglomeration, Defluidization, Refuse-derived Fuels

INTRODUCTION

Recently, some incineration processes have become more productive and economical with the increased utilization of the heat available from refuse-derived fuels (RDFs). Fluidized bed incineration has been considered to be a suitable technology for RDFs. However, RDFs of high alkalinity occasionally undergo bed agglomeration in a fluidized bed combustor, despite the use of relatively low temperatures (700-900 °C). In the worst case scenario, rapid sintering can lead to severe agglomerate formation, resulting in defluidization and subsequent shut-down of the incinerator [1].

Bed agglomeration is an ash-related problem that is particularly associated with the content of alkalis, such as sodium and potassium. The alkali component in ash and mineral matter (mostly the Si component) can form alkali silicate melts at the typical operating temperature of fluidized bed incineration [2,3]. The initial adhesion between sticky bed particles leads to the formation of bed agglomerates, followed by further ash-bed particle interactions [3]. Therefore, several researchers have studied methods to mitigate the agglomeration problem, primarily by reducing the formation of these alkali silicate melts [4-6].

Grubor et al. [4] investigated the inhibitory effect of adding iron oxide (Fe_2O_3) and corundum (Al_2O_3) on bed agglomeration during the fluidized bed incineration of a biomass. They reported that following the addition of iron oxide, no sintering occurred, regardless of the amount of alkalis (Na+K) introduced. Moreover, iron oxide was more effective than corundum in preventing bed agglomeration, while silica sand was not suitable as a bed material for the incineration of a biomass with a high alkaline content in the ash. Additives have been found to exhibit either chemical or physical dilution effects, depending on the extent of the interaction between the additive and the ash particles [5]. Under conditions in which the $Fe_2O_3/(Na_2O+K_2O)$ molar ratio was greater than unity, Grubor et al. [4] and Lee et al. [7] reported that only Fe_2O_3 could react with alkalis because of the higher reaction rate between Fe_2O_3 and sodium or potassium relative to SiO_2 and alkalis. Despite these studies, the interaction between the ash compounds and the bed particles and additives incorporated into the agglomerates are poorly understood.

Therefore, in the present study, we devised a thermodynamic equilibrium model simulation [8], to investigate the effect of adding iron oxide on the prevention of bed agglomeration during the fluidized bed incineration of RDFs.

MODEL SIMULATION

The present study evaluated the use of Fe_2O_3 as an additive to prevent bed agglomeration in fluidized bed incinerations involving two different RDFs with high agglomeration potentials using a thermodynamic equilibrium model. We used the Gibbs free energy minimization method and the extensive thermochemical database of HSC Chemistry [8], which contains the enthalpy (H), entropy (S), and heat capacity (C) data for more than 17,000 chemical compounds. This model has been used to estimate the equilibrium compositions of chemical compounds at high temperature by several researchers [9-12]. The model calculated the amounts of the $Na_2O \cdot 2SiO_2$, $Na_2O \cdot SiO_2$, and $K_2O \cdot 4SiO_2$ melts that contributed to agglomeration [1,13], so that the potential for bed agglomeration could be predicted.

The compositions of the fuels are considered as the input data for the thermodynamic equilibrium model simulation. They are calculated based on the heat balance and operating conditions of actual combustion. The operating conditions considered were the superficial velocity (u_0=1.5 m/s), air/fuel ratio (λ_T=1.2), temperature (T_b=600-1,200 °C), and pressure (1 bar). Silica sand is used as a bed material,

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Table 1. Compositions of fuels used in this study

	RDF 1	RDF 2	Palm fiber*		RDF 1	RDF 2	Palm fiber*
Proximate analysis (wt%)				Ash analysis (wt%)			
Moisture	10.0	6.5	36.4	SiO_2	3.3	39.0	63.2
Volatile matter	82.4	86.7	46.3	Al_2O_3	0.3	1.0	4.5
Fixed carbon	-	-	12.0	CaO	27.7	9.9	ND
Ash	7.6	6.8	5.3	Fe_2O_3	0.3	1.0	3.9
Ultimate analysis (dry basis, wt%)				K_2O	28.4	29.0	9.0
C	46.7	45.2	47.2	MgO	3.1	2.2	3.8
H	5.9	6.6	6.1	Na_2O	0.7	0.4	0.8
O	35.6	38.5	36.8	P_2O_5	7.6	4.7	2.8
N	2.6	1.2	1.4	TiO_2	ND	0.4	0.2
S	0.2	0.2	0.3				
Cl	0.6	1.0	ND				
Ash	8.4	7.3	8.3				

