

Effect of Ash Compositions on Air Pollutant Emissions during Fluidized Bed Sludge Incineration

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Abstract—A simulation using a thermodynamic equilibrium model was performed to predict the effect of ash compositions on the behavior of air pollutants during fluidized bed sludge incineration. To investigate emission characteristics, the incineration temperature, air-fuel ratio (λ_f) and contents of calcium and chlorine were chosen as major operating parameters. For the analyses of the desulfurization of SO_x and the pollutant emissions by the limestone addition, the Ca/S molar ratio was changed from 0.5 up to 7.0. According to the simulation, NO_x was not influenced markedly by the air-fuel ratio, though greatly influenced by operating temperature. The effect of desulfurization with limestone addition was greatly influenced by ash composition, and desulfurization occurred over the Ca/S molar ratio of 5.5. This was attributed to the fact that the reactivity of the P component in ash to the added CaO was higher than that of sulfur in fuel.

Key words: Ash Composition, Desulfurization, Phosphoric Compound, Equilibrium Model

INTRODUCTION

The concentration of air pollutant emissions in the fluidized bed incineration process is greatly affected by operating condition and their compositions of the wastes [Cooper and Alley, 1986; Yan et al., 1999; Zevenhoven-Onderwater et al., 2000]. Therefore, in order to understand the characteristics of air pollutant emissions and to reduce them, methods for establishing optimum operating conditions of waste should be developed.

To date, the optimum operating conditions have been determined through several combustion experiments based on compositions of waste and fuel. But, there is considerable difficulty in carrying out this task; consequently, studies on predicted modeling, based on concentrations of combustible parts and heavy metals, have been partially carried out [Desrches-Ducarne et al., 1998].

However, existing predicted model studies are focused on the basic elements of combustible contents, which lead to large discrepancies. The reasons for the discrepancies are due to the lack of considerations for the amount of ash and its chemical composition [Desrches-Ducarne et al., 1998; Jang et al., 2001].

There is an especially wide difference between the measured and the predicted values of SO_x concentration in waste incineration without consideration of ash content and composition. In addition of limestone to desulfurize, it can be theoretically expected the perfect desulfurization in an equimolar Ca/S ratio. But, most operations are done with excessive limestone injection in practical incineration of waste. The reason is that the utilization rate of sorbent according to the structural properties and particle distribution of limestone and the contact efficiency between limestone and sulfur oxides are considered in practical incineration process. However, in order to predict the behavior of air pollutant emission more accurately in the incineration process, studies on the ash compositions must also be

carried out.

Consequently, the prediction of equilibrium compositions of air pollutants from waste incineration processes was carried out with considering ash compositions besides the major elements. The emission characteristics of air pollutants were evaluated with operating parameters such as incineration temperature, air-fuel ratio and Ca/S ratio according to limestone addition.

MODEL SIMULATION

In this study, HSC Chemistry [Outokumpu Research, 1999], which is a thermodynamic equilibrium model using the Gibbs free energy minimization method, was applied to predict emission behaviors of air pollutants considering both the major elements and ash composition.

To investigate the emission characteristics of air pollutants, incineration temperature, air-fuel ratio and the rate of limestone addition were chosen as major operating parameters. The air fuel ratio (λ_f) and the Ca/S molar ratio were changed to 2.0 and 7.0, respectively. The compositions of sewage sludge were listed in Table 1. The re-

Table 1. Compositions of sewage sludge used in the experiment

| Proximate analysis (wt%) | | Ash analysis (wt%) | |
|--------------------------|-------|-------------------------|-------|
| Moisture | 21.00 | SiO_2 | 49.60 |
| Combustibles | 30.64 | Al_2O_3 | 18.37 |
| Ash | 48.36 | P_2O_5 | 14.30 |
| Ultimate analysis (wt%) | | TiO_2 | 0.84 |
| C | 14.30 | CaO | 5.43 |
| H | 2.72 | MgO | 1.30 |
| N | 2.33 | Na_2O | 1.15 |
| S | 1.45 | K_2O | 2.14 |
| O | 17.99 | | |
| Ash | 61.22 | | |

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sults of analysis were considered as the input data of the model used in this study.

