Prediction of Gaseous Pollutants and Heavy Metals during Fluidized Bed Incineration of Dye Sludge

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Abstract–This research provides an equilibrium model for predicting both the emission of gaseous pollutants and the fate of heavy metals during incineration of biologically treated dye sludge in a bench-scale fluidized bed incinerator. Major gaseous pollutants and hazardous trace heavy metals have been also measured under various operating conditions. The predicted values, which were derived by using a thermodynamic equilibrium model, can be used to determine the optimum operating parameters and the risk associated with hazardous waste incineration by means of verifying experimental data. However, prediction of NO_x emission using a thermodynamic equilibrium model during incineration of waste was not simple. The reason is that the variation of NO_x emission during incineration of waste was affected by the various operating parameters, such as air-fuel ratio (λ_T), primary air factor (λ_1/λ_T), combustor geometry, method of heat release, and preheating of combustion air. According to the distributions of Cr and Pb simulated by the equilibrium model, all of the Cr in the feed was retained in the ash as the solid phase of Cr_2CO_3. However, most Pb was retained in the ash during incineration as the solid phase of $PbSO_4$, or heterogeneously deposited onto the fly ash as PbO(g) when the combustion gas becomes cool.

Key words: Thermodynamic Equilibrium Model, Gaseous Pollutants, Trace Metals, Dye Sludge, Fluidized Bed Incineration

INTRODUCTION

In recent years, there has been increasing concern about the amount and quality of dye sludge that has to be disposed of. Finding an economically and environmentally acceptable method to dispose of dye sludge has been required. Among several methods available to treat and dispose of dye sludge, incineration has been known to be the most effective one [Kawaguchi, 1985; Bayens and Geldart, 1978]. However, the dye sludge contains minor and trace elements, such as sulfur, chlorine, and heavy metals, which are released during incineration. In assessing the environmental impact caused by the incineration of dye sludge, it is important to determine the fate of the toxic elements that may provide a source of health hazard. Some of these elements are easily volatilized at typical combustion temperatures, and then enriched on the very fine particles elutriated from the bed and also found in vapor form in flue gas.

Several investigators reported that the fluidized bed incineration, due to its lower combustion temperature, can minimize the concentration of potentially toxic and trace elements released from flue gas emissions, resulting in enriching the elements in ash and slag formations. Similarly, particulate fines released from cleaning systems are expected to contain a lower concentration of the toxic and trace elements on the particle surface. Furthermore, the fluidized bed incinerator has the potential to capture SO_2 by means of introducing a desulfurizing agent such as limestone or dolomite to the bed [Valk et al., 1987; U.S. EPA, 1981; Gibbs and Hampartsoumian, 1984; Yaverbaum, 1977].

During the fluidized bed incineration process, including the introduction of desulfurizing agent, therefore, the minor and trace elements can interact with either a desulfurizing agent or other compounds such as gaseous combustion products and/or particulate matters. In addition, because the composition of solid wastes is heterogeneous and changes momentarily, it is difficult to maintain the optimum operating conditions on sites.

A thermodynamic equilibrium model principally delineates the stable phases that can form under specific operating conditions. When both analytical and thermodynamic data are assimilated, the reaction mechanisms and pathways of minor and trace elements in the incineration process may be proposed. Furthermore, the model can reduce expenses required for conducting the emission testing of minor and trace elements, and determine the optimum operating conditions during incineration of wastes in the field.

In this research, therefore, the gaseous pollutants and heavy metals produced during incineration of dye sludge were predicted with a thermodynamic equilibrium model. The model simulation used for determining the distribution of major combustion gas and trace metal species was performed according to the content of chlorine in the sludge. And, the equilibrium concentrations of major gaseous pollutants and trace metals were also obtained in case of adding lime into the bed to control the gases of HCl and SO_x.