*Werther et al. [10]

and the ratio of the bed material to each fuel is kept constant. An iron oxide (Fe_2O_3) additive was fed into the bed to prevent bed agglomeration in fluidized bed incinerations. The $Fe_2O_3/(K_2O+Na_2O)$ molar ratio was assumed to be varied to 2.0 with the consideration of the Fe_2O_3 in the ash composition.

Table 1 shows the compositions of the fuels used in this study. As shown in Table 1, the compositions of the two RDFs with high potassium content and agglomeration potential were compared to that of a palm fiber with low alkali content [14] and agglomeration potential.

RESULTS AND DISCUSSION

1. Prediction of Bed Agglomeration

The potential for bed agglomeration can be evaluated by calculating the amount of alkali silicate melts produced from combustion, since $Na_2O{\cdot}2SiO_2$ (mp 874 °C), $Na_2O{\cdot}SiO_2$ (mp 1,089 °C) and $K_2O{\cdot}4SiO_2$ (mp 770 °C) melts have high viscosities and form an initial coating layer on the bed particles [2,15]. Therefore, to predict the potentials for bed agglomeration of the two RDFs and palm fiber, the amounts of alkali silicate melts were calculated by using a thermodynamic equilibrium model. The results are shown in Fig. 1.

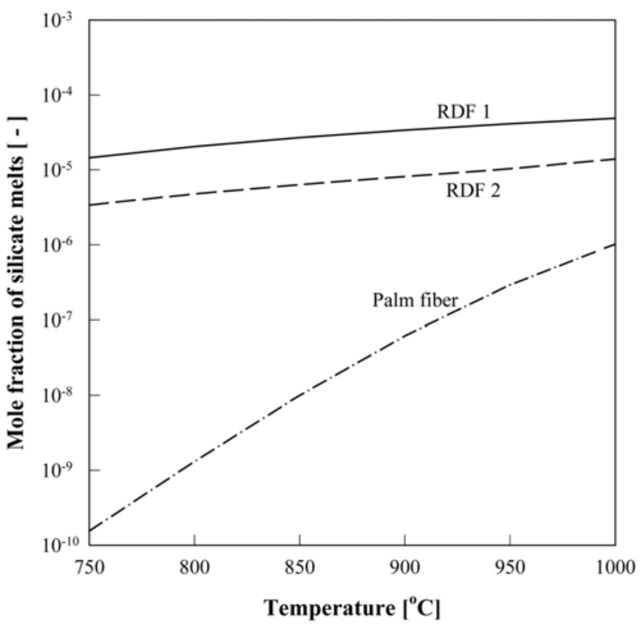

Fig. 1. Characteristics of silicate melts produced as a function of the temperature during the incineration of the RDFs and palm fiber.

As shown in Fig. 1, RDF 1 and RDF 2 have relatively high potentials for bed agglomeration compared with the palm fiber, and the amount of silicate melts produced from the incineration of RDF 1 or 2 was 2-4 orders of magnitude higher than that produced from palm fiber. Moreover, RDFs with high content of potassium components produced the highest levels of silicate melts, which were primarily potassium silicate melts.

In the case of palm fiber, a low level of silicate melts was produced, such that no bed agglomeration or ash-related problems occurred. However, the mole fractions of silicate melts produced from the incineration of palm fiber were strongly affected by the operating temperature, whereas that produced from incineration of the RDFs was not.