A model simulation was carried out to predict the effect of ash compositions on the emission level of air pollutants in a fluidized bed incineration of sewage sludge using a thermodynamic equilibrium model (HSC chemistry). Equilibrium assumption implies infinite reaction times and perfect mixing in the incineration system. Thus, the equilibrium composition represents the most stable chemical composition within a system under a specific state. Thermodynamically, this composition is corresponding to the one where the system free energy is minimized. The calculated equilibrium composition would reveal the preferred chemical speciation under a specific state, which in turn, suggests potential chemical reactions, which may occur within the system.

The sewage sludge used in the model simulation consisted of moisture, ash, C, H, N, S and O. The incinerator was assumed to operate at 400-1,200 °C of temperature range, 0-100% excess air and 1.0 atm pressure. The desulfurizing agent (CaO) was fed into the bed for the purpose of the SO₂-removal. The Ca/S molar ratio was assumed to be varied from 1.31 to 7.0 with the consideration of the CaO in the ash composition. In addition, the molar ratio of chlorine to sulfur was assumed to be varied from 0.01 to 3.0 to investigate the effect of chlorine content on the gas emissions.

RESULTS AND DISCUSSION

1. The Emission Characteristics of Air Pollutants

The total air-fuel ratio (λ_T) and bed temperature are major operating parameters in fluidized bed incineration. The emission of air pollutants was remarkably affected by the major two operating parameters, and thus their effects were predicted by model calculation.

The molar fraction of major exhaust gas with the total air-fuel ratio (λ_T) during the fluidized bed incineration of sewage sludge was profiled in Fig. 1. The concentration of nitrogen oxides (NO_x) in the

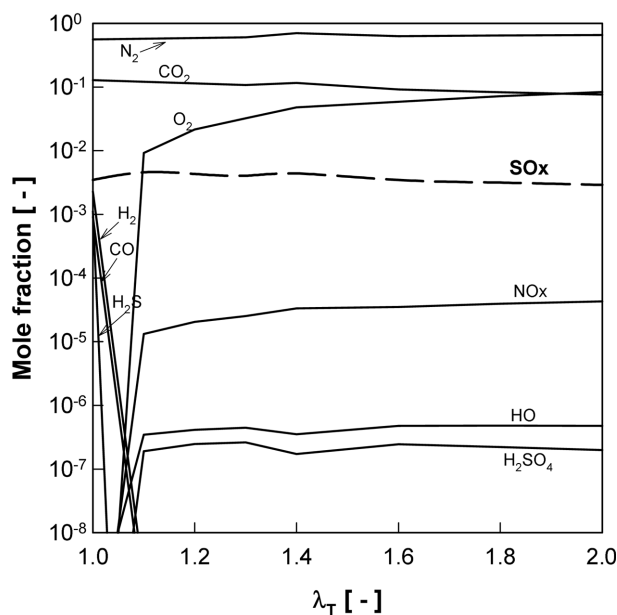


Fig. 1. The mole fraction of major air pollutants with total air-fuel ratio (T=800 °C).

exhaust gas was low, but the sulfur oxides (SO_x) were estimated as a high concentration. From these results, it is necessary to control sulfur oxides in the fluidized bed incineration of sewage sludge.

As shown in Fig. 1, the effect of the excess air on the emission level of nitrogen oxides slightly increased, but the concentration of sulfur oxides decreases slightly with an increase of total air-fuel ratio. With a simulation results, this can be explained that the higher excess air leads to the higher partial pressure of oxygen in the incinerator, and thus the oxidization rate of the nitrogen component in the sludge increased with the increase of the total air-fuel ratio.

Generally, most of the sulfur in the fuel was oxidized due to the high conversion rate of sulfur in the incineration process [Gibbs and Hampartsoumian, 1984]. The partial pressure of oxygen increased with the increase of the total air-fuel ratio, and thus the conversion rate of the sulfur component increased, but the emission level of sulfur oxides was highly affected by the dilution effect owing to a large amount of the excess air.

The concentration and species of the air pollutants varied with the operating temperature in the fluidized bed incineration of sewage sludge. The emission characteristics of air pollutants with an operating temperature of the 400-1,200 °C range are illustrated in Fig. 2. As shown in Fig. 2, the major air pollutants in the flue gas are the SO_x, NO_x, CO and H₂SO₄, and most of the sulfur component was converted to the sulfur oxides (SO_x) above the temperature of 800 °C. The concentration of hydrogen sulfate (H₂SO₄) at a low temperature was comparatively high, but the hydrogen sulfate (H₂SO₄) was converted to the sulfur oxides (SO_x) when the temperature increased to the typical incineration condition. From these results, when the operating temperature of the air pollutant controlling devices decreased for the purpose of the sulfur oxides control, some measures must be taken to cope with the corrosion of the controlling devices due to the increase of the H₂SO₄.

