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博士学位論文

**Study on condensation behavior of heavy metal  
vapors in air and oxy-fuel combustion**

空気燃焼および Oxy-Fuel 燃焼における  
重金属蒸気の凝縮挙動に関する研究



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# CONTENTS

ABSTRACT.....	I
LIST OF FIGURES .....	IV
LIST OF TABLES .....	VII
<b>CHAPTER 1 INTRODUCTION.....</b>	<b>1</b>
1.1 BACKGROUND OF THE RESEARCH.....	1
1.1.1 Fossil fuel combustion .....	1
1.1.2 Environmental impacts in coal and waste-fired power plants .....	4
1.1.3 Oxy-fuel combustion of pulverized coal.....	9
1.2 REVIEW OF PREVIOUS STUDIES .....	11
1.2.1 Occurrence of trace elements in coal .....	11
1.2.2 Transformation and condensation behavior of trace elements in air and oxy-fuel combustion .....	13
1.2.3 Control of trace elements during coal combustion .....	18
1.2.4 Oxy-fuel combustion technology.....	21
1.3 PURPOSE OF THIS STUDY .....	22
1.4 OUTLINE OF THIS THESIS .....	23
REFERENCES.....	26
<b>CHAPTER 2 EFFECT OF INORGANIC PARTICULATES ON THE CONDENSATION BEHAVIOR OF LEAD AND ZINC VAPORS UPON FLUE GAS COOLING.....</b>	<b>41</b>
2.1 INTRODUCTION .....	41
2.2 EXPERIMENTAL SECTION.....	43
2.2.1 Sample preparation .....	43
2.2.2 Experimental setup and conditions .....	43
2.2.3 Samples characterization .....	46
2.2.4 Thermodynamic pseudo- equilibrium model.....	46

2.3. RESULTS AND DISCUSSION.....	47
2.3.1 Condensation of Pb and Zn vapors without particulates in flue gas.....	47
2.3.2. Interaction of Pb and Zn with particulates in flue gas .....	49
2.3.3 Interaction mechanisms of Pb and Zn vapors with particulates .....	52
2.4. CONCLUSIONS .....	58
REFERENCE .....	60
<b>CHAPTER 3 CONDENSATION BEHAVIOR OF HEAVY METAL VAPORS UPON FLUE GAS COOLING IN OXY-FUEL VERSUS AIR COMBUSTION.....</b>	<b>62</b>
3.1 INTRODUCTION .....	62
3.2 EXPERIMENTAL.....	65
3.2.1 Experimental setup and conditions .....	65
3.2.2 Thermodynamic pseudo-equilibrium model.....	67
3.3 RESULTS AND DISCUSSION.....	69
3.3.1 Condensation behavior of Pb and Zn vapors in single mode without particulates .....	69
3.3.2 Condensation behavior of Pb and Zn vapors in mixture mode.....	74
3.3.3 Condensation mechanism of metal vapor species .....	77
3.3.4 Condensation of Pb and Zn vapors with particulates in air and oxy-fuel conditions.....	80
3.4 CONCLUSIONS .....	84
REFERENCES.....	86
<b>CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS .....</b>	<b>89</b>
4.1 CONCLUSIONS .....	89
4.2 RECOMMENDATIONS FOR THE FUTURE WORKS.....	91

## ABSTRACT

Coal and waste-fired power plants currently provide over 40% of the world's electricity, while environmental problems are created during coal and waste combustion. In particular, the emission of ultrafine particulate matter, namely  $PM_{1-10}$  for the particulates with heavy elements and being formed by vaporization-condensation and the trace elements condensation behavior have been much concerned. Also these problems were extensively investigated, the formation of ultrafine particles which is mainly attributed to vaporization-condensation mechanism of trace elements during coal combustion is very complicated and the condensation behavior of trace elemental vapors with the flue gas cooling is not very clear, especially for the formation of species of trace elements as a function of the temperature of flue gas, which greatly affects the toxicity and leaching performance of trace elements.

On the other hand, regarding oxy-fuel combustion of coal, the information of ash and transformation and condensation behavior of trace elements is scarce until now. Even the trend of trace elements behavior between traditional combustion and oxyfuel combustion is not united in the researchers. High partial pressure of  $CO_2$  around char surface can trigger extra gasification reaction and affect the vaporization of trace elements. The flue gas recirculation with impurities such as  $HCl$ ,  $SO_2$  and  $H_2O$  during oxy-firing conditions possibly results in the change of transformation and condensation behavior. These also need to be confirmed by experimental observation.

This thesis consists of three parts related to the vaporization and condensation behavior of trace element during flue gas cooling.

- 1) the influence of  $HCl$ ,  $SO_2$ ,  $H_2O$  and oxide particulates on condensation behavior of trace metals during flue gas cooling;
- 2) the homogeneous nucleation and heterogeneous condensation behavior of trace metals during flue gas cooling;
- 3) the differences of condensation behavior of trace metals between traditional combustion and oxy-fuel combustion

## **Chapter 1**

### **Introduction**

In this section, the environmental impacts in coal-fired power plants were introduced. An overview of the air pollutants emission during air and oxy-fuel combustion of coal was given. Based on the state of the art of these problems, the research purposes in this thesis were outlined.

## **Chapter 2**

### **Effect of Inorganic Particulates on the Condensation Behavior of Lead and Zinc Vapors upon Flue Gas Cooling**

Three oxides of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  as inorganic particulates were placed individually in flue gas cooling section to mimic pre-existing particulates in flue gas and examine their impact on the fate of Pb and Zn compound vapors. The effect of gaseous components including HCl,  $\text{SO}_2$  and  $\text{H}_2\text{O}$  on the heterogeneous condensation of Pb and Zn compound vapors on particulates grains has also been clarified. The presence of particulates in flue gas exerted remarkable influence on the fate of Pb and Zn compound vapors. Pb compound vapor was found being captured by  $\text{Al}_2\text{O}_3$  as Pb-Al-O at the temperature above 823K through chemical reaction, regardless flue gas composition. Zn preferentially transformed into  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnO}$  respectively on the presence of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  above 823 K. The presence of  $\text{SO}_2$  inhibited the chemical reactions of Pb and Zn vapors with particulates. Such an inhibitory effect was however compensated by the introduction of steam to flue gas. The presence of particulates in flue gas promoted the condensation of Pb and Zn compound vapors at higher temperature in comparison to the blank conditions, through heterogeneous nucleation, which in turn offset the effect of super-cooling. Moreover, the formation of sulfate was increased since the presence of particulates in flue gas triggered the condensation of sulfates vapors at high temperature and then reduced its partial pressure in flue gas, facilitating the sulfation reaction. Adjusting the concentrations of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  in flue gas can prevent the formation of chloride of Pb and Zn, which is notorious for its toxicity and corrosion propensity during solid waste incineration.

## Chapter 3

### Condensation behavior of heavy metal vapors upon flue gas cooling in oxy-fuel versus air combustion

Vaporization of Pb and Zn-loaded model compounds has been carried out in a lab-scale rotary kiln reactor to clarify their condensation behavior upon flue gas cooling in both air-firing and oxy-fuel combustion modes. The influence of flue gas impurities including HCl, SO<sub>2</sub> and H<sub>2</sub>O has been examined systematically. For the two metals existing separately in the reactor, namely at single mode, both preferentially condensed as chlorides in the presence of HCl, under air-firing and oxy-fuel conditions. SO<sub>2</sub> and steam in flue gas promote chloride into sulfide at high temperature. It was noticed that the deposition propensities of Pb and Zn vapors under oxy-fuel condition of the single mode were slightly enhanced than that in air-firing condition. This is due to a lower Lewis number of oxy-fuel combustion that is in favor of the formation of highly polydispersed fine particles. However, this discrepancy was diminished in the case that both two metals co-exist as the mixture mode in the reaction system. At the mixture mode from 700 K to 400 K, the condensation fraction of either Pb or Zn was confirmed higher than that in the single mode, due to an enhanced heterogeneous nucleation of Zn vapors on PbSO<sub>4</sub> nuclei.

## Chapter 4

### Conclusions

The main results obtained from this work and some recommendations for the future works were summarized in this section.

**Key words:** trace elements, flue gas cooling, homogenous/ heterogeneous, oxy-fuel combustion



## LIST OF FIGURES

Figure 1-1. Figure 1-1. Total Primary Energy Supply by resource 1993, 2011 and 2020.

Figure 1-2. Historical trend of world's coal production/consumption.

Figure 1-3. Sources of electric power generated

Figure 1-4 Power generation efficacy achievement of waste incineration facilities and estimated results

Figure 1-5 Ash formation mechanisms for trace elements

Figure 1-6. Global CO<sub>2</sub> emissions by sector and scenario

Figure 1-7 Schematic of an oxyfuel pulverized coal fired power plant

Figure 1-8. Modes of occurrence of trace elements in coal.

Figure 1-9 Volatility of metals categorised within a PF furnace

Figure 2-1. Schematic of the experimental apparatus.

Figure 2-2 Schematic of a thermodynamic pseudo-equilibrium model on the condensation of metallic vapors during flue gas cooling.

Figure 2-3 Condensation of Pb and Zn vapors without particulates in flue gas under different conditions. The three columns from left to right for each temperature respectively represent 0% SO<sub>2</sub>, 0.2% SO<sub>2</sub> and 0.2% SO<sub>2</sub> plus 8% H<sub>2</sub>O. P denotes impinger.

Figure 2-4 Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl /N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

## LIST OF FIGURES

Figure 2-5 Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl/SO<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

Figure 2-6 Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl/SO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

Figure 2-7 Total fraction of Pb-Al-O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO retained in particulates under different flue gas composition.

Figure 2-8 Zn compounds at 1073K, 823K and 573K with CaO (left column) and CaSO<sub>4</sub> (right column) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere.

Figure 2-9 Comparison of model calculation with experimental results in HCl/N<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub> atmosphere.

Figure 2-10 Comparison of model calculation with experimental results in the present of SO<sub>2</sub> and steam in flue gas.

Figure 3-1 Temperature profile of cooling zone in a reactor

Figure 3-2 Schematic of a thermodynamic pseudo-equilibrium model on the condensation of metallic compound vapors during flue gas cooling.