To investigate the possible reasons for the observed differences in the amounts of silicate melts produced from two kinds of RDF and the palm fiber, the behaviors of Na-compounds and K-compounds with respect to the operating temperatures for RDF 1 and palm fiber were examined. RDF 1 and palm fiber produced the highest and lowest levels of silicate melts, respectively, and it has been reported that palm fiber has a very low potential for bed agglomeration [12].

Fig. 2 shows the distribution of K-compounds produced during fluidized bed incineration of RDF 1 and palm fiber as a function of the operating temperature. For RDF 1 combustion, KCl(*l*) and $K_2O{\cdot}2SiO_2$ were the dominant compounds over the entire temperature range. The levels of potassium silicate melts, such as $K_2O{\cdot}4SiO_2(l)$, increased with rising temperature, reaching a high mole fraction of 3.1×10^{-5} at temperatures above 900 °C, while the amount of K_2SO_4 decreased (Fig. 2(a)). For palm fiber combustion, K_2SO_4 and $K_2O{\cdot}F_2O_3$ were the dominant compounds at temperatures below 900 °C, while as the temperature increased, the levels of KPO_3 and K-Al-

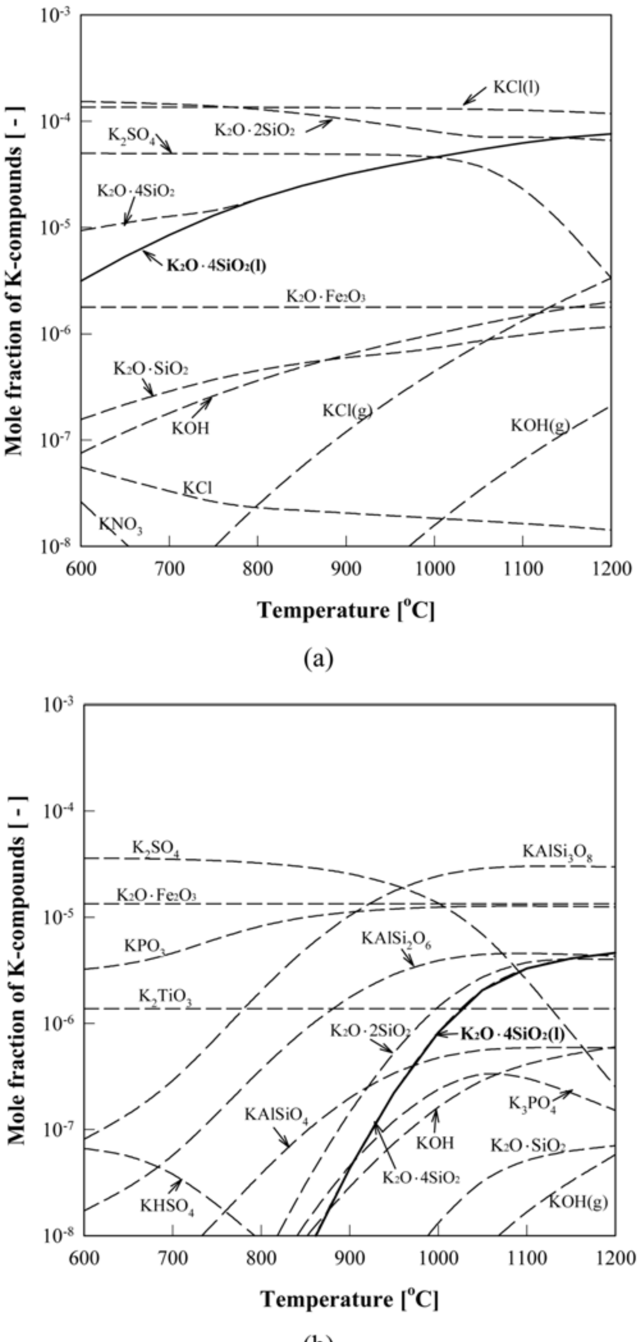

Fig. 2. Mole fractions of typical potassium products with respect to the operating temperature during the combustion of (a) RDF 1 and (b) palm fiber.