EXPERIMENTAL

As described in the previous research [Lee et al., 1992], the in-

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Table 1. Compositions of dye sludge and coal used in the experiment

Proximate analysis (wt%)			Ultimate analysis (wt%, dry basis)		
	Dye sludge	Coal		Dye sludge	Coal
Moisture	80.60	7.20	C	30.90	69.79
Volatile matter	10.07	29.13	H	4.84	4.26
Fixed carbon	3.73	54.59	N	7.17	4.46
Ash	5.60	9.08	S	2.54	0.31
			O	25.70	11.40
HHV (kcal/kg)	3258	6572	ash	28.85	9.78

cinerator is fabricated with stainless steel. The bed section in the incinerator is: ID of 0.26 m and height of 1.2 m, and the freeboard section is ID of 0.35 m and height of 2.0 m. As an air distributor, the stainless steel plate contained a 1.96% opening area ratio in a triangular arrangement.

During the incineration experiments, the bed was initially filled with sand as a bulk bed material. To start up the incinerator, the fluidizing air produced from a compressor was divided into primary and secondary flows, and then preheated by the air preheaters, and injected into both the bed and the freeboard section. At the same time, LPG was supplied until the bed temperature reached a temperature of 500 °C. Then, the airflow, the feed rate of dye sludge and bituminous coal as an auxiliary fuel were gradually increased until the bed temperature reached a predetermined value.

During co-incineration of dye sludge and coal, the dye sludge and coal were fed into the bed by 2 sets of screw feeders, respectively. As shown in Table 1, the sludge has about 80% moisture content, and feed rate of sludge ranges from 20 g/min to 50 g/min under the whole experimental conditions. The ratio of dye sludge to coal was 2 by weight basis. The ash produced from the bed was not re-

moved because the pressure drop of the bed did not occur under the whole experimental conditions. The compositions of dye sludge and coal used in this research are shown in Table 1.

Once steady state incineration conditions were established, the ash sampled from the bed and collected by cyclones were weighed once an hour and were analyzed for combustible content, calorific values, and heavy metals. To analyze the metal concentrations in the flue gas, the gas was also sampled. The concentrations of gaseous pollutants (SO_2, NO_x, CO) in the incineration gas, which was collected from each gas sampling line, were measured by using an automatic gas analyzer.

For analysis of heavy metals in the dye sludge and the ash taken from various output streams of the incinerator, the samples were digested with HF-aqua regia, and then analyzed by atomic absorption spectrometry (AAS) or inductively coupled argon plasma spectrometry (ICP). Source Assessment Sampling System (SASS) with addition of 0.5 M nitric acid solution was used to collect the gaseous heavy metal elements in the flue gas [Hughes and Littlejohn, 1987].

RESULTS AND DISCUSSION

1. Model Simulation

Chemical equilibrium is usually described by either of two equivalent formulations, such as equilibrium constants or minimization of free energy. However, the equilibrium constant method has several disadvantages. These include difficulty in the use of components, in testing the some condensed species, and in extending the generalized method for nonideal equations of state. For these reasons, the free-energy minimization method is usually utilized.

At equilibrium the free energy of a system is minimized. By combining this fact with mass conservation constraints it is possible to develop a series of algebraic equations that can be solved to determine the equilibrium composition of a given system. A computer program was developed to solve this of equations [Gordon and
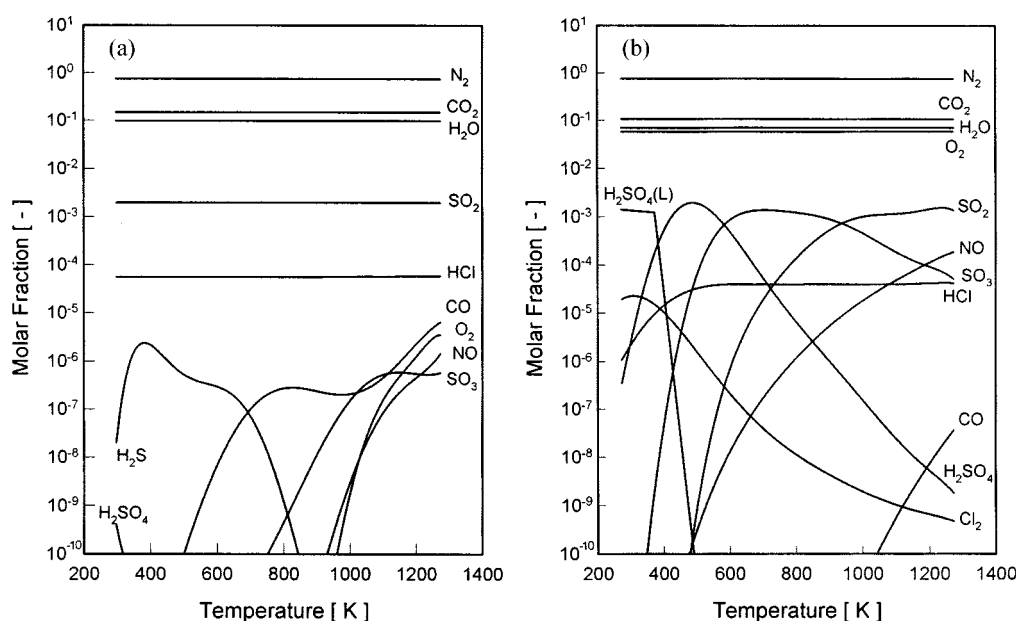
Fig. 1. The molar fraction of major gaseous pollutants as a function of temperature with 0.1% of chlorine content [(a); 0% of excess air, (b); 40% of excess air].