Figure 3-3 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl under single mode

Figure 3-4 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single mode

Figure 3-5 SEM picture of deposit and particle size distribution at 803K in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub> under single mode

Figure 3-6 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl under mixture mode

## LIST OF FIGURES

Figure 3-7 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under mixture mode

Figure 3-8 Comparison of model calculation with experimental results under single mode.

Figure 3-9 Comparison of  $\alpha$  values in air-firing and oxy-fuel conditions with HCl under single and mixture modes

Figure 3-10 Comparison of  $\alpha$  and  $\beta$  values in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single and mixture modes

Figure 3-11 Condensation of Pb and Zn vapors with particulates in flue gas under 0.2%HCl, 0.1%SO<sub>2</sub>, 5%O<sub>2</sub>, 10%H<sub>2</sub>O. In each picture, the left columns represents air condition, the right column represents oxy-fuel condition.

Figure 3-12 Condensation of Pb and Zn vapors with particulates in flue gas of 0.2%HCl, 0.1%SO<sub>2</sub>, 5%O<sub>2</sub>, 10%H<sub>2</sub>O under mixture mode. In each picture, the left columns represents air condition, the right column represents oxy-fuel condition.

Figure 3-13 Zn compounds at 1073, 823 and 573 K with 0.5g CaO (left) and 0.8g CaO (right) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O atmosphere.

Figure 3-14 Zn compounds at 1073, 823 and 573 K with 0.5g CaO (left) and 0.5g CaCO<sub>3</sub> (right) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O atmosphere.

## LIST OF TABLES

Table 1-1. Continental/regional share of proven coal reserves, annual production, and annual consumption in 2008

Table 1-2 Fuel analysis of coals and selected supplementary fuels

Table 1-3 Volatile impurities in waste fuels

Table 1-4. Trace elements distribution in coal

Table 2-1. Reaction gas composition.

Table 2-2. Possible reactions of  $\text{PbCl}_2$  and  $\text{ZnCl}_2$  vapors with particulates and their Delta G under different temperature.

Table 2-3. Total mole ratio of sulfate/chloride of Pb and Zn in the deposits at 1073 K, 823 K and 573 K.

Table 3-1. Gas composition of the feeding

# Chapter 1

## Introduction

### 1.1 Background of the Research

#### 1.1.1 Fossil fuel combustion

Annually, increasing industrialization and population will need to be underpinned increased energy consumption worldwide. For example, the world's consumption of non-renewable fossil fuels such as coal, oil, and gas was over 10,000 million tonnes of oil equivalent ( $4.19 \times 10^{14}$  Joules) in 2007.[1] Increasing industrialization and population will ultimately need to be underpinned by increased energy consumption worldwide. As the most important fuel for electricity generation and industries, fossil fuel will have a major role to play in meeting future needs. Fossil fuels including coal, oil and gas provide more than 80% of global primary energy requirements according to the report of World Energy Resources in 2013. Figure 1-1 portrays the total Primary Energy Supply by resource 1993, 2011 and 2020.[2]

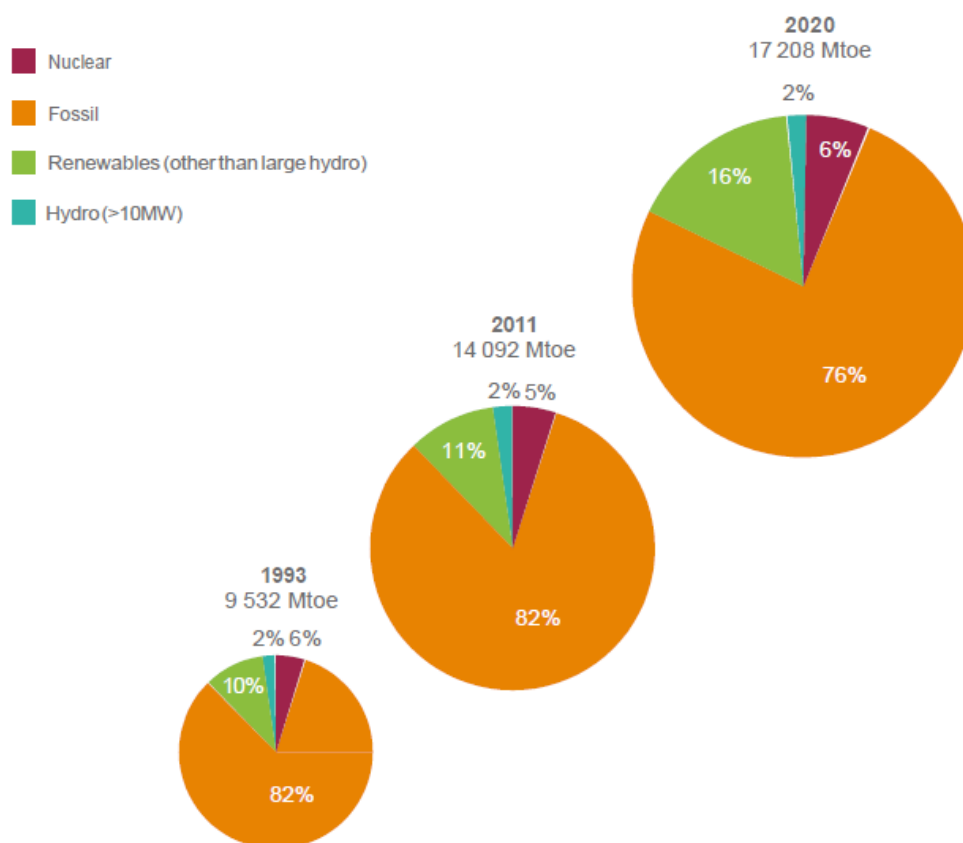


Figure 1-1. Total Primary Energy Supply by resource 1993, 2011 and 2020  
(Source: WEC Survey of Energy Resources 1995, World Energy Resources 2013  
and WEC World Energy Scenarios to 2050 [2]).

Oil and natural gas liquid (NGL) which are significantly for technology, socio-economic and industrial growth of nations are two basic components of the world energy portfolio. They also continuously drive international competition among major consuming nations, particularly in developing countries, and make these countries to seek ways and means of securing sufficient energy for improving their socio-economic and technological status. As of 2010, the amount of world's proven oil and NGL is estimated at about 1,380 billion barrels of oil equivalent [1]. As the most important fuel for electricity generation and industries, coal have a major role in energy source in many areas of the world. Table 1-1 displays the annual production and consumption of the world in 2008.[3] Coal play a significant role in various industrial processes such as power generation, cement production and steel and aluminum industry. Figure 1-2 displays the production and consumption of world's

coal over the past three decades. The proved coal reserves worldwide estimated to be approximately about 861,000 million tonnes.[3] In many countries, coal is mainly used for producing electricity, especially in developing countries, for example, 81% in China, 93% in Poland and 94% in South Africa.[4] The approximately 60% of global coal reserves is collectively held by the USA, the Russian Federation, and China. The global demand of coal is projected to grow by 60% from now to 2030, over 50% of which is due to increased demand by power generation sectors in China and India [5]. In fact, a plentiful supply of indigenous coal can afford as a primary energy source in China and India to provide their rapidly growing economies. While it is worth noting that coal, in its conventional way of use, is one of the most polluting energy sources, especially in terms of greenhouse gas (GHG) emission [6].

Table 1-1. Continental/regional share of proven coal reserves, annual production, and annual consumption in 2008 (Source of data: WEC [3])

Continent/Region	Reserve	Production	Consumption
Africa	3.68%	3.79%	2.77%
North America	28.49%	16.94%	
South America	1.45%	1.30%	
Asia	26.51%	56.82%	61.18%
Europe	30.78%	15.14%	15.50%
Middle East	0.14%	0.04%	
Oceania	8.94%	5.97%	1.61%
Total	(Mtoe)	421,900	3,470

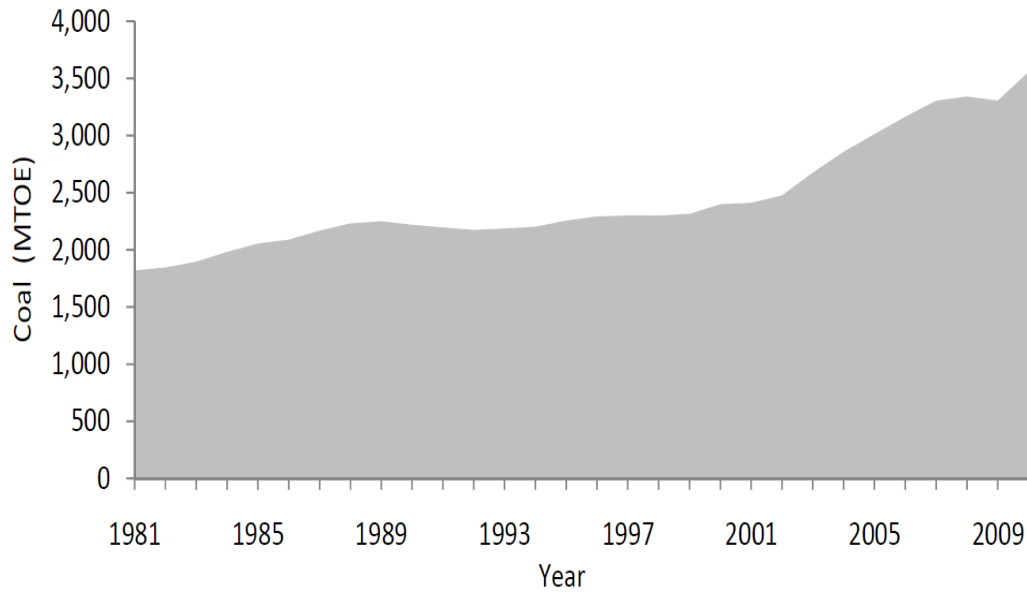


Figure 1-2. Historical trend of world's coal production/consumption (Source of data: BP [1]).

### 1.1.2 Environmental impacts in coal and waste-fired power plants

According to previous report, it appears to be in the long term, that coal will continue to play a significant role in the power generation sector worldwide, as can be seen in Figure 1-3. However, the abundant use of coal has become a cause of concern due to their adverse effects on the environment.