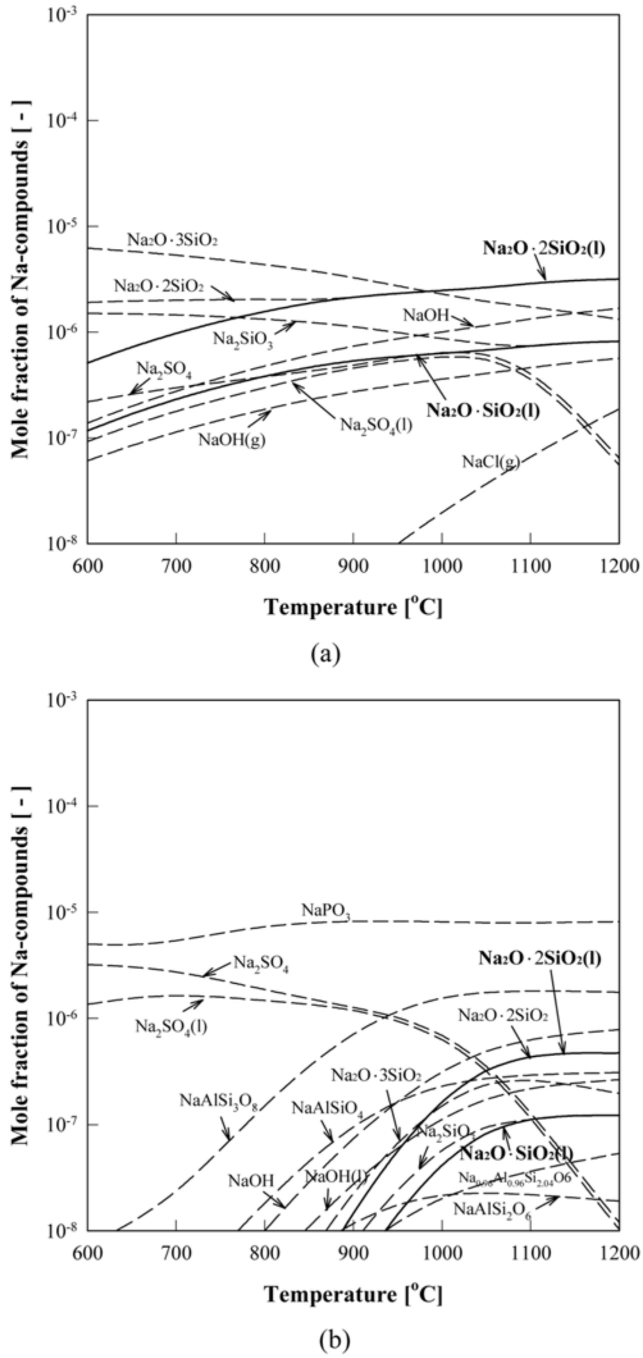

Fig. 3. Mole fractions of typical sodium products with respect to the operating temperature during the combustion of (a) RDF 1 and (b) palm fiber.

Si increased. The levels of silicate melts, such as $K_2O{\cdot}4SiO_2(l)$, also increased with increasing temperature, albeit to a low mole fraction of $<10^{-5}$ (Fig. 2(b)). The mole fraction of potassium silicate melt during fluidized bed incineration of palm fiber was lower than that for RDF 1, since the K component of palm fiber was considerably lower than that of RDF 1 (Table 1).

The distribution of Na compounds produced during the fluidized bed incineration for the RDF 1 and palm fiber is illustrated in Fig. 3 as a function of the operating temperature. For RDF 1 combustion, Na-Si compounds predominated over the entire temperature range, and the amounts of $Na_2O{\cdot}2SiO_2(l)$ and $Na_2O{\cdot}SiO_2(l)$ increased with increasing temperature (Fig. 3(a)). However, for palm fiber combustion, $NaPO_3$ was the predominant Na-compound over the entire temperature range, and although the level of $Na_2O{\cdot}2SiO_2(l)$ increased with increasing temperature, it had a lower mole fraction of $<10^{-6}$ (Fig. 3(b)). In addition, despite having similar levels of Na components, RDF 1 produced higher levels of sodium silicate melts than did the palm fiber.