Mcbride, 1971; Lee, 1988].

A model simulation was done to predict the emission level of air pollutants and to evaluate the fate of heavy metals by using a thermodynamic equilibrium model. The model was especially developed for predicting equilibrium composition during coal or solid waste combustion.

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 that may occur within the system. The solid wastes used in the model simulation were assumed to consist of C, H, N, S, and Cl. The trace metals considered were just 100 ppm of lead (Pb) and chromium (Cr), respectively. The incinerator was assumed to operate in the 700-1,200 K temperature range, 0-40% excess air, and 1.0 atm pressure. In addition, SO_2-removal efficiencies were assumed to be obtained up to 90% through the addition of desulfurizing agent (CaO) into the bed.

1-1. Major Gaseous Pollutants

The effect of excess air on the distribution of major gaseous pollutants produced under the conditions of 200-1,400 K temperature range, and 0.1% chlorine content in the waste is illustrated in Fig. 1(a) and (b). The concentration of nitrogen oxide (NO) plotted in Fig. 1(b) was significantly higher than the concentration in Fig. 1(a) simulated without excess air. This is because the amount of the NO (g) was reduced into the gaseous nitrogen (N_2) by the reducing atmosphere that was formed with decreasing excess air.

Although the Cl_2(g) concentration increases with either increasing excess air or decreasing temperature, the concentration of gaseous hydrogen chloride (HCl) is higher than Cl_2(g) under the whole conditions simulated. However, the effect of the excess air on the variation of HCl concentration was almost not apparent. Increasing the excess air content up to 40% reduces the SO_2 molar fraction at temperature below 900 K, while enhancing the molar fraction of
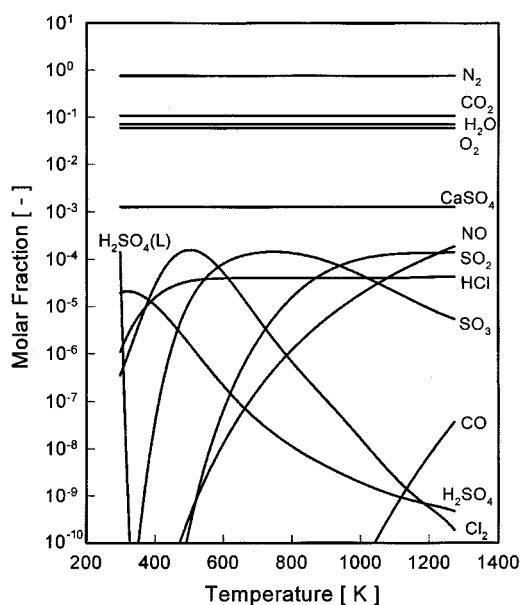

Fig. 2. The molar fraction of major gaseous pollutants as a function of temperature under the conditions of 0.1% of chlorine in the waste and 90% SO_2-removal.

SO_3 and H_2SO_4.