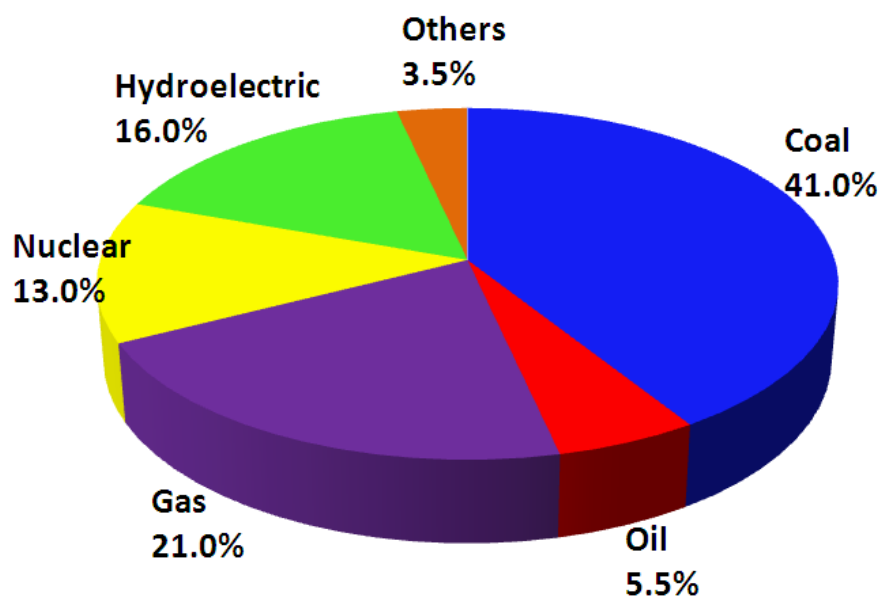


Figure 1-3. Sources of electric power generated((IEA) 2009[5])



The adverse effects on the environment of coal and waste combustion is that when coal and waste is burned to generate electricity, the combustion releases a combination of toxic chemicals into the environment, including trace elements (heavy metals and so on), carbon dioxide (CO<sub>2</sub>), oxides of sulphur (SO<sub>x</sub>) and nitrogen (NO<sub>x</sub>) and particulate matter (PM).[7-9] These pollutions have become a major environmental health concern over the world. The fuel characteristics of waste fuels are very different from those of typical coals as shown in Table 1-2 and 1-3. In the case of sewage sludge the figures in the table assume additional drying. The heating values of sewage sludge and straw are considerably lower than coal. The ash contents are considerably higher. The moisture content of some waste fuels is lower than that of most coals, but in others can be an order of magnitude higher. The fuel nitrogen sulphur and heavy metals levels of wastes can sometimes be higher and sometimes lower than those of coal. All these properties need to be considered when cofiring wastes with coal. [10]

Table 1-2 Fuel analysis of coals and selected supplementary fuels

	Hard coal	Brown coal	Wood	Straw	Dried sewage sludge
Moisture, raw, %	5.1	50.4	33	10.6	3
Ash, dry, %	8.3	5.1	0.34	6.1	45.1
Volatile matter, dry, %	34.7	52.1	83.2	74.4	49.5
C, dry, %	72.5	65.9	48.7	47.4	25.0
H, dry, %	5.6	4.9	5.7	4.5	4.9
S, dry, %	0.94	0.39	0.05	0.05–0.11	1.1
Cl, dry, %	0.13	<0.1	<0.1	0.4–0.73	<0.1

Table 1-3 Volatile impurities in waste fuels

Fuel	Volatile impurities
Municipal solid waste	S (0.1–0.9%)
	N(0.5–0.6%)
	Cl(0.5–0.9%)
	F(0.01–0.02%)
	Heavy metals (Cd, Hg, Pb, Zn, Cr, As)
Biomass	S(0.01–0.1%)
	N(0.1–1.0%)
	Cl(0.0–0.2%)
Tyres	S(1.2–1.6%)
	Heavy metals (Zn)

It is known that incineration plants for municipal waste also generate these 3 problems. From about 1960, Japan began disposing urban garbage by incineration, and today, Japan possesses the world's leading garbage incineration facilities. In the fiscal year 2009, there were 1243 incineration facilities in Japan, incinerating garbage using several methods - stoker furnaces, fluidized bed furnaces, and gasification fusion resource furnaces with the objective of ash recycling. Stoker furnaces account for 70% of all furnaces, and improvement of this type of furnace is progressing rapidly as the showing of Fig 1-4.[11]

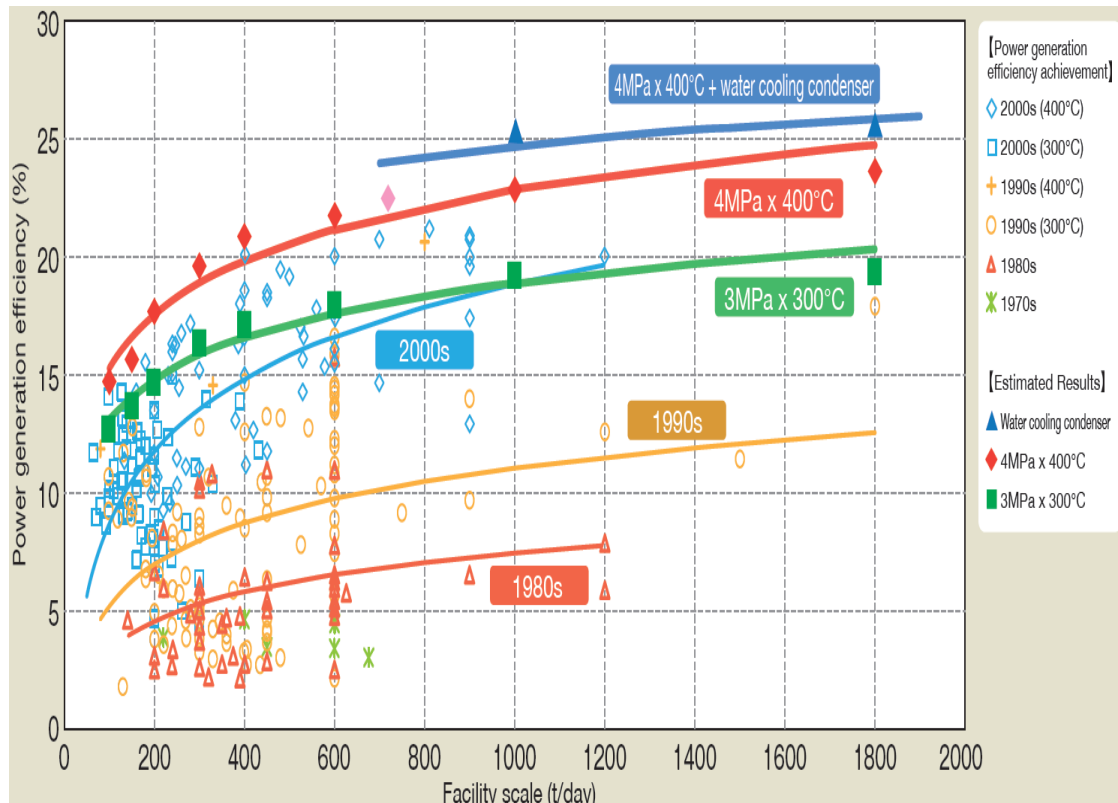


Figure 1-4 Power generation efficacy achievement of waste incineration facilities and estimated results

**Trace elements:** Trace elements such as mercury, lead and zinc present in coal are known to be of concern for public health. Coal and waste-fired power plants have resulted in emission of several tons of trace elements in environment. These elements mostly evaporate during combustion and condense either homogeneously as sub-micron ash or heterogeneously onto already existing fine ash, the formation mechanisms of trace elements are showed in figure 1-5.[12] This environment problem has been paid high attention by many countries recently. Although the concentration of these elements in coal is extremely low, which are the constituents with concentration below 100 ppm.[13] The harmful effect is significant because of the enormous amounts of coal burned each year.[14] The portion of these elements in gas phase will be in the form of metallic compound fumes with the decrease of flue gas temperature through nucleation.[15-21] The fumes deposited from atmosphere may accumulate in soils over time or may be accumulated to toxic levels within the food chain. This accumulation of toxic elements in the atmosphere, soils, or the food

chain is of major environmental concern.[22] Even for the portion of trace elements retained in fly ash, the subsequent treatment through land filling can lead to their leaching and then pollute soil and underground water.

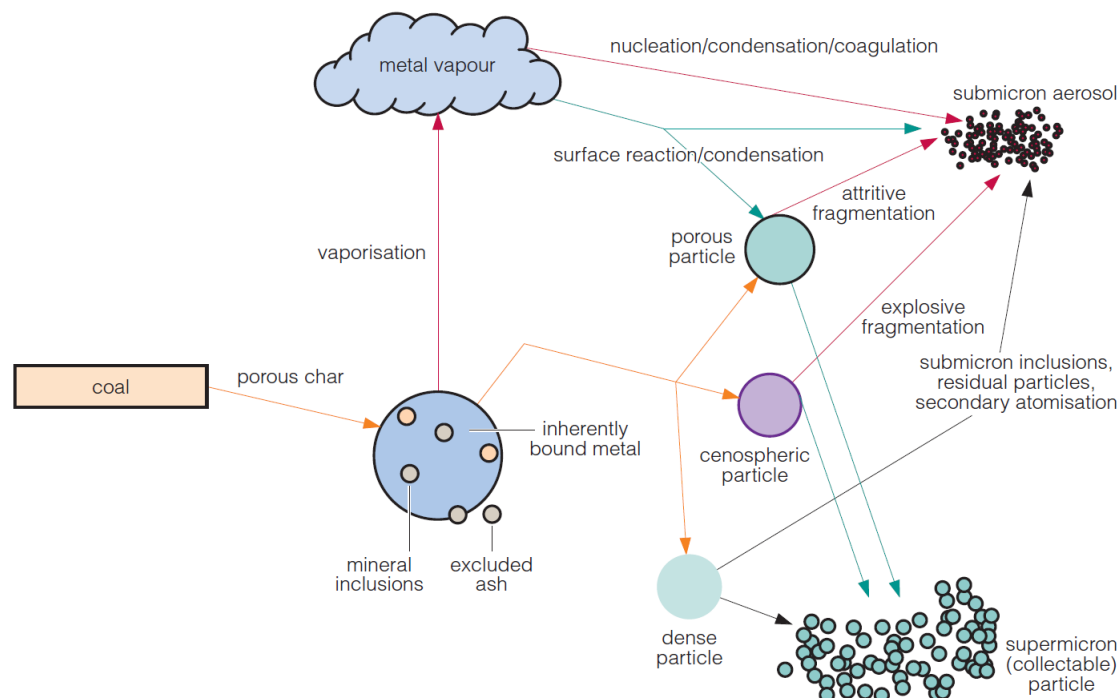


Figure 1-5 Ash formation mechanisms for trace elements (IEA Clean Coal Centre,2012)

PM: Mineral matters, minor elements and halogens are the mainly elements which are included in the particle matters emission as the coal burning. The particle matters can be classified into three size ranges: nucleation mode, accumulation mode and coarse mode.[23,24] They can impact not only the respiratory systems of people but also affect the local visibility and cause dust problems. Furthermore, some trace elements were often enriched in fine particles,[25,26] the subsequent treatment through landfilling can lead to their leaching and the then pollutes soil and underground water.

CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub>: The elements which contain C, H, O, N and S react with oxygen at high temperature during coal burning to form CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub> causing environmental impacts. CO<sub>2</sub> in the atmosphere can cause global warming, while NO<sub>x</sub> and SO<sub>x</sub> cause acid rain in the combustion of coal. Furthermore NO<sub>x</sub> emission also can destroy the ozone layer and cause ozone hole. Under the Clean Air Act (CAA), National Ambient Air Quality Standards (NAAQS) have been set for six so-called

‘criteria’ pollutants including nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO) and etc. To match these emission limitations, air pollutant control device (APCD) must be installed in coal-fired power plant.

### 1.1.3 Oxy-fuel combustion of pulverized coal

CO<sub>2</sub> is considered to be the major greenhouse gas (GHG) contributing to global warming. Since the beginning of the industrial revolution in about 1850, the average atmospheric concentration of CO<sub>2</sub> has increased from 280 ppm to 370 ppm and as a result, the average global temperature has increased between 0.6 °C and 1 °C in the same time period.[27] So reduction emission of CO<sub>2</sub> is major factor of the global warming has long been clamored. Figure 1-6 shows CO<sub>2</sub> emission rate in each industrial sector in 2009 and 2050.[28]

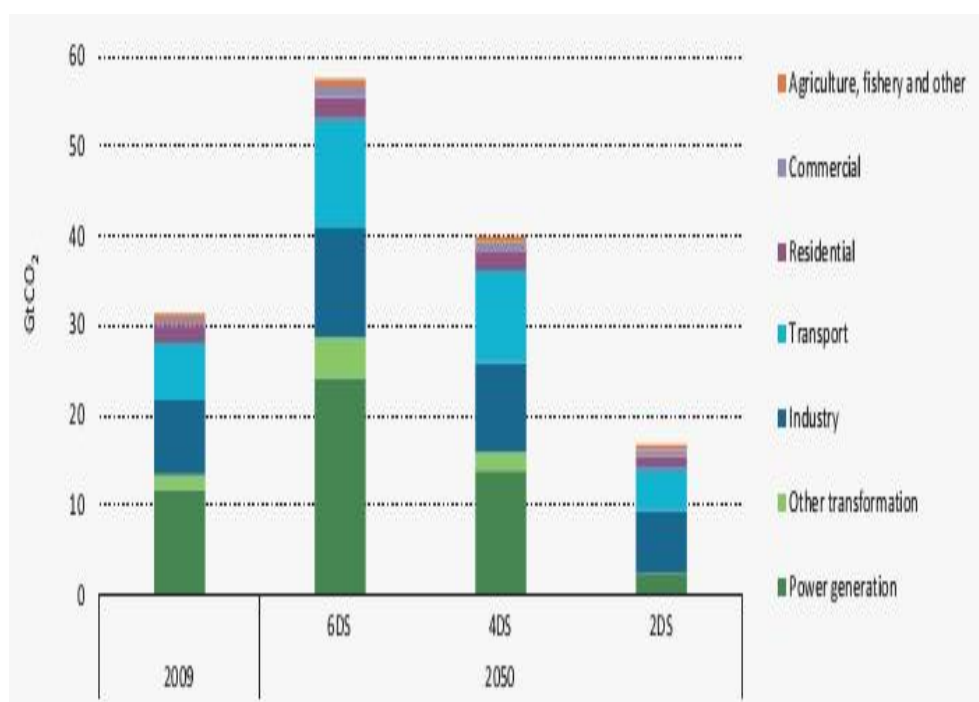


Fig. 6. Global CO<sub>2</sub> emissions by sector and scenario(Energy Technology Perspectives 2012 (IEA))

Electricity production from coal combustion causes a great emission of greenhouse gas, the major contributor being CO<sub>2</sub> which has been linked to global warming. The combustion of coal emits 1.3 times more CO<sub>2</sub> than oil and 1.7 times

more than gas. More than 28% of global carbon dioxide emission is from coal fired power plant. Oxy-fuel combustion is one of the options for controlling CO<sub>2</sub> emission in coal-fired power plant. This technology was first applied in coal combustion for CO<sub>2</sub> capture until the early 1990s and the combustion trials were completed by IHI in the late 1990s. Based on these developments, oxy-fuel technology has now evolved from pilot-scale to several planned demonstration scale projects. A schematic of an oxy-fuel pulverized coal power is shown in figure 1-7.[29] As it shows, we can simply describe the process as follows: eliminating nitrogen from the oxidant by burning the fuel in either nearly pure oxygen or a mixture of nearly pure oxygen and a CO<sub>2</sub>-rich recycled flue gas resulting in a product flue gas from the boiler containing mainly carbon dioxide and water vapor. It contains air separation unit for oxygen supply, pulverized coal combustion (PC) or circulated fluidized bed (CFB) boiler under oxy-firing with gas recirculation for temperature control, and a CO<sub>2</sub> compression unit for meeting the requirement and specification of CO<sub>2</sub> transport and sequestration.

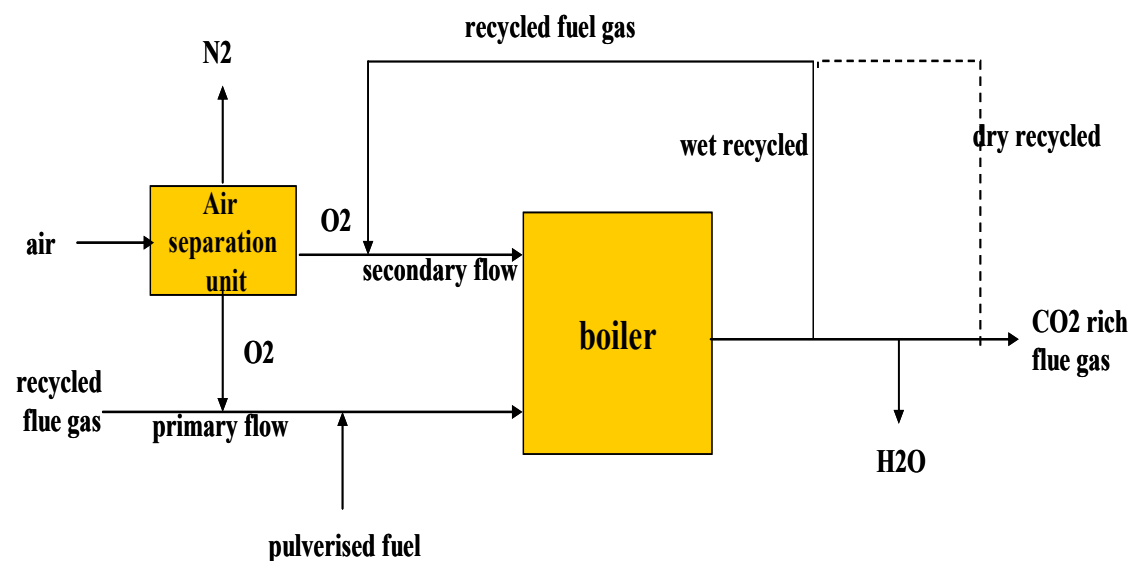


Figure 1-7 Schematic of an oxyfuel pulverized coal fired power plant

Comparing with traditional combustion, oxy-fuel combustion method has the following merits due to the feature shown in the previous section.

1. We do not need to separate CO<sub>2</sub> from flue gas and we can store the captured CO<sub>2</sub> directly (Purification of CO<sub>2</sub> may be needed depending on the way of transportation or storage.);

2. We expect improvement of combustion efficiency due to oxygen enrichment;
3. Boiler efficiency in oxyfuel combustion is higher than that in air combustion in the same operating condition since the amount of flue gas decreases;
4. NO<sub>x</sub> emission decreases since NO<sub>x</sub> in flue gas is reduced by recirculating flue gas into boiler. Therefore there is a possibility that De-NO<sub>x</sub> plant becomes unnecessary;
5. We can downsize FGD because the amount of flue gas decreases. In addition, when we install CO<sub>2</sub> purification plant, we do not need FGD since desulfurization can be done in CPU;
6. We can apply the oxyfuel combustion technology to the modification of the existing power plant as well as newly installed power plant.

## **1.2 Review of previous studies**

According to above discussion, the emission of trace elements, PM and SO<sub>x</sub>, NO<sub>x</sub>, PM, CO<sub>2</sub> is the main environmental problems in coal-fired power generation. Since the overview of the formation of sulfur, nitrogen, PM and their control has been given elsewhere [30-34], they will not be discussed here. In this section, the occurrence and condensation behavior of trace elements during coal and waste combustion, as well as the studies related to oxy-fuel combustion of coal will be elucidated in detail.

### **1.2.1 Occurrence of trace elements in coal**

Coal contains significant quantities of trace metals almost. These elements can be divided into three groups, based on their concentration, including major elements, minor elements and trace elements.[35-37] Trace elements in coals are associated in several forms, including inorganic, organic associations and mineral associations.[38-39] US National Research Council classified trace elements into 5 group of environmental concern, which as following[40]:

1. Greatest concern group, including As, B, Cd, Hg, Mo, Pb, Se;
2. Moderate concern group, including Cr, Cu, Ni, V, Zn;
3. Minor concern group, including Ba, Co, Ge, Li, Mn, Sb, Sr;
4. Radioactive elements, including Rn, Th, U;
5. Very low concentration group, including Be, Sn, Te, Tl.