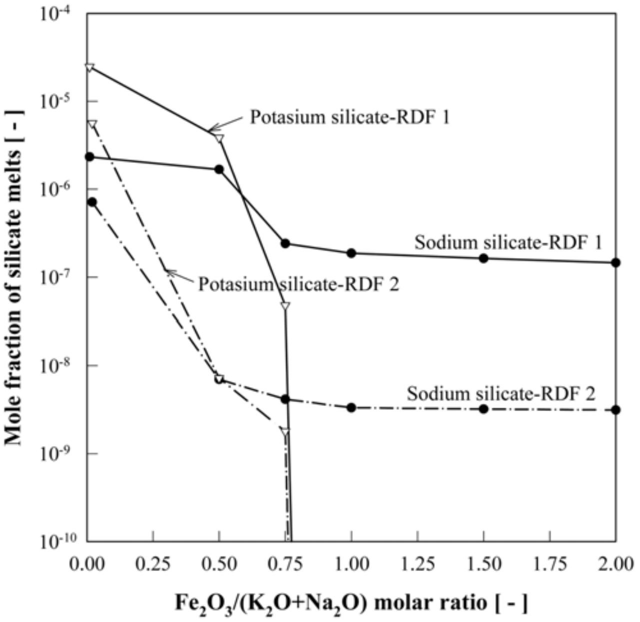

Fig. 4. Mole fractions of silicate melts as a function of the Fe_2O_3/(K_2O+Na_2O) molar ratio during the fluidized bed incineration of RDFs at 850 °C.

Several researchers have reported that Na component has a higher affinity for P component than for Si component, and that the reactivity of P component for Ca component is higher than for other ash compounds [11,12]. RDF 1 has a higher P component content than palm fiber but it also has a high content of Ca component. Therefore, the levels of Na-Si compounds produced from incineration of RDF 1 were high because almost all P component reacted with Ca component, resulting in the formation of negligible levels of Na-P compounds.

2. Prevention of Bed Agglomeration by Iron Oxide Addition

Tangsathitkulchai and Tangsathitkulchai [3] have reported that iron oxide is an effective additive to prevent the formation of alkali silicate melts, primarily because the Na and K alkali components react readily with Fe_2O_3, resulting in the formation of high-melting-point compounds.

Fig. 4 shows the mole fraction of the potassium and sodium silicate melts produced during the incineration of the RDFs according to the molar ratio of Fe_2O_3/(K_2O+Na_2O) at 850 °C. Incineration of the RDFs at 850 °C resulted in sharply decreased mole fractions of the potassium silicate melts, with increased molar ratios of Fe_2O_3/(K_2O+Na_2O) and lower molar ratio (0.75).

Similarly, the levels of sodium silicate melts produced during the incineration of RDF 1 and RDF 2 decreased with increasing molar ratios of Fe_2O_3/(K_2O+Na_2O), whereas the mole fractions of the sodium silicate melts were scarcely changed at the molar ratio of Fe_2O_3/(K_2O+Na_2O) >0.75. From these results, we conclude that Fe component has a much higher affinity for K component than for Na component.

To quantify the effect of Fe component on the formation of sodium silicate melts, the behavior of the Na components in the RDFs following iron oxide addition was investigated. The results are shown in Fig. 5.