The emission level of the nitrogen oxides (NO_x) increased with operating temperature. This could be explained by the formation rate

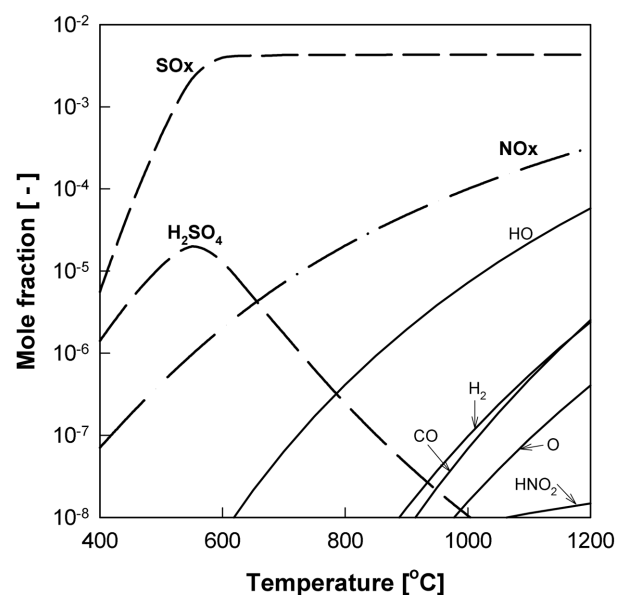


Fig. 2. The mole fraction of gaseous pollutant with operating temperature ($\lambda_T=1.2$).

of the fuel- NO_x and thermal- NO_x increase with operating temperature due to the higher oxidation rate of the nitrogen component in the sludge and nitrogen gas in the combustion air in the higher temperature condition [Zeldovich et al., 1947; Fenimore, 1971].

2. The Effect of the Ca/S Molar Ratio on the Emission Characteristics

Lime or limestone injection is usually used for the purpose of desulfurization during the incineration process [Lin et al., 1994; Seo et al., 1999]. Determination of the limestone dose is usually estimated on the Ca/S molar ratio basis. The extent of desulfurization is remarkably dependent on the purity and the particle size of the limestone injected in the practical incineration process, and calcination and sulfation of the limestone are very sensitive to operating temperature. Thus, perfect desulfurization is not possible when the limestone is injected into the bed as a theoretical molar ratio of the Ca/S. In addition, the gaseous SO_x reacts heterogeneously with the solid phase of the CaO, and the utilization of sub-micro pores of limestone is limited, and thus the practical injection rate of limestone is much higher than the theoretical molar ratio [Lin et al., 1994; Seo et al., 1999].

Fig. 3 shows the concentration of air pollutants with regard to the Ca/S molar ratio and without consideration of the ash compositions. Theoretically, perfect desulfurization was accomplished at the Ca/S of 1.3, as shown in this result. But the high efficiency of desulfurization can be obtained practically in the incineration process over 3.0 of the Ca/S molar ratio [Seo et al., 1999]. The predicted values by the thermodynamic equilibrium model were especially different from the measured values experimentally for waste, which had high ash content. It was supposed that the ash components in the waste might participate in the desulfurization reaction [Seo et al., 1999]. Therefore, model simulation was performed with consideration of ash compositions, such as the SiO_2 , Al_2O_3 , P_2O_5 , CaO, MgO, Na_2O , TiO_2 and K_2O , and the Ca/S molar ratio was also predetermined on a raw ash basis without adding limestone.