However, as the excess air was reduced, more SO_2 was formed. Fig. 2 shows the distribution of major gaseous pollutant when the model analysis was carried out at 40% excess air and 90% SO_2-removal with lime injection. As shown in this figure, the effect of the lime injection on the variation of HCl concentration is insignificant, while the concentration of sulfur oxides is remarkably decreased. From the result, it is found that the reactive affinities of the sulfur oxides (SO_x(g)) to the lime (CaO(s)) are much higher than that of the gaseous hydrogen chloride (HCl(g)).
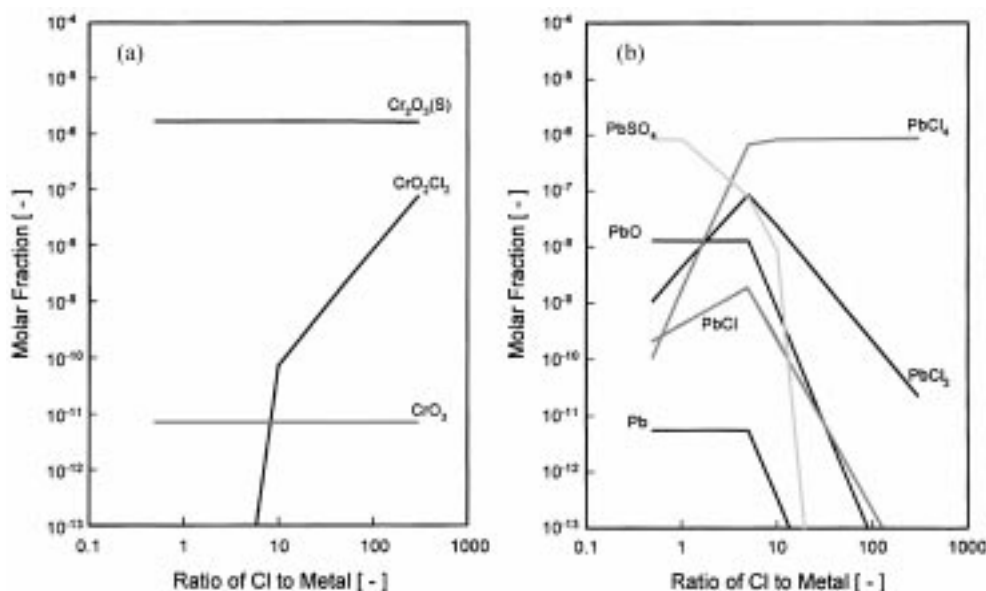
1-2. Trace Metal Compounds

Fig. 3. The variation of the molar fraction of metal compounds with the ratio of chlorine to metal species under 20% of excess air and 1,073 K of temperature: [(a); chromium, (b); lead.

All of the trace element is assumed to be available at the incineration reactions for the thermodynamic equilibrium analysis. When the metals are presented with chlorine together, it is expected that the formation characteristics of metal chlorides will become different. To investigate the effect of chlorine content in the waste on the behavior of the trace metals (Cr and Pb) selected in this study, the simulation conditions were determined with a temperature of 1,073 K, excess air of 20% (air-fuel ratio of 1.2), and a ratio of chlorine to metal species ranging from 5×10^{-1} to 3×10^{2} by weight basis.

Fig. 3 shows the result of the calculation performed with varying amounts of chlorine as mentioned above. As shown in Fig. 3, the chromium compounds have different properties in comparison to the lead compounds. Under oxidizing conditions, the reaction of the Cr in the waste with combustion gases leads to the formation of chromium oxide (Cr_2O_3) as shown in Fig. 3(a).

When the ratio of chlorine to metal exceeds 100, a little amount of volatile chromium oxychloride phase (CrO_2Cl_2) was formed through the reaction of $Cr_2O_3(s)$ and gaseous HCl as described in Eq. (1). However, all of the lead compounds are vaporized to the volatile phase under the conditions simulated as shown in Fig. 3(b).
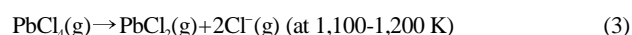
$$Cr_2O_3(s) + 4HCl(g) + 3/2O_2(g) \rightarrow 2CrO_2Cl_2(g) + 2H_2O(g) \qquad (1)$$