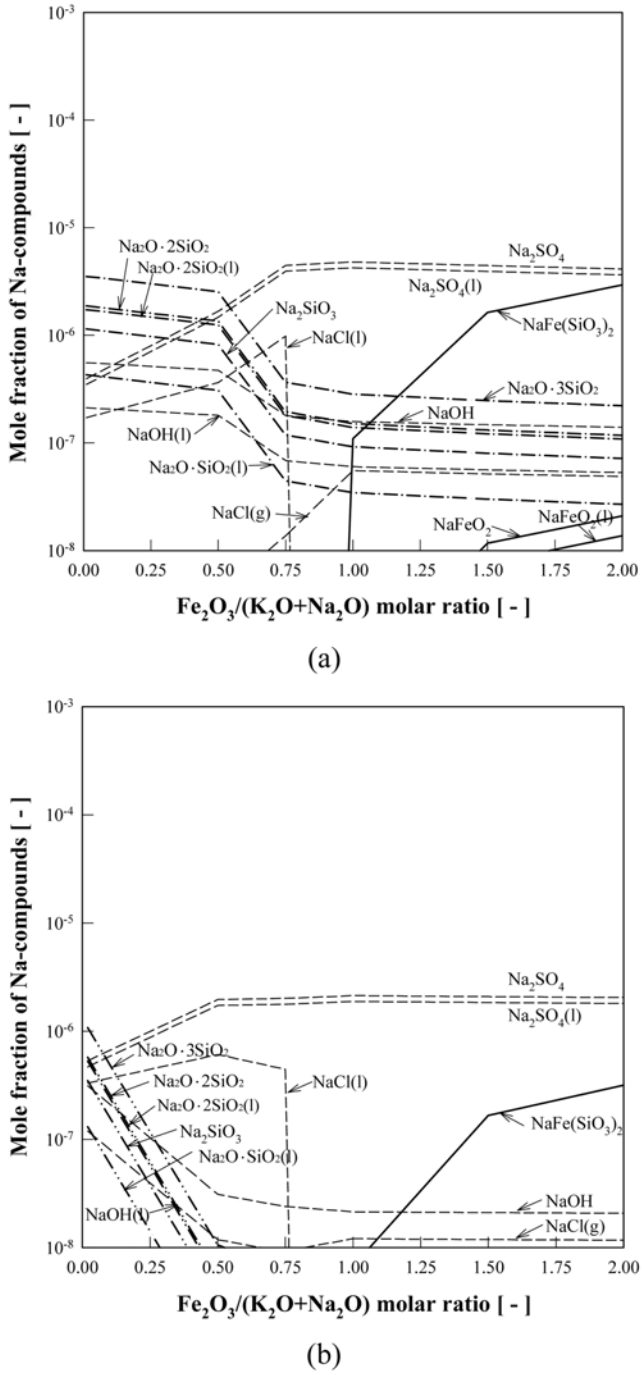

Fig. 5. Mole fractions of typical sodium products with respect to the molar ratio of Fe_2O_3/(K_2O+Na_2O) during the combustion of (a) RDF 1 and (b) RDF 2 at 850 °C.

The mole fractions of the Na-Si compounds decreased with increasing molar ratios of Fe_2O_3/(K_2O+Na_2O), and the levels of the Fe-Na compounds increased significantly at molar ratios of Fe_2O_3/(K_2O+Na_2O) >1.0 as shown in Fig. 5.

This, it appears that the formation of sodium silicate melts can be effectively reduced by the addition of Fe components. However, the mole fractions of the sodium silicate melts were virtually unchanged at Fe_2O_3/(K_2O+Na_2O) molar ratios >0.75, as described above. Therefore, the behavior of Fe component was investigated to