Fig. 4 shows the emission level of the air pollutants with the op-

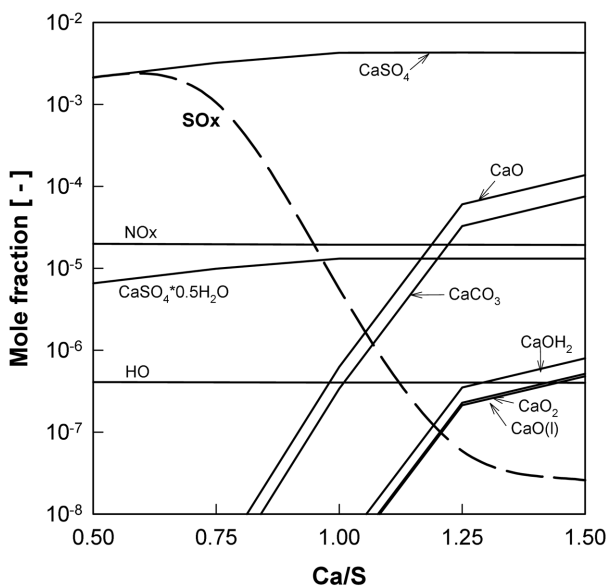


Fig. 3. The mole fraction of air pollutants with Ca/S ratio ($T=800$ °C, $\lambda_r=1.2$).

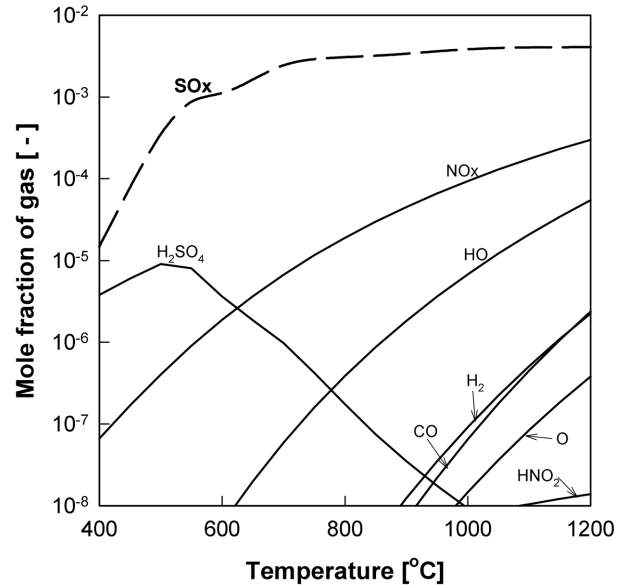


Fig. 4. The mole fraction of gaseous pollutants with operating temperature ($\lambda_r=1.2$, $\text{Ca/S}=1.3$).

erating temperature. Although the limestone was not injected, the Ca/S molar ratio was 1.3 due to the high content of the CaO in the sewage sludge, but a desulfurization reaction did not occur. This result differs entirely from the desulfurization efficiency obtained without the consideration of ash compositions as shown in Fig. 3. Therefore, more limestone was required to reduce the sulfur oxides.

As shown in Fig. 5, the desulfurization reaction slightly occurred at 5.5 of the Ca/S molar ratio, and then a remarkable effect of reduction was obtained at 6.5 of the Ca/S. As mentioned above, the desulfurization reaction started as the Ca/S molar ratio exceeded 5.5 in an incineration of the sewage sludge. The injected limestone

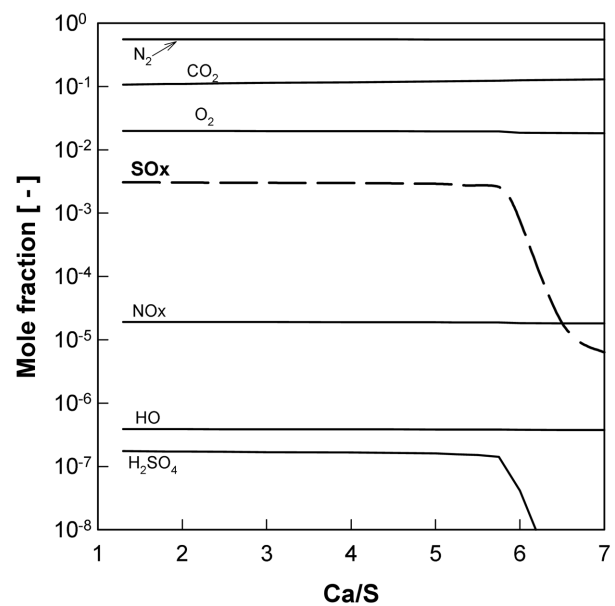


Fig. 5. The mole fraction of gaseous pollutants with Ca/S ratio ($T=800$ °C, $\lambda_r=1.2$).