Xu et al classified trace elements into four main group with concentration >50 ppm, 10–50 ppm, 1–10 ppm, and <1 ppm, after investigated the mean values of concentrations of trace element contents in more than 1500 coal samples.[41] Although the trace elements are classified into different group depending on different standards, the distribution of trace elements are differ significantly between coals from different sources and even between coals from the same seams, according to some researchers.[42-58] Querol et al. extensive investigated trace elements distribution in both coals and wastes, their findings are summarized as Table 1-4.[52]

Table 1-4 Trace elements distribution in coal[52]

Affinity	Mineral	group	Mineral
Inorganic	Clay minerals and feldspars	Kaolinite	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y and rare earth elements
		Montmorillonite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb S, Sb, Se, Ti, W and Zn
	Iron sulfides	Pyrite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb S, Sb, Se, Ti, W and Zn
		Sphalerite	
	Carbonates	Calcite, Dolomite, Ankertie	Ca, Co and Mn
Organic	Sulfates	--	Ba, Ca, Fe and S
	Heavy minerals	Tourmaline	B
	N, S, Be, B, Ge, V, Wand Zr (B exhibits partial association with tourmaline in the heavy fraction, and V with clay minerals).		

However, for purpose of having a realistic assessment and prediction of the emission of trace elements during the coal utilization processes, such as combustion and gasification, it is necessary to have knowledge about the content and mode of trace elements in different coals. Since different mode will show different behavior in the combustion process, such as the elements associating mostly with organic and



sulfide fractions in coal tend to vaporize and then adsorb on fine particles as the decreasing of flue gas temperature, elements combining mainly with the excluded minerals which most probably form the coal ash. Fig. 1-8 illustrates the modes of occurrence of trace elements in coal, according to the research of Clarke and Sloss. As the Fig.8 shows trace elements in coal can be divided into two categories: organic associated and inorganic associated in coal matrix. Metals intimately associated with the organic material may be either chemically bound or physically bound. It has often been suggested that the organic associated are those bound to the functional groups such as the carboxylic acid (-COOH), phenolic hydroxyl (-OH), imino (=NH) or as part of element complexes and chelates. Regarding the characterization of organic bound metal in raw coal, the indirect methods with an initial segregation of coal or its mineral matter followed by characterization of each fraction are used, including sequential leaching and size/density-segregation.[59-61]

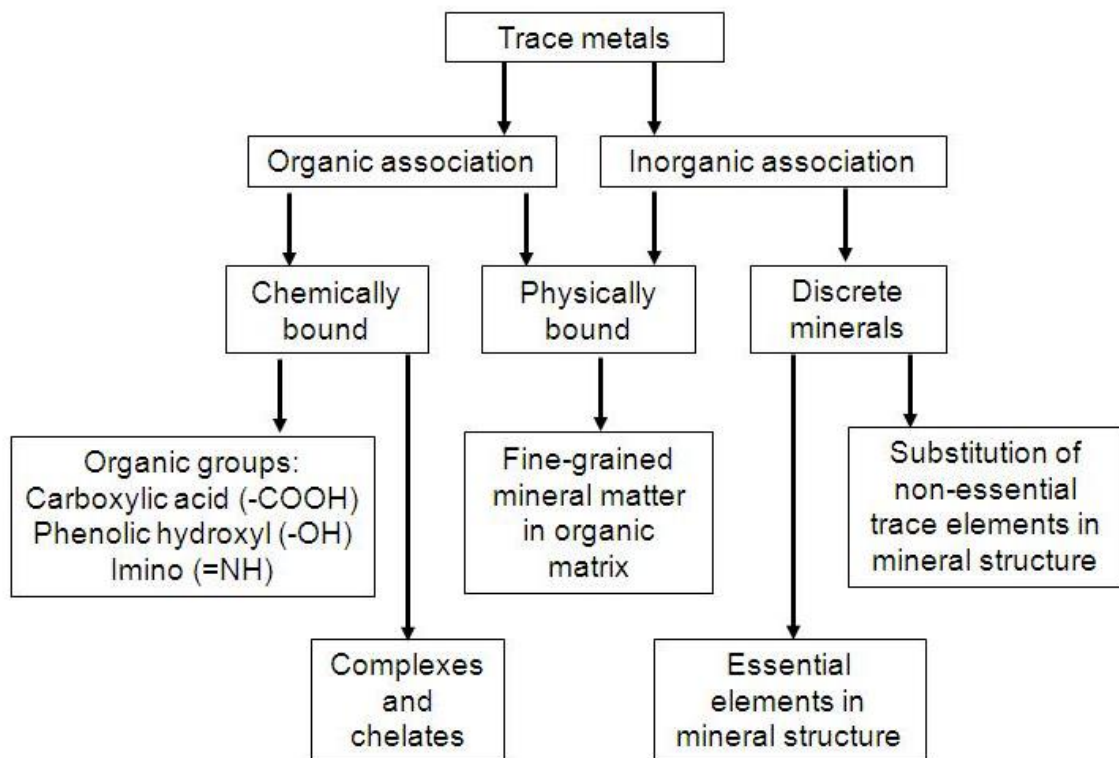


Figure 1-8. Modes of occurrence of trace elements in coal.

## 1.2.2 Transformation and condensation behavior of trace elements in air and oxy-fuel combustion

During combustion, with excellent heat and complex physic-chemical reaction, toxic elements could release from feed coal and enter atmosphere.[62-68] The transformation and emission of trace elements is dependent on a large number of factors including their original mode of occurrence, combustion conditions and the interaction between elements in the combustion process. Extensive research on the toxic elements transformation behaviors in pulverized coal combustion system reported that the behaviors of toxic elements are determined by the coal composition, combustion atmosphere, physic-chemical characteristic and combustion technology.[69-74] These trace elements mostly evaporate during coal combustion and then condense either homogeneously as sub-micron particles which is difficult to be captured or heterogeneously onto already existing fine ash. The minerals of individual coal, mineral grains and the volatility of trace elements are strongly influence on the retention of trace elements in fly ash particles. Usually, the high reflectivity component of coal containing higher concentration of minerals burns comparatively slowly to cause retention of some of trace elements in selected ash particles, especially those with low volatility. Thus the emission mode of trace elements is strongly linked with nature of coal and formation of fine particles. S. Singh W separated behavior of trace elements into three broad groups, as shown in Figure 1-9.[75] Class 1: Elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash. They include Ba, Ce, Cs, Mn and Th; Class 2: Elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size. They are typically the chalcophile such as As, Cd, Cu, Pb, Sb, Se and Zn; Class 3: Elements which vaporize most readily. They are concentrated in the vapor or gas phase and are depleted in all solid phase, such as Br, Hg and I. He also suggests that the Zn may well be forming a submicron aerosol, based on the behaviour of trace metals within a furnace, and ZnO will not contribute to in-furnace slagging, due to ZnO volatilising to Zn forming a vapour aerosol able to pass through the combustion chamber.

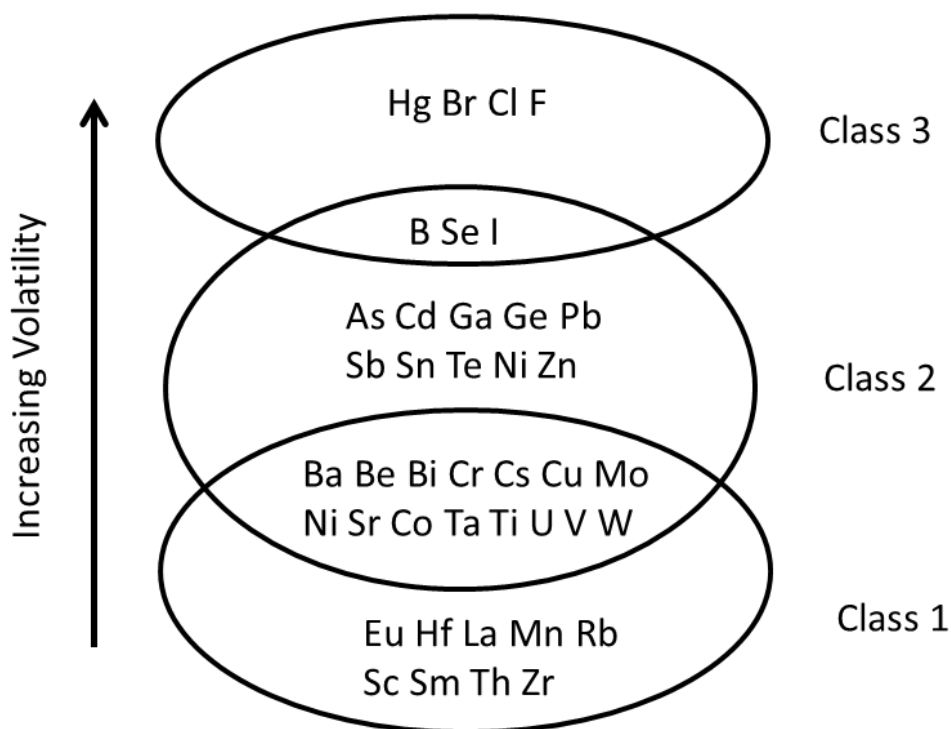


Figure 1-9 Volatility of metals categorised within a PF furnace

Quan Tang investigated the trace elements in feed coal, fly ash, bottom ash and FGD gypsum samples which were collected from two different CFPPs at Huainan, the results showed that Concentrations of thirteen major and trace elements in these samples were determined by inductively coupled plasma atomic emission spectrometry (B, Ti, Mn, Ni and Zn), inductively coupled plasma mass spectrometry (Cd, Co, Cr, Cu, Pb, Sn and V) and atomic fluorescence spectroscopy (As). The results show that most of the trace elements were concentrated in the fly ash, only Fe and Mn were enriched in the bottom ash. [76] Chuncai Zhou investigated toxic elements behaviors using a 330 MW coal gangue circulated fluidized bed co-combustion power plant equipped with electrostatic precipitators, the results show that As, Cd, Cu, Pb, Se and Sn which have a volatilization ratio more than 20% and are enriched mainly in fly ash, while Co, Cr, Mn and V which have low volatilization (65%) and are equally distributed between bottom and fly ash. [77] Anna A. Raeva developed a method that can be used to simulate the microenvironmental conditions of interest using a modified Graphite Furnace Atomic Absorption Spectrometer (GFAAS). Activation energies determined were used to predict the mechanism of element vaporization/atom formation. [78] According to the research of Chuncai Zhou,

the trace elements can be roughly classified into two groups depending on their volatilize tendencies: (a) first cluster with high volatilize tendency (Ni, Cu, Zn, Cd, Sn Pb and As); (b) second cluster, represented (Co, Cr and V), represent the low volatilize tendencies.[79]

Being an element associated with sulphides in coal, a marked surface association of Pb in ash might be expected. Around 50–60% Pb is estimated to be in surface association in fly ash [80], although the findings of Warren and Dudas [81] suggest that the majority of Pb is probably associated with the internal glassy matrix of fly ash, and is therefore not readily leached even under extended acidic. weathering[82] also reported a dominant silicate association. Pb was found to be highly insoluble and virtually immobile (b1% and often b0.1%) in both acidic and alkaline-natured fly ash samples, irrespective of the pH and the leaching test [83-86] Despite the well known affinity for sulphur during combustion, Zn would appear to have an important glass association (50–60%) in UK fly ash.[87] Kim and Kazonich[88] found an even distribution of Zn between the silicate and non-silicate fractions.