The volatile compounds of lead sulfate ($PbSO_4$), lead tetrachloride ($PbCl_4$), lead dichloride ($PbCl_2$), lead chloride (PbCl), lead oxide (PbO), and elemental lead (Pb) are subjected to form when Pb is released from the wastes and reacts with the combustion gases. When the ratio of chlorine to metal reaches 5 or higher, $PbCl_4$ is the predominant gaseous compound while lead sulfate ($PbSO_4$) is predominant below the ratio of 5. Therefore, it can be concluded that lead tetrachloride ($PbCl_4$) will be usually produced in the waste incineration process, but it will be controlled as the forms of lead sulfate and lead oxide by the flue gas cooled by passing through the air pollution control devices.

To investigate the behavior of lead with lime injection, the molar fraction of each metal species in the lead compounds contained in the combustion gases is plotted in Fig. 4. When the lime was not introduced, lead tetrachloride ($PbCl_4$) was the predominant species below 600 K, as shown in Fig. 4(a). Between 800 and 1,100 K, the concentration of $PbCl_4$ decreases, while the volatile $PbCl_2$ content in the effluent stream increases.

As the SO_x emission decreases with lime injection, lead is bound with chlorine resulting in forming lead tetrachloride in significant concentration in the volatile phase. As shown in Fig. 4(b), $PbCl_4$ is the thermodynamically favored gaseous compound of lead at 1,100 K, being replaced by lead oxide above 1,200 K through the following reactions:

$$PbCl_4(g) + 2H_2O(g) \rightarrow Pb(g) + 4HCl(g) + O_2(g) \qquad (2)$$

$$PbCl_4(g) \rightarrow PbCl_2(g) + 2Cl^-(g) \text{ (at 1,100-1,200 K)} \qquad (3)$$

$$PbCl_2 + H_2O \rightarrow PbO + 2HCl \qquad (4)$$

However, the Eq. (3) reaction will occur in 800-1,100 K of temperature ranges without lime injection as previously mentioned.

2. Comparison of Predicted and Experimental Values

To verify the concentration of gaseous pollutant predicted by the equilibrium model, the predicted and experimental values of the concentration of SO_x and NO_x with regard to the operating parameters including λ_T and T_b were illustrated in Table 2. As shown in Table 2, the predicted concentration of SO_2 was almost same as experimental values in given conditions. However, the concentration of NO_x predicted by the model was a little lower than that of NO_x measured from experiment. The simulation analysis using the thermodynamic equilibrium model can not accurately determine the NO_x emission in waste incineration system. The reason is that the variation of NO_x emission during incineration of waste is affected by the various operating parameters, such as air-fuel ratio (λ_T), primary air factor (λ_1/λ_T), combustor geometry, and method of heat release and preheating of combustion air, etc.

To determine the fate of trace metals in dye sludge during the fluidized bed incineration, it is required to calculate the partitioning
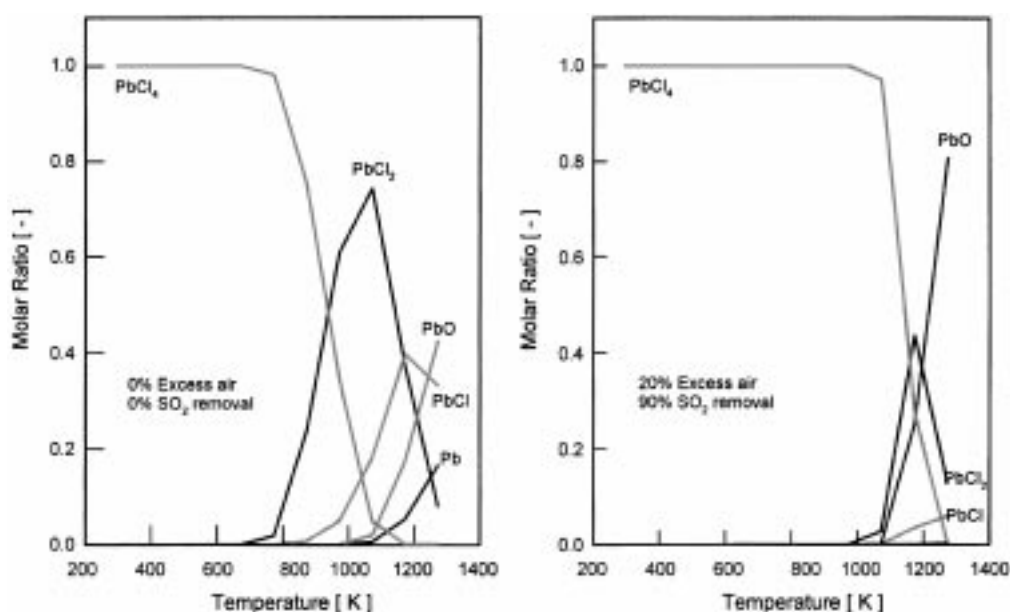