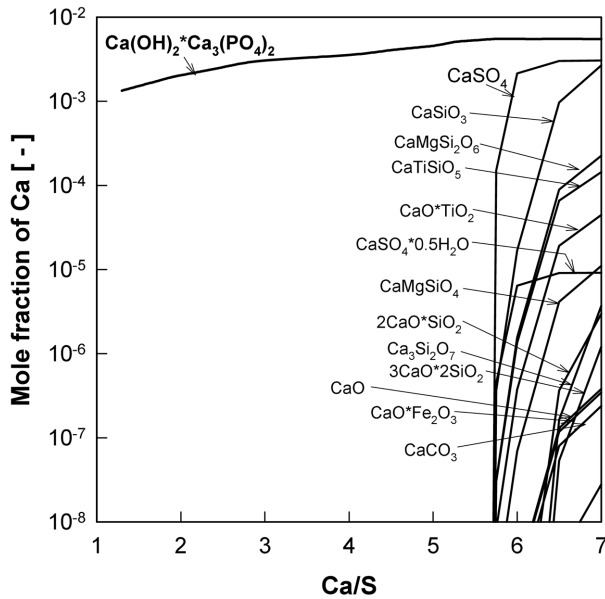


Fig. 6. The concentration of Ca compounds with Ca/S ratio ($T=800$ °C, $\lambda_r=1.2$).

reacting with any component in the ash compositions can explain this.

The variations of the calcium compounds in the ash with the Ca/S molar ratio are plotted in Fig. 6. As shown in Fig. 6, the $\text{Ca(OH)}_2 \cdot \text{Ca}_3(\text{PO}_4)_2(\text{s})$ among the various Ca-compounds was the most dominant compound in the whole of the conditions. And then some of the compounds such as the $\text{CaSO}_4(\text{s})$, $\text{CaSiO}_3(\text{s})$, $\text{CaMgSi}_2\text{O}_6(\text{s})$ and so on were usually produced as the Ca/S molar ratio exceeded 5.5. Therefore, the desulfurizing reaction by the limestone injected started at 5.5 of the Ca/S molar ratio, and then the ash components could react with the remaining Ca-component after it reacted with sulfur

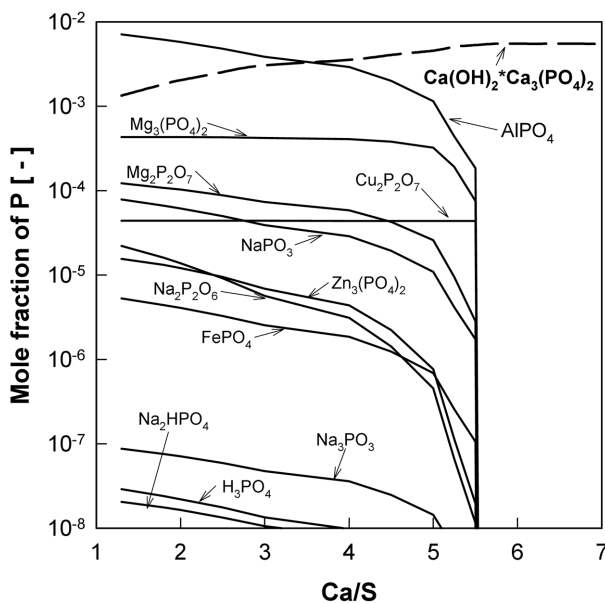


Fig. 7. The concentration of P compounds with Ca/S ratio ($T=800$ °C, $\lambda_r=1.2$).

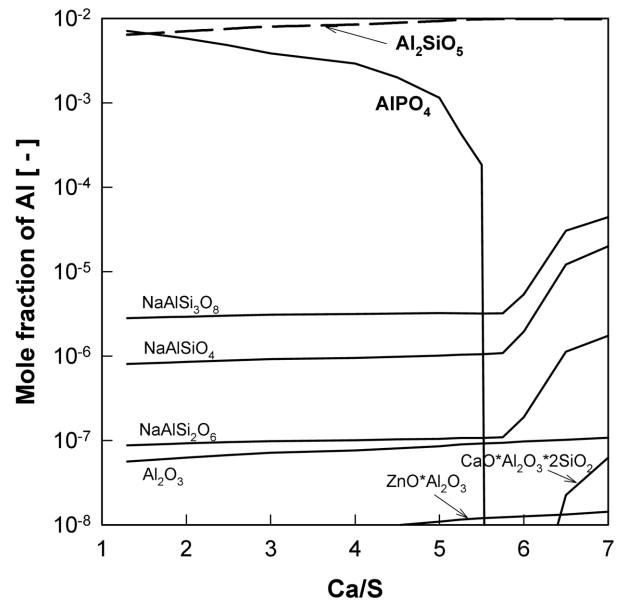


Fig. 8. The concentration of Al compounds with Ca/S ratio ($T=800$ °C, $\lambda_r=1.2$).

and phosphorus.