Nielsen investigated the formation of deposits by condensation in the SNL-MFC, the results indicated that the partial pressure of SO<sub>2</sub> in the combustor had a pronounced effect on the molar ratio for the high temperature experiments, but not for the low-temperature experiments.[89] The incineration of waste will produce many heavy metals both in fly ash and bottom ash, the former generally has higher metal concentration than the latter if the large, unburned metal fragments from the bottom ash are excluded.[90] And the concentrations of trace elements in ashes from incinerator are very high comparing with background levels in the environment. For instance, if comparing to average concentrations of heavy metals found in soil globally, it is clear that bulk ash (combined fly + bottom ash) contains elevated amounts of many metals.[91,92] In addition, the process of incineration greatly enhances the mobility and bioavailability of trace elements compared with raw municipal waste. [93] Consequently, the process of incineration greatly enhanced the potential for leaching of metals into the environment from ashes dumped in landfill than from ordinary waste. A study on incinerator ashes from veterinary college

incinerators in which animal carcasses are burned found that levels of metals varied considerably between incinerators. [94-96] Quann et al.[97] have investigated a back oxidation of reduced state species, as gases formed during the process of combustion or gasification of coal move away proximity of char from the high temperature to low temperature zone, the decreasing of temperature and increase of oxygen partial pressure provided the driving force for condensation and homogeneous nucleation, once the critical nucleus radius is reached, which in turn results in the growth of extremely fine ash particles as the result of inter-particle collision and fusion, which is referred to “coagulation”. Further char vaporization will result in the growth of condensation particles by heterogeneous condensation, on the surface of the homogeneously condensed aerosol before they are able to nucleate.[98]

Knowledge of trace element behaviour during Oxy-fuel combustion is important for the control of pollutants and emissions, necessary for the development of Oxy-fuel as an efficient and CO<sub>2</sub> capturing technology using brown coal/lignite. Although few experimental data are available on Oxy-fuel combustion, prior study considered only bituminous coal. The study of trace element emissions from brown coals/lignites, during Oxy-fuel combustion has never been explored. During oxy-combustion, the gas composition inside the boiler differs greatly from that of conventional combustion with air.[99] Very little has been documented on the fate of trace elements in the coal during oxy-firing, and no meaningful conclusions were gleaned from the literature. Some authors have reported results for mercury [100–105] and for other trace elements (As, Pb, Cd, Se) [105–107] released under O<sub>2</sub>–CO<sub>2</sub> coal combustion. Most of these studies reveal different trends for trace element emissions during oxy-fuel and air combustion. However results obtained have been seen to be highly dependent on the type of coal. O. Font evaluated the fate of trace elements and the properties of oxy-combustion residues in a 90kWth bubbling fluidized bed (BFB) oxy-combustion pilot plant fed with coal and limestone, the results indicated that low gas temperature and high-Ca content promotes condensation on fly ash collected in the bag filters.[108] Bithi Roy used thermodynamic equilibrium calculations to predict the trace elements (Cr, As, Se and Hg) speciation during Oxy-fuel combustion of Victorian brown coal at

different temperatures and then compared with the results from air combustion. It was found that the amount of toxic hexavalent chromium ( $\text{Cr}^{6+}$ ) species, such as  $\text{CrO}_2(\text{OH})_2$ , in the vapour phase was greater for Oxy-fuel combustion than that for air combustion, while at low temperature the distributions of toxic arsenic and selenium species in Oxy-fuel combustion showed almost the same behaviour as in air combustion.[109] M.L. Contreras compared the environmental impact of trace elements emissions in oxy-fuel combustion with that in conventional combustion through the analysis of thermodynamical equilibrium calculations (HSC 6.1) based on Gibbs energy minimization. The results indicate that, total mercury and cadmium vaporization have been seen to increase during oxyfiring, although results are strongly influenced by the fuel composition. The main differences encountered in trace elements speciation during oxyfiring, in contrast to conventional combustion, are related to variations produced in chlorine speciation in the combustion atmosphere (specially with biomass fuels) and also, to the large excess of  $\text{CO}_2$  in the oxy-fuel atmosphere which could interact with ash forming compounds, promoting variations in trace metals volatilization.[110]

### **1.2.3 Control of trace elements during coal combustion**

As mentioned above, the toxic trace elements in coal will distribute in combustion residues and gas phase after combustion. Especially for these elements belonged to Classes 2 and 3, which possess a high vaporization propensity. An alternative technology for the control of trace elements emission is to prevent the metal vapors forming during combustion process and minimize the formation of metal vapors at the hot-end of the coal combustion process. Different control technologies of reducing emission of trace elements have been employed in coal utilization processes. The foremost technology is pre-utilization removal of trace elements from coal. A significant portion of minerals in coal is removed by a number of methods which is closely associated with association of trace elements in coal. Those trace

elements which associated with minerals are easy to be removed in the process of coal cleaning. Prakash K. Singh investigated the possibility of removal of environmentally sensitive trace elements from coal through treatment with mixed bacterial consortium; they found the consortium could efficiently remove over 80% of metals like Ni, Zn, Cd, Cu and Cr while the removal of Pb was nearly 45%, after samples were subjected to a mix of bacterial consortium, under controlled conditions. [111] Minami et al.[112] using air dense medium fluidized beds (ADMFB) were able to reject a substantial fraction of mercury in original coal while retaining acceptable combustible fraction. The next technology is to capture trace elements in the process of combustion or post combustion using different methods such as adsorption of trace elements on the clay materials, condensation of trace elements onto the smaller fly ash particles, and capturing the trace elements by using adsorbents [113] during combustion or during post-combustion scrubbing. Particularly, extensive research works have been focused on reducing the emission of mercury by a variety of adsorbents. The second strategy normally includes Spray dryer absorption systems, Wet scrubbers and Sorbent injection. A typical Spray dryer absorption system includes a reagent preparation system, a spray dryer absorber and a dust collector. Flue gas enters the spray dryer, where it is contacted by a cloud of finely atomized droplets of reagent. The flue gas temperature decreases and the humidity increases as the reagent slurry simultaneously reacts with acid gases and evaporates to dryness. Wet scrubbers control the emission of vapor phase through gas cooling and collection of the resulting condensed fine trace elements particulates. The most commonly used wet scrubbers for this type of service are the electrostatically enhanced wet scrubbers and the condensing wet scrubber. Various research works have been fixed on the interaction between trace metals and various sorbents.[114-120] In the experiments of Riess et al. [121], the sorption of arsenic under reducing conditions at 1073K was investigated. They found that fly ash, bauxite,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and corundum are suitable for the retention of arsenic. Copper-containing sorbents show good sorption performance for arsenic, due to the formation of Cu<sub>3</sub>As. Mahuli et al. [122] investigated the sorption mechanism of hydrated lime on arsenic vapors under medium (673-873K) and high temperature

(873-1273K) conditions. The capture mechanism of  $\text{Ca}(\text{OH})_2$  does not involve a simple physical adsorption but proceeds by means of an irreversible chemical reaction leading to a solid product. Sorption of arsenic by fly ash is found to be reversible and physical in nature. Meanwhile, their group [123] also used  $\text{Ca}(\text{OH})_2$  to capture selenium vapors and found the medium temperature range of 673-873K is favorable for the reaction to occur and leads to high selenium sorption. Diaz-Somoano et al. [124] studied the retention capacity of solid sorbents for Cd species present in coal gasification flue gas at high temperature. In their work, kaolin, limestone, alumina and fly ash were used as sorbents. It has been found that the amount of cadmium captured by kaolin, limestone and alumina was negligible. Fly ash has the most efficient for retaining Cd in gasification atmosphere. Gullett et al. [125] tested sorbents injection into the pilot scale high-temperature furnace during coal combustion and their results indicated a reduction in concentrations of Sb, As, Hg and Se in submicron particles when hydrated lime and limestone were injected. Yao et al. [126] used aluminosilicate and calcium-based sorbent to capture Pb and Cd in a drop tube furnace. Kaolin was found to be a relatively effective sorbent for Pb and Cd capturing. Their results further showed that the capture ability depended on chemical compositions and specific surface area of the sorbents. HCl in flue gas caused a little decrease in the capture ability of aluminosilicate-based sorbents. Fiona Low injected silica-based additive for the inhibition of ash slagging and fouling to investigate the influence of silica on the behaviour of the aforementioned trace elements, the results showed that Addition of the silica-based additive was shown to provide competing reactions for the heterogeneous transformation of the trace elements and hence altering their relationships the group encompassing As, Cr, Mn, and V, witnessed a noticeable reduction in enrichment across all boiler positions upon using the silica-based additive. The group; Ba, Co, Ni and Zn, have depleted concentrations irrespective of the use of the silica-based additive. For the rest of the trace elements particularly Be, Cu, and Pb, they have intertwining trends between the different RE sections, and also between the two combustion cases of the raw coal and coal mixed with the silica-based additive. [127]

Few studies are published about oxy-fuel combustion on fluidized bed (FB)



boilers, and most of them focused on the fundamentals of this power generation technology, mainly on flame characteristics, heat transfer patterns, and NO<sub>x</sub> and SO<sub>x</sub> release and abatement.[128–131] Research on trace elements is extremely scarce. Few articles on Hg speciation[132–134] and modelling studies on the behaviour and emissions of other trace elements[135] have been published. Consequently, develop research on the fate of trace elements and on properties of oxy-combustion residues, is then of special relevance, especially taking into account the expected implementation of oxy-combustion technology in the forthcoming years.