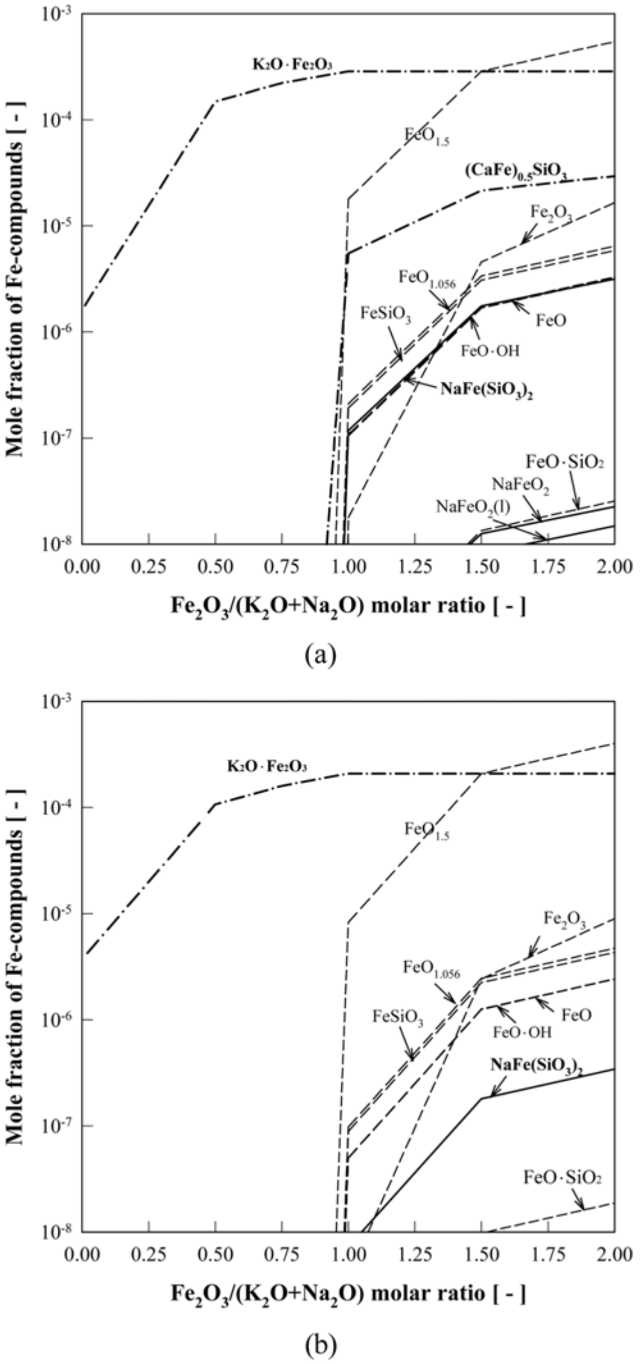

Fig. 6. Mole fractions of Fe-compounds as a function of the $Fe_2O_3/(K_2O+Na_2O)$ molar ratio during the fluidized bed incineration of (a) RDF 1 and (b) RDF 2 at 850 °C.