The consumption rate of the limestone added for the removal of the sulfur oxides was significantly affected by the phosphorous content in the ash. As shown in Fig. 7, the various phosphuretted compounds, such as $\text{Ca(OH)}_2 \cdot \text{Ca}_3(\text{PO}_4)_2(\text{s})$, AlPO_4 , $\text{Mg}_3(\text{PO}_4)_2$, $\text{Mg}_2\text{P}_2\text{O}_7$, NaPO_3 and so on, were usually produced at a low Ca/S molar ratio. As mentioned above, the desulfurization did not occur up to 5.5 of the Ca/S molar ratio.

The molar fraction of $\text{Ca(OH)}_2 \cdot \text{Ca}_3(\text{PO}_4)_2(\text{s})$ was increased with the Ca/S molar ratio, but the P-compounds reacted with the Al, Na and Mg component which were dissociated and converted to the phosphuretted calcium compound. From these results, the reactivity of the P-component to the injected limestone (Ca) was the highest in comparison to other ash compounds in this study.

According to the behavior of the P-component, therefore, the behavior of the Al-, Na- and Mg-compounds was significantly dependent on the fate of the P compounds. As shown in Fig. 8, most of the Al-component was usually formed to the Al_2SiO_5 and AlPO_4 , but the AlPO_4 was decreased and converted to the Al_2SiO_5 and other oxides by the increases of the Ca/S ratio.

Similar trends could be also observed in the magnesium (Mg) and the sodium (Na) components. As shown in Figs. 9 and 10, the phosphuretted compounds were converted to the oxides coupled with the Ca, Si and Al components with the increase in the Ca/S molar ratio. Most of the Mg-component was usually formed to the $\text{Mg}_3(\text{PO}_4)_2$ and MgSiO_3 up to around 5.0 of the Ca/S ratio, but the MgSiO_3 was the dominant compound with an increase in the Ca/S ratio. The sodium component was usually formed to the Na_2SO_4 and NaPO_3 , but the NaPO_3 was decreased and converted to the $\text{NaAlSi}_3\text{O}_8$ and other oxides by the increases of the Ca/S ratio.

In the case of the high phosphorous containing waste, the determination of the Ca/S molar ratio should be considered for the sulfur and phosphorous contents in the waste. Applying the stoichiometric reaction, the formation mechanism of the Ca-P compound

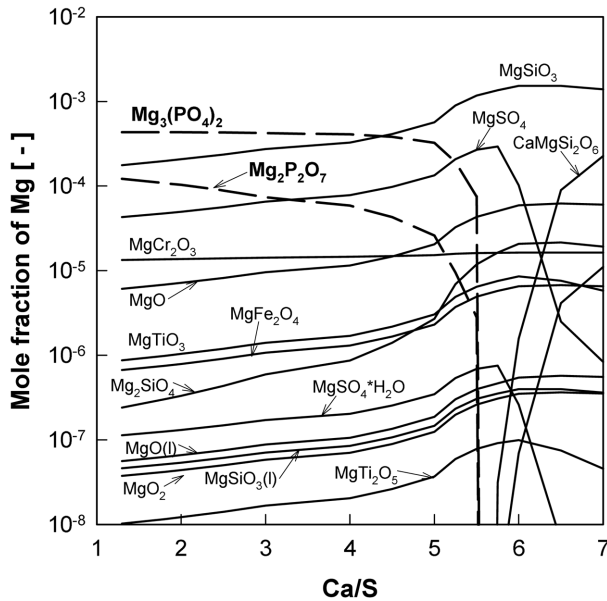


Fig. 9. The concentration of Mg compounds with Ca/S ratio ($T=800\text{ }^{\circ}\text{C}$, $\lambda_r=1.2$).