### **1.2.4 Oxy-fuel combustion technology**

As one of the leading options for power generation with CO<sub>2</sub> capture, Oxy-fuel combustion has been established primarily from pilot-scale studies.[136-138] Oxy-fuel combustion has been found to differ from air combustion in several ways, including flame temperature and ignition, heat capacity, density of flue gas, radiative properties of the furnace gases, char reactivity, reduced NO<sub>x</sub> and SO<sub>x</sub> emissions, since of many different properties between N<sub>2</sub> and CO<sub>2</sub>, summarized as below:[139]

Ignition, flame propagation and stability: Shaddix et al.[140] tested the ignition and de-volatilization characteristics of both a high-volatile bituminous coal and a subbituminous coal using a single-particle imaging at a gas temperature of 1700 K over a range of 12-36% O<sub>2</sub> in both N<sub>2</sub> and CO<sub>2</sub> diluent gas. The use of CO<sub>2</sub> retards the onset of ignition and increases the duration of de-volatilization because of the higher molar specific heat of CO<sub>2</sub> and its tendency to reduce the local radical pool. Kiga et al.[141], they employed a microgravity facility to measure the flame propagation speed in a coal-dust cloud for the study of ignition characteristic of pulverized coal in a CO<sub>2</sub>-rich atmosphere. It was found that the flame propagation speed in O<sub>2</sub>/CO<sub>2</sub> atmosphere is lower than that in O<sub>2</sub>/N<sub>2</sub>. Arias et al.[142] have reported that the burnout of coals with a mixture of 79%CO<sub>2</sub>/21%O<sub>2</sub> is lower than in air, but an improvement is achieved when the oxygen concentration is 30% or 35%.

Combustion and burnout: Gani et al. reported that de-volatilization and char combustion are delayed and that the calculated particle temperatures are lower in the presence of CO<sub>2</sub>. The reason can be attributed to the differences in the thermal and transport properties of N<sub>2</sub> and CO<sub>2</sub>. [143] SKIPPY modeling by Shaddix et al. demonstrated that the temperature of char particles are strongly impacted by the high endothermicity of the reaction of CO<sub>2</sub> with char, even for assuming reaction rate that fail to yield substantial flux for CO<sub>2</sub> gasification.[144]

Heat transfer: Buhre et al. found that the major contribution of the heat transfer from a flame is thermal radiation from water vapors, carbon dioxide, soot, and carbon monoxide in air combustion. While in oxyfuel combustion with RFG, the radiative heat transfer from the flame will change due to significantly increasing of the concentration of carbon dioxide and water vapor. As carbon dioxide and water having high thermal capacities comparing with nitrogen, it will lead to an increase in the heat transfer in the convective section of the boiler.[145] Andersson et al. have researched radiative heat transfer in lignite fired oxyfuel flames. The results indicated that the temperature, and the total radiation intensity of the oxyfuel flames, increased with decreasing flue gas recycle rate when flue gas recycle rate was varied to keep the stoichiometry the same in all cases but the oxygen fraction in the RFG ranged from 25 vol% to 29 vol%. [146]

### **1.3 Purpose of this study**

As summarized above, Coal and waste-fired power plants currently provide over 40% of the world's electricity, while the problems of emission limited the utilization of coal and waste. Also these problems were extensively investigated, the formation of ultrafine particles which is mainly attributed to vaporization-condensation mechanism of trace elements during coal combustion is very complicated and the condensation behavior of trace elemental vapors with the flue gas cooling is not very clear, especially for the formation of species of trace elements as a function of the temperature of flue

gas, which greatly affects the toxicity and leaching performance of trace elements. Moreover, for the control technology of trace elements, the ash properties are potentially shifted by the addition of adsorbents and in turn alter the leaching of trace elements in fly ash. But, the increase of operation cost caused by the use of adsorbents should be considered for commercial power plant. In contrast, adjusting the mineral composition through the combustion of blending coal, which is a reliable technology and has been widely used in many power plants, is expected to reduce the emission of trace elements and prevent their leaching from fly ash. This assumption need to be confirmed by experimental observation.

On the other hand, regarding oxy-fuel combustion of coal, the information of ash formation and transformation and condensation behavior of trace elements is scarce until now. Even the trend of trace elements behavior between traditional combustion and oxyfuel combustion is not united in the researchers. High partial pressure of CO<sub>2</sub> around char surface can trigger extra gasification reaction and affect the vaporization of trace elements. The flue gas recirculation with impurities such as HCl, SO<sub>2</sub> and H<sub>2</sub>O during oxy-firing conditions possibly results in the change of transformation and condensation behavior. These also need to be confirmed by experimental observation.

Accordingly, the purposes of this work include:

- Investigation on the homogeneous nucleation and heterogeneous condensation behavior of trace metals during flue gas cooling;
- Investigation on the influence of HCl, SO<sub>2</sub>, H<sub>2</sub>O and oxide particulates on condensation behavior of trace metals during flue gas cooling;
- Investigation on the differences of condensation behavior of trace metals between traditional combustion and oxy-fuel combustion.

## **1.4 Outline of this thesis**

The content of this thesis contains seven chapters as outline below.

Chapter 1 is current chapter, which consists of background of this work, review of previous work and the purpose of this study.

In chapter 2, The presence of particulates in flue gas exerted remarkable influence on the fate of Pb and Zn compound vapors. Pb compound vapor was found being captured by  $\text{Al}_2\text{O}_3$  as Pb–Al–O at the temperature above 823 K through chemical reaction, regardless flue gas composition. Zn preferentially transformed into  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$  and ZnO, respectively on the presence of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and CaO above 823 K. The presence of  $\text{SO}_2$  inhibited the chemical reactions of Pb and Zn vapors with particulates. Such an inhibitory effect was however compensated by the introduction of steam to flue gas. The presence of particulates in flue gas promoted the condensation of Pb and Zn compound vapors at higher temperature in comparison to the blank conditions, through heterogeneous nucleation, which in turn offset the effect of super-cooling. Moreover, the formation of sulfate was increased since the presence of particulates in flue gas triggered the condensation of sulfates vapors at high temperature and then reduced its partial pressure in flue gas, facilitating the sulfation reaction. Adjusting the concentrations of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  in flue gas can prevent the formation of chloride of Pb and Zn, which is notorious for its toxicity and corrosion propensity during solid waste incineration.

In chapter 3, Vaporization of Pb and Zn-loaded model compounds has been carried out in a lab-scale rotary kiln reactor to clarify their condensation behavior upon flue gas cooling in both air-firing and oxy-fuel combustion modes. The influence of flue gas impurities including HCl,  $\text{SO}_2$  and  $\text{H}_2\text{O}$  has been examined systematically. For the two metals existing separately in the reactor, namely at single mode, both preferentially condensed as chlorides in the presence of HCl, under air-firing and oxy-fuel conditions.  $\text{SO}_2$  and steam in flue gas promote chloride into sulfide at high temperature. It was noticed that the deposition propensities of Pb and Zn vapors under oxy-fuel condition of the single mode were slightly enhanced than that in air-firing condition. This is due to a lower Lewis number of oxy-fuel combustion that is in favor of the formation of highly polydispersed fine particles. However, this discrepancy was diminished in the

case that both two metals co-exist as the mixture mode in the reaction system. At the mixture mode from 700K to 400K, the condensation fraction of either Pb or Zn was confirmed higher than that in the single mode, due to an enhanced heterogeneous nucleation of Zn vapors on  $\text{PbSO}_4$  nuclei.

In chapter 4, the major conclusions obtained from this work and recommendations for future works are summarized in this section.

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## Chapter 2

# Effect of inorganic particulates on the condensation behavior of lead and zinc vapors upon flue gas cooling

### 2.1 Introduction

Incineration is one of the common technologies for the treatment of municipal solid waste (MSW), as it can reduce the volume of waste by up to 90% and recover the energy for power generation [1-2]. However, MSW contains large quantity of heavy metals which are partially released out of stack in gas phase upon incineration, raising environmental concern [3]. Lead (Pb) and zinc (Zn) are two typical heavy metals in solid waste and usually possess relative high concentration either in bottom ash or in fly ash [4]. The heavy metals retained in ash are also of concern, as they could transfer into water systems or soil upon leaching into rainwater and/or underground water. Among the species for heavy metals, the chlorides are most hazardous, due to their high toxicity and solubility. Moreover, lead and zinc chlorides can trigger operating problems during MSW incineration, *e.g.* corrosion of super-heater tube since the existence of lead and zinc chlorides drastically lower the melting point of deposits [5-8]. Hence, it is essential to investigate the transformation behavior of lead and zinc vapors to minimize their chloride formation during MSW incineration.

Lead and zinc during MSW incineration undergo initial vaporization from flame zone, subsequently condensing during flue gas cooling through nucleation and/or chemical reactions with pre-existing solid particles or other gaseous components (*e.g.* sulfur and moisture). The fates of these two metals during MSW incineration are affected by numerous factors including incineration operating conditions and the original properties of MSW. Both experimental observations and thermodynamic equilibrium prediction have confirmed that the chlorine concentration in MSW is one key factor affecting the vaporization of lead and zinc [9-12]. Increase in the ratio of sulfur/chloride in flue gas shifts the transformation of lead and zinc from chlorides toward sulfates [3]. Apart from gas components, the ultra-fine particulates containing the refractory elements are also supposedly dominant in flue gas. Their existence has the potential to alter the condensation propensity of Pb and Zn compound vapors through complex chemical reactions and/or heterogeneous nucleation. Zinc retained in waste combustion bottom ash and fly ash has been found to partially combine with Si and Al. Lead of oxide, chloride and sulfate were detectable in the deposits collected from super heater area during MSW combustion [13]. Additionally, Pb vapor has also been confirmed being captured by kaolinite through chemical reaction at high temperature [14-16], the reaction rate of which is potentially retarded once the chlorine being introduced into the combustion system [14,16]. In contrast, limestone is not an effective sorbent for the capture of Pb compound vapors [14,15].

