Thermodynamic equilibrium analyses of transformation and partition of Pb during sludge incineration

Haimeng Hou¹²,*
¹ Shenyang Academy of Environmental Sciences, Shenyang, China
² Liaoning Provincial Key Laboratory for Urban Ecolog, Shenyang, China
*Corresponding author e-mail: houhaimeng520@163.com

Abstract. The chemical thermodynamic equilibrium analyses were used to explore the migration and transformation of Pb during sludge incineration, and the influences of S, Cl and adsorbents were also studied. The results show that the main form of Pb is PbO(g) and PbCl(g) at 1000K due to its high volatility. Chlorine will promote the volatilization of Pb, reduce the initial volatile temperature, and increase volatilizing rate, while the effect of sulfur is not obvious. Al₂O₃ and SiO₂ can all form solid state compound with Pb, thus inhibiting its volatilization.

1. Introduction
Incineration is one of the main disposal technologies of sewage sludge, which has the excellent reduction effect. However, the secondary pollutants produced from sewage sludge incineration limit its application. Sewage sludge contains heavy metals such as Cu, Cd, Cr, Mn, Pb, and Zn, which produce heavy metal pollutants during incineration, as the form of solid or gaseous state [1-4]. Pb is one of the main heavy metals in sewage sludge with a high content, and it is easy to volatilize. S and Cl in sludge also affect the volatilization of Pb. Incineration of waste and sludge is an important source of Pb pollution in the atmosphere. Therefore, it is significant to explore the migration and transformation of Pb during sewage sludge incineration, which could figure out the reaction and transformation process of Pb and provide theoretical basis for Pb emission control.

The chemical thermodynamic equilibrium analyses can determine the direction and limit of chemical reaction under certain condition by the minimization theory of Gibbs free energy. The chemical thermodynamic equilibrium analyses is an important theoretical tool to explore the transformation of heavy metals in solid fuel incineration, which has been widely used in the study of trace elements migration in the process of coal, waste and biomass incineration[5-8]. In this paper, the migration and transformation Pb during sewage sludge incineration were investigated by the chemical thermodynamic equilibrium analyses, while the effects of S, Cl and adsorbents were also studied.

2. Methods
The FactSage 6.1 chemical thermodynamic equilibrium calculation software was used in this study. It is based on the Gibbs free energy minimum method, which can be used to solve chemical equilibrium and phase equilibrium [9-10].

In the process of thermodynamic equilibrium calculation, the characteristic parameters of sludge were input into the software, including basic element components C, H, O, N, S and Cl, the main mineral elements Si, Al, Ca, Fe, Mg and K, the major heavy metal elements Cd, Cr, Cu, Mn, Pb and
Zn, and the N₂ and O₂ in combustion-supporting air. The incineration temperature is 400-1600K, and the pressure is an atmospheric pressure. The solid and gaseous products generated by incineration can be obtained by equilibrium calculations. The effects of incineration temperature, the contents of S and Cl, and the addition of Al₂O₃ and SiO₂ were explored. The average value of several kinds of sludge was used in this study.

3. Results and discussion

3.1. The form and distribution of Pb

The thermodynamic equilibrium analysis of Pb during sludge incineration was presented in Figure 1. During sludge incineration, the main forms of Pb are PbSO₄ (s), PbCl₂ (g), PbO (g) and PbCl (g), which are variable under the different temperature. At 400~1100 K, Pb exists mainly in the form of PbSO₄(s) and PbCl₂(g). PbSO₄(s) gradually converts to PbCl₂(g) from 500K, and completely decompose at 1100K. When the temperature reaches 1100K and continues to rise, PbCl₂(g) is gradually converted to PbO(g) and PbCl(g). The main form of Pb is PbO(g) when temperature rises to 1400K. During sludge incineration, the main forms of Pb are PbSO₄(s) and PbCl₂(g) at low temperature, while change to PbCl₂(g), PbO(g) and PbCl(g) at high temperature.

![Fig. 1. Thermodynamic equilibrium distribution of Pb during sludge incineration.](image)

3.2. The effect of S and Cl

During sludge incineration, heavy metals and their compounds could react with chlorides under high temperature[11-12]:

\[ M + Cl_2 \rightarrow MCl_2 \]

\[ M + 2HCl \rightarrow MCl_2 + H_2 \]

\[ MO + 2HCl \rightarrow MCl_2 + H_2O \]

The thermodynamic equilibrium analysis results of the influence of sulfur and chlorine on Pb volatilization during sludge incineration were shown in Figure 2. When there was no chlorine in the combustion system, Pb volatilized at 900K and completely evaporated at 1000K, and the main gaseous phase is PbO (g). In the presence of chlorine, the temperature in which Pb begins to volatilize is reduced to 400K, and decreases with the increase of chlorine content. The main volatilization products are PbCl₄(g) and PbCl₂(g), while the solid state of Pb also changed to PbCl₂(s) at low temperature, which indicates that the chlorine affects the form of Pb during the whole combustion process.