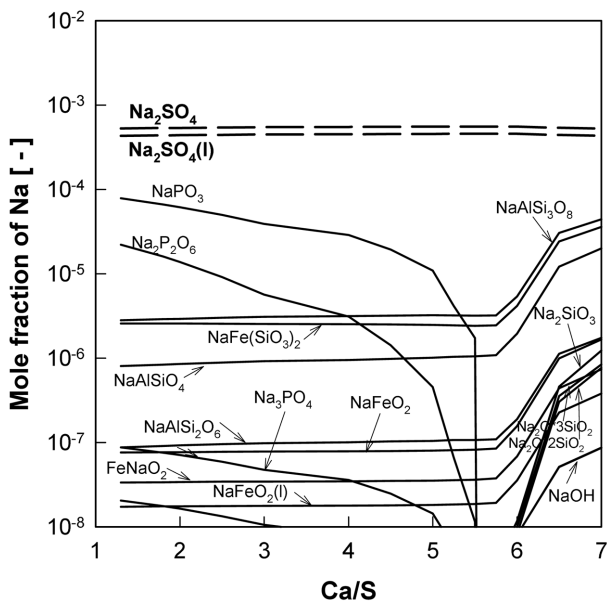
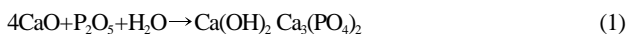


Fig. 10. The concentration of Na compounds with Ca/S ratio ($T=800\text{ }^{\circ}\text{C}$, $\lambda_r=1.2$).

predicted by the model simulation may be as follows:



The theoretical molar ratio of the calcium to the phosphorous was 2 times more than shown in the Eq. (1). The molar ratio of S, Ca and P content based on the value listed in Table 1 was about 1 : 1.3 : 2.7, and 2.01 of the molar ratio of the Ca to the P was equivalent to 5.5 of the Ca/S molar ratio. This implies that the desulfurization reaction started at the Ca/S molar ratio of 5.5 and over. Therefore, the determination of the limestone injection rate using the Ca/(S+P) molar ratio is the more reasonable manner during the incin-

eration of the waste containing a high phosphorous content. The optimum rate of limestone injection was observed at the Ca/(S+P) molar ratio of 3.3 and upward.

In the practical incineration process, however, the desulfurization efficiency can be reached at 90% or more at the Ca/S molar ratio of 3.0 [Seo et al., 1999]. The differences between the predicted and practical values were caused by the facts that the CaO content in the ash was involved in the calculation of the Ca/S molar ratio, and the particle size of the limestone was not considered in the model simulation. If the CaO content in the ash is not considered, then the Ca/S molar ratio becomes 4.2, which is somewhat higher than the practical value. In a practical incineration process, a large amount of the limestone injected is transported into the freeboard section without remaining in the bed due to the wide range of the size distribution of the limestone particle. Thus, a lower amount of limestone than the predicted value is required [Lin et al., 1994; Seo et al., 1999].

CONCLUSIONS

This study was performed to predict emission characteristics of air pollutants using a thermodynamic equilibrium model, and to establish basic data for an optimum operating condition, which was able to reduce the emission level of air pollutants. The results obtained in this study are as follows;

The concentration of sulfur oxides decreased slightly with an increase of total air-fuel ratio. Most of sulfur component was converted to the SO_x above the temperature of $800\text{ }^{\circ}\text{C}$. On the other hand, the nitrogen oxides (NO_x) were slightly increased under the excess air condition. The emission level of the nitrogen oxides (NO_x) increased with the increase of operating temperature. This could be explained by the formation rate of the fuel- NO_x and thermal- NO_x which increased with an increase of operating temperature due to the higher oxidization rate of the nitrogen component in the sludge and nitrogen in the combustion air.

Without considering ash compositions, theoretically, perfect desulfurization could be accomplished at the Ca/S molar ratio of 1.0. Although the limestone was not injected, the Ca/S molar ratio was 1.3 due to the high content of the CaO in the sewage sludge, but the self-desulfurization reaction did not occur. This can be explained by the reaction between included CaO and any component in the ash.

Because the Ca component preferentially reacted to the P component, the desulfurizing reaction by the injected limestone was significantly affected by the phosphorous content in the ash. The behavior of ash components such as Al, Na, and Mg was also affected by the Ca-P compound. Therefore, the determination of the limestone injection rate using the Ca/(S+P) molar ratio had a more reasonable manner during the incineration of the waste containing a higher phosphorous content.

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