Fig. 4. The molar ratio of lead compound as a function of temperature with 0.1% of chlorine content.

Table 2. The comparison of predicted and experimental values of gaseous pollutants (U_0=1.1 m/s)

λ_T (-)	T_b (°C)	Experimental		Predicted	
		SO_2 (ppm)	NO_x (ppm)	SO_2 (ppm)	NO_x (ppm)
Effect of overall air-fuel ratio (λ_T)					
1.0	850	1136.3	179	1070.4	-
1.1	850	1099.7	92	901.3	34.3
1.2	850	1046.3	114	797.4	47.4
1.3	850	769.2	88	726.0	55.3
1.4	850	810.2	99	658.3	62.2
Effect of bed temperature (T_b)					
1.2	750	798.5	82	688.1	18.4
1.2	800	864.6	86	754.7	30.2
1.2	850	1046.3	189	797.4	47.4
1.2	900	752.6	401	826.5	71.7

Table 3. Partitioning coefficient of heavy metals in the output streams

Element	T_b (°C)	k_{Xb}	k_{Xc}	k_{Xg}	Σk_i
Cr	750	0.710	0.341	-	1.051
	850	0.690	0.328	-	1.018
	850	0.700	0.339	-	1.039
	900	0.660	0.360	-	1.020
Pb	750	0.590	0.366	-	0.956
	800	0.620	0.308	-	0.928
	850	0.491	0.483	-	0.974
	900	0.389	0.513	-	0.902

k_{Xi} (=m_{Xi}/m_{Xs}); The ratio of output to input mass flow rate of heavy metal.

coefficient (k_{Xi}) of heavy metals, which was derived from the mass flow rate of heavy metals in each streams (m_{Xi}). Table 3 shows the partitioning coefficient (k_{Xi}) of heavy metals in the output streams of the incinerator under various operating bed temperatures. The sum of k_{Xi} means the total recovery of metals. From the observed results, it is noted that the heavy metals, such as Cr and Pb, can be quantitatively retained in the output stream ash during incineration of dye sludge in the fluidized bed incinerator.

As described in Table 3, the partitioning coefficient k_{Xb} is higher than k_{Xc}, and the partitioning coefficient k_{Xg} is negligible. From this result, it is found that the more metals are retained in the bed material than carryover ash, and the metal content in flue gas were not detected during the experiment. As shown in Table 3, the sum of k_{Xi} is about 1, which shows that almost 100% of metals entering the incinerator is recovered. The amount of total metals recovered during this experiment was found to be higher than those reported by other investigators [U.S. EPA, 1985; Dewling and Manganelli, 1980]. For higher recoveries, it can be said that the fluidized bed incineration has a potential for reducing the trace metal emissions due to less volatilization occurring at low incineration temperature.

Table 4 shows the distribution of metal compound simulated by equilibrium model under various experimental conditions. As shown in Table 4, the chromium species in the fed was converted to chromium oxide of solid phase ($Cr_2O_3(s)$) under given experimental conditions. Therefore, it is found that all of the chromium compound was retained in the bed material and fly ash. A similar trend was observed for the lead compound from the result of model analysis at low temperature. As mentioned above, however, the partitioning coefficient k_{Xc} for Pb increased with bed temperature (T_b). This trend can be explained as that the portion of gas phase of PbO increased with increasing T_b as shown in Table 4. It is expected that the Pb compound was almost retained in the ash as the form of solid phase of $PbSO_4$ or heterogeneously deposited on the fly ash as PbO(g) when combustion gas became cool. As described in Table 3, the partitioning coefficient, k_{Xc} for Pb was higher than for Cr. Also, the sum of k_{Xi} for Pb was lower than 1, because a small amount of Pb(g) and PbO(g) might have been discharged with the flue gas and fly ash not collected by cyclone, and deposited onto the duct surface.