Sulfur has some influence on the thermodynamic equilibrium distribution of Pb. When there was no sulfur in the fuel, the main forms of Pb are PbCO₃(s), PbO(s), PbO(g) and Pb(g), and Pb begins to volatilize at 900K. When sulfur was present in the fuel, the main forms of Pb were PbSO₄(s), PbO(g)
and Pb(g), while the temperature in which Pb began to volatilize rises to 1100K due to the formation of sulfate.

![Graph](image1)

![Graph](image2)

Fig.2. The effect of S and Cl on Pb volatilization.

3.3. The effect of adsorbents

The addition of adsorbents such as alumina and silicon dioxide can adsorb heavy metals during sludge incineration, which is an effective way to control heavy metals emission. Figure 3 show the effects of Al₂O₃ and SiO₂ on Pb volatilization. It is shown that Al₂O₃ has obvious adsorption effect on Pb at 400~1200K, while all Pb react with Al₂O₃ to form (PbO) (Al₂O₃)₆ (s), which delays the volatilization of Pb compared with non-adsorbent. SiO₂ also has adsorption effect on Pb. Pb will combined with SiO₂ to form PbSiO₃ (s) at 400~1100K, which delays the volatilization of Cd.

![Graph](image3)

Fig. 3. The effect of Al₂O₃ and SiO₂ on Pb volatilization.

4. Conclusion

The FactSage 6.1 chemical thermodynamic equilibrium calculation software was applied to explore the migration and transformation of Pb during sludge incineration, and the influences of S, Cl and adsorbents were also studied. The results indicate that:

1) Pb has strong volatility and is mainly found in flue gas and fly ash at high temperature during sludge incineration. The main forms of Pb are PbO (g) and PbCl (g) at 1000K, which are PbO (g) at 1200K.
(2) Chlorine promotes the volatilization of Pb obviously, and reduces the initial temperature of its volatilization and increases the volatilization rate, which is due to the formation of metal chloride with low boiling point. Sulfur also inhibits the volatilization of Pb by the generation of PbSO₄.

(3) Alumina and silicon dioxide have some adsorption effect on Pb owing to due to the generation of (PbO)(Al₂O₃)(s) and PbSiO₃(s).

References
[1] F. Frandsen, Trace Elements from Coal Combustion. Technical University of Denmark, 1995, pp. 115-138.
[2] MH Lopes, P Abelha, N Lapa, JS Oliveira, I Cabrita, The behaviour of ashes and heavy metals during the co-combustion of sewage sludges in a fluidised bed, Waste Management. 23 (2003) 859-870.
[3] D Marani, CM Braguglia, G Mininni, F Maccioni, Behaviour of Cd, Cr, Mn, Ni, Pb, and Zn in sewage sludge incineration by fluidised bed furnace, Waste Management. 23 (2003) 117-124.
[4] Tie Mei, Song Linlin, Hui Xiujuan, Zhang Chaohong, Study on Chemical Forms Distribution Characteristics of Heavy Metals in Municipal Sewage Sludge, Environmental Protection Science. 05 (2012) 36-40.
[5] Y Chen, YG Zhang, LI Qinghai, YG Zhuo, CH Chen, Equilibrium Analysis of Sorbents Behavior on Cd Adsorption Under MSW Incineration Conditions, Journal of Combustion Science and Technology. 14 (2008) 239-245.
[6] Chang Yu Wu, Timothy Barton, A Thermodynamic Equilibrium Analysis to Determine the Potential Sorbent Materials for the Control of Arsenic Emissions from Combustion Sources, Environmental engineering science. 18 (2001) 177-190.
[7] Meng Yun, Zhang Junying, Zhong Qin, Zheng Chuguang, Wang Ben, Development of thermodynamics equilibrium prediction of trace arsenic and selenium speciation during coal combustion, Techniques and Equipment for Environmental Pollution Control. 3 (2002) 1-5.
[8] Liu Jingyong, Sun Shuiyu, Thermodynamic equilibrium analysis of heavy metals speciation transformation and distribution during sewage sludge incineration, The Chinese Journal of Nonferrous Metals. 20 (2010) 1645-1654.
[9] Bale C W, Chartrand P, Degterov S A, FactSage thermochemical software and databases, Calphad. 26 (2002) 189-228.
[10] Bale C W, Belisle E, Chartrand P, FactSage thermochemical software and databases-recent developments, Calphad. 33 (2009) 295-311.
[11] SV Vassileva, C Braekman-Danheuxb, P Laurant, T Thiemann, A Fontana, Behavior, capture and inertization of some trace elements during combustion of refuse-derived char from municipal solid waste, Fuel. 78 (1999) 1131-1145.
[12] MB Folgueras, RM Díaz, J Xiberta, I Prieto, Volatilisation of trace elements for coal–sewage sludge blends during their combustion, Fuel. 82 (2003) 1939-1948.