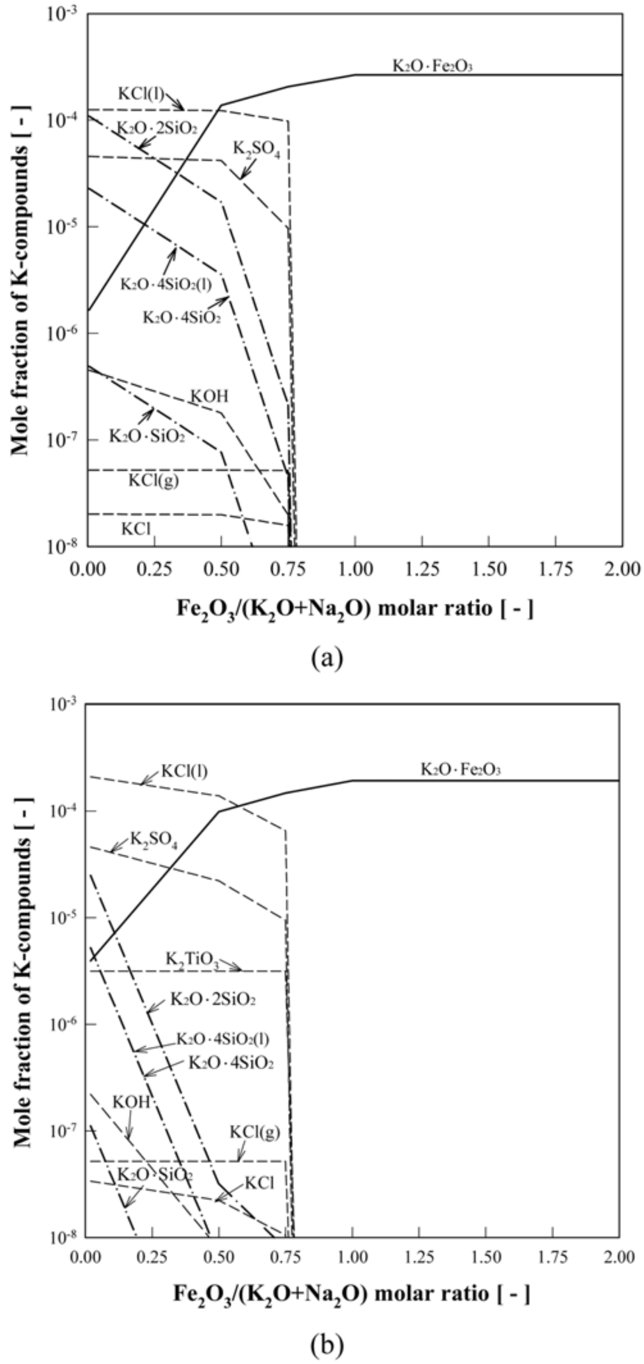

Fig. 7. Mole fractions of typical potassium products with respect to the molar ratio of $Fe_2O_3/(K_2O+Na_2O)$ during the combustion of (a) RDF 1 and (b) RDF 2 at 850 °C.

understand why the levels of sodium silicate melts were not reduced to as great an extent as the potassium silicate melts. The results are illustrated in Fig. 6.

RDF 1 and RDF 2 displayed similar tendencies, although a higher concentration of $(CaFe)_{0.5}SiO_3$ was formed in the case of RDF 1. It was estimated that the formation of $(CaFe)_{0.5}SiO_3$ influenced the preventative effect of iron oxide addition on bed agglomeration, and that the levels of silicate melts were not greatly reduced. Furthermore, the affinities of Fe component for the other components ranged from the highest affinity for K component to a lower affinity for Ca component to the lowest affinity for Na component.

Fig. 7 shows the mole fraction of K-compounds produced during the incineration of the RDFs 1 and 2 according to the molar ratio of $Fe_2O_3/(K_2O+Na_2O)$ at 850 °C. At 850 °C, the mole fractions of most of the K compounds, including the potassium silicate melts, decreased with increasing molar ratios of $Fe_2O_3/(K_2O+Na_2O)$ for both RDF 1 and RDF 2. However, the level of $K_2O{\cdot}Fe_2O_3$ increased dramatically with increasing $Fe_2O_3/(K_2O+Na_2O)$ molar ratios, and this was the predominant compound at ratios >0.5.

The results obtained in the present study are similar to those reported by Covey et al. [16], Grubor et al. [4], and Lee et al. [7]. Covey et al. [16] reported that Fe component reacted more readily with K components than Si component as follows:

$$Fe_2O_3+K_2O \rightarrow 2KFeO_2 \quad (1)$$

$$Fe_2O_3+K_2SO_4 \rightarrow K_2O \cdot Fe_2O_4+SO_2 \quad (2)$$

Therefore, it was recognized that the reactivity of K component for Fe component predominated over those for Si, Cl, S, and Ti components. Furthermore, it was confirmed that the formation of silicate melts was significantly reduced by the addition of iron oxide, leading to the conclusion that iron oxide addition during fluidized bed incineration of RDFs with high alkali contents is effective for preventing bed agglomeration.

CONCLUSION

From the results of the simulation, using a Gibbs free energy minimization thermodynamic equilibrium model, the potential for bed agglomeration during the fluidized bed incineration of refuse-derived fuels can be predicted. Moreover, silicate melts are important compounds with low melting points owing to a tendency to cause bed agglomeration.

The results show that the extent of bed agglomeration can be effectively reduced by adding only small amounts of iron oxide to the bed due to the higher affinity of K component to Fe component to Si component. The amounts of silicate melts that resulted in bed agglomeration were reduced as the $Fe_2O_3/(K_2O+Na_2O)$ molar ratio increased, up to an equimolar value (1.0). At higher molar ratios of $Fe_2O_3/(K_2O+Na_2O)$, there was no tendency for decreased sodium silicate melts and no potassium silicate melts were detected. In conclusion, for the combustion of fuels with a high content of K components in the ash, the potential for bed agglomeration may be effectively reduced by adding small amounts of iron oxide.

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