CONCLUSIONS

A thermodynamic equilibrium model was used to predict the emission of gaseous pollutants and the fate of heavy metals during the incineration of dye sludge. From the results of the model simulation and experiment, it was found that the reactive affinity of the

Table 4. Effect of operating parameters on the distribution of metal compound

λ_T (-)	T_b (°C)	Molar fraction of metal compounds						
		Cr		Pb				
		$Cr_2O_3(s)$	$Cr_2S_3O_{12}(s)$	Pb(g)	PbO(g)	PbS(s)	PbS(g)	$PbSO_4(s)$
Effect of overall air-fuel ratio (λ_T)								
1.0	850	1	0	0.444	0.444	0	0.111	0
1.1	850	1	0	-	0.401	-	-	0.599
1.2	850	1	0	-	0.384	-	-	0.616
1.3	850	1	0	-	0.407	-	-	0.593
1.4	850	1	0	-	0.451	-	-	0.549
Effect of bed temperature (T_b)								
1.2	750	1	0	-	0	-	-	1
1.2	800	1	0	-	0.015	-	-	0.985
1.2	850	1	0	-	0.384	-	-	0.616
1.2	900	1	0	-	1	-	-	0

sulfur oxides ($SO_x(g)$) to the lime ($CaO(s)$) was much higher than that of the gaseous hydrogen chloride ($HCl(g)$). And, the concentration of HCl gas was not affected by the excess air and lime addition at a combustion temperature.

When the ratio of chlorine to metal was 5 or higher, $PbCl_4$ was the predominant gaseous compound, while lead sulfate ($PbSO_4$) was predominant below the ratio of 5. When reducing the SO_x emissions by lime injection, the lead species in the waste was bound with chlorine as forming lead tetrachloride in a significant concentration in the volatile phase. Thermodynamically, $PbCl_4$ was the favored gaseous compound of lead up to 1,100 K, but it was replaced by lead oxide above 1,200 K.

The predicted concentration of SO_2 was almost same as experimental values under given conditions. However, the concentration of NO_x predicted by the model was a little lower than that of NO_x measured from experiments.

It is noted that heavy metals, such as Cr and Pb, can be quantitatively retained in the output stream ash during the incineration of dye sludge in a bench-scale fluidized bed incinerator. According to the distributions of Cr and Pb simulated by the equilibrium model, all of the Cr in the feed was retained in the ash as the solid phase of Cr_2CO_3. However, most Pb was retained in the ash during incineration as the solid phase of $PbSO_4$, or heterogeneously deposited onto the fly ash as $PbO(g)$ when the combustion gas became cool. As described in Table 3, the partitioning coefficient, k_{xc} for Pb was higher than for Cr. Also, the sum of k_{Xi} for Pb was lower than 1, because a small amount of $Pb(g)$ and $PbO(g)$ might have been discharged with the flue gas and fly ash not collected by cyclone, and deposited onto the duct surface.

ACKNOWLEDGEMENT

NOMENCLATURE

k_{Xg} : partitioning coefficient of heavy metal in flue gas [μg/g]

k_{Xb} : partitioning coefficient of heavy metal in ash sampled from the bed [μg/g]

k_{Xc} : partitioning coefficient of heavy metal in fly ash collected by cyclones [μg/g]

m_{xg} : mass flow rates of heavy metals in flue gas [μg/min]

m_{xs} : mass flow rates of heavy metals in dye sludge [μg/min]

m_{xb} : mass flow rates of heavy metals in ash drained from the lower bed [μg/min]

m_{xc} : mass flow rates of heavy metals in fly ash collected by cyclone [μg/min]

T_b : bed temperature at 20 cm above the air distributor [$^{\circ}$C]

U_o : primary superficial gas velocity [m/s]

λ_T : total air-fuel ratio to theoretical air flow rate [-]

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