Based on the above literature review, one can conclude that the presence of either inorganic particulates or gaseous components including SO<sub>2</sub>, HCl and steam in flue gas is influential in the fate of Pb and Zn compound vapors. The capture of metal vapors by different sorbents has been widely investigated in CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O atmosphere and a theoretical model was also developed to simulate the interaction between metal compound vapors and solid sorbents [17-19]. Our previous work has investigated the condensation behavior of metallic vapors upon flue gas composition without particulates in air condition. However, the flue gas from MSW incineration contains HCl, SO<sub>2</sub> and H<sub>2</sub>O, which are supposed to affect the speciation of lead and zinc as well as the particulate composition, thereby making the interaction of metallic

vapors with particulates, as well as the vapor condensation complex. Our previous work has investigated the condensation behavior of metallic vapors upon flue gas composition without particulates in incineration system [19]. A thermodynamic pseudo-equilibrium model was developed to evaluate the effect of super-cooling and sulfation reaction of metallic vapors on the condensation of metallic vapors [20]. This work aims to augment our previous study to provide detailed information on the fate of Pb and Zn compound vapor upon flue gas cooling during MSW incineration. Three compounds of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  were employed and placed individually in flue gas cooling section to simulate inorganic particulates in MSW incineration. The gaseous components of  $\text{HCl}$ ,  $\text{SO}_2$  and steam were introduced into flue gas to systematically examine their effects on the interaction of Pb and Zn vapors with particulates. The new knowledge is expected to help optimize the incineration process parameters to reduce the propensity of toxicity and corrosion caused by the lead and zinc chlorides during MSW incineration.

## **2.2 Experimental section**

### **2.2.1 Sample preparation**

Pb- and Zn- bearing model compounds were made and employed for incineration throughout this study. Porous titanium dioxide ( $\text{TiO}_2$ ) were immersed in Pb- and Zn-containing solution for 2 h, respectively, and then dried at 313 K in a rotary evaporator. The metal-containing solution was made by the dissolution of 0.5 g metallic acetate in 20 ml deionized water. The resulting dry heavy metal-laden  $\text{TiO}_2$  powders were eventually calcined at 773 K in a muffle furnace for 2 h to remove the organic moieties.

### **2.2.2 Experimental setup and conditions**

Incineration experiments were conducted in a lab-scale electrically heated rotary kiln furnace reactor with a multiple-stage flue gas cooling zone, as shown in Fig.2-1. The detail description of the reactor has been described elsewhere [20, 21]. The model

waste sample of Pb or Zn was put on the bottom of the inner tube, which was quickly moved into the outer tube once the temperature was up to 1223 K. The HCl-containing gas was introduced into inner tube to vaporize the heavy metals loaded in porous TiO<sub>2</sub>. A motor was used to rotate the inner tube to eliminate the gas diffusion resistance. The resulting metal compound vapors from inner tube flow into a vertical cooling section with three stages with temperature of 1073K, 823K and 573K respectively. SO<sub>2</sub> and H<sub>2</sub>O were injected into outer tube to adjust flue gas composition and examine their effects on the reactions of Pb and Zn compound vapors with particulates during flue gas cooling.

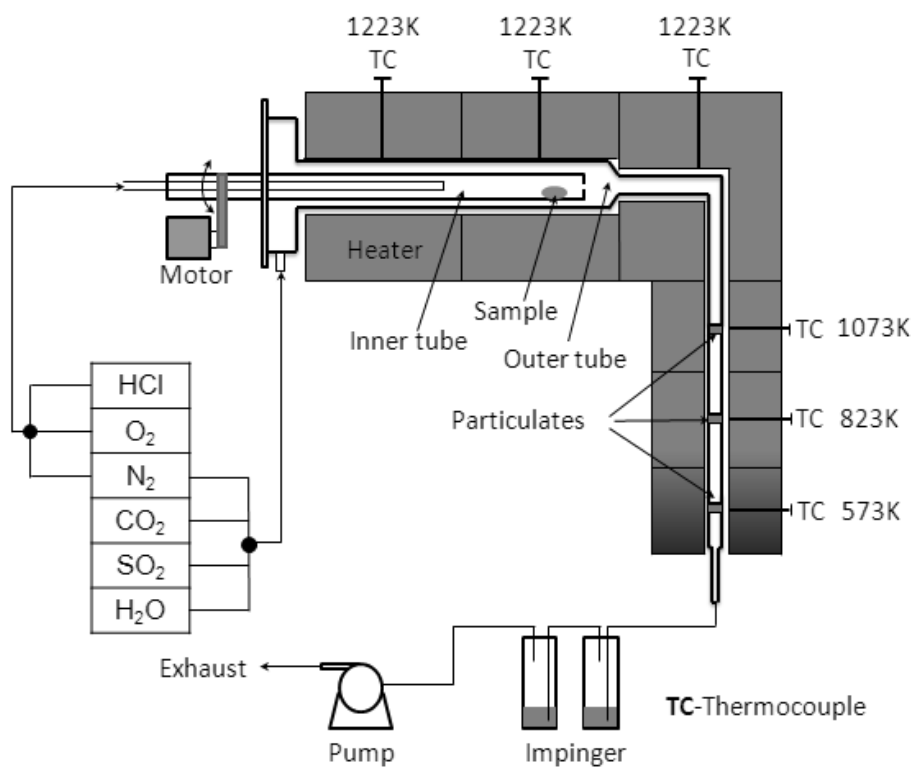


Fig. 2-1. Schematic of the experimental apparatus.

The reaction gas composition was given in table 2-1. The flow rate and concentration of HCl, O<sub>2</sub> and N<sub>2</sub> in inner tube were remained constant throughout all experimental conditions to generate an identical amount of Pb or Zn compound vapor. The behavior of Pb and Zn compound vapors upon flue gas cooling was examined under three atmospheres including 0% SO<sub>2</sub>, 0.2% SO<sub>2</sub> and 0.2% SO<sub>2</sub> plus 8% steam, introduced from outer tube. The vaporization of metal loaded in TiO<sub>2</sub> in inner tube was continued for 20 min in each run, and the total gas flow rate in cooling section



remained at 1.4 L/min, resulting in the presence of 0.038% of Pb and 0.029% of Zn compound vapors in flue gas. The cooling rate of flue gas in the cooling section is about 100 K/s to simulate flue gas cooling process in a real system. Since the vaporization of metals is greatly dependent on the HCl partial pressure, HCl concentration of 2000ppm in flue gas was chosen for obtaining a satisfactory experimental accuracy. Although the SO<sub>2</sub> concentration used in these experiments are maybe higher than that in real MSW incinerator, the mole ratio of HCl/SO<sub>2</sub>, a key factor of determining the partitioning of metal species, is comparable to realistic incinerator.

Table 2-1. Reaction gas composition.

	Gas species	Concentration, vol.%
Inner tube	O <sub>2</sub>	5
	HCl	0.2
	N <sub>2</sub>	Balance
	SO <sub>2</sub>	0,0.2
Outer tube	H <sub>2</sub> O	0,8
	CO <sub>2</sub>	12
	N <sub>2</sub>	Balance

The active Al<sub>2</sub>O<sub>3</sub> with diameter of 1-2 *mm* and Fe<sub>2</sub>O<sub>3</sub> and CaO with diameter of 10-150 *μm* were tested in the cooling section. For each run, 0.5 g inorganic particulates were put on each cooling stage where a silica thimble filters was located for flue gas to pass through. The quartz wool was used to disperse the particulates as uniformly as possible. Two impingers containing 1M HNO<sub>3</sub> were installed downstream the cooling section to capture the non-condensable Pb and Zn vapors. There are two possible mechanisms to affect the fate of metal compound vapors upon flue gas cooling: condensation of metal compound vapors and interaction of metal compound vapors with inorganic particulates [19]. Therefore, two kinds of experiment were designed to separate the role of above two possible mechanisms: 1) Experiments were first conducted without inorganic particulates in flue gas, termed as blank condition hereafter, to investigate the condensation behavior of metal compound vapors during flue gas cooling; and 2) Experiments were carried out with inorganic particulate in flue gas to examine their effect on the fate of metal compound

vapor upon flue gas cooling through the comparison of the results with that of blank condition.

### 2.2.3 Samples characterization

X-ray diffraction (XRD, Rigaku RINT) was employed for determining the crystalline species in deposits. The concentrations of metals and anions of the deposit were quantified using atomic absorption spectrophotometer (AAS, Shimadzu AA-6200) and ion chromatography (IC, Shimadzu) with a CDD-6A conductivity detector, respectively. The results from replication experiment indicated a minor error less than 5% in this experiment. Metallic species retained in inorganic particulates were subjected to X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-3300) characterization using Mg K $\alpha$  (1253.6 eV) as the excitation source. C1s energy of carbon atom (284.6 eV) was used to calibrate the binding energy of other atoms. The Pb and Zn-bearing species retained in particulates were determined and quantified through the comparison of the binding energy of Pb (4f<sub>7/2</sub>) and Zn (2p<sub>3/2</sub>) with that of a series of standard samples.

### 2.2.4 Thermodynamic pseudo- equilibrium model

Apart from potential chemical reactions of metal vapors with inorganic particulates, the presence of inorganic particulates in flue gas possibly affects the condensation of metal compound vapors through heterogeneous nucleation in terms of the deposition of a metallic vapor species at a given temperature. To help understand the condensation mechanisms of Pb and Zn vapors upon flue gas cooling, a thermodynamic pseudo-equilibrium model was developed using ChemApp linked with FactSage 6.2 database. The schematic of the model is shown in Fig. 2-2. The detail description of this model has been given elsewhere [21]. In brief, a variable,  $\alpha$ , in the model is used to describe the proportion of a metal vapor which does not condense on a certain cooling stage, namely super-cooling. The value of  $\alpha$  was optimized by curve-fitting the experimental results without particulates in flue gas in

HCl/O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub> atmosphere, which was further applied to the other conditions with SO<sub>2</sub> and/or steam entering the outer tube. Another variable,  $\beta$ , was employed to evaluate the extent of overall sulfation reaction in the process of flue gas cooling when SO<sub>2</sub> and/or H<sub>2</sub>O were introduced into flue gas. The flue gas compositions and the amount of condensed metal compound vapor determined under an experiment condition were used as input for the modeling. The output includes the metal species in both gas and solid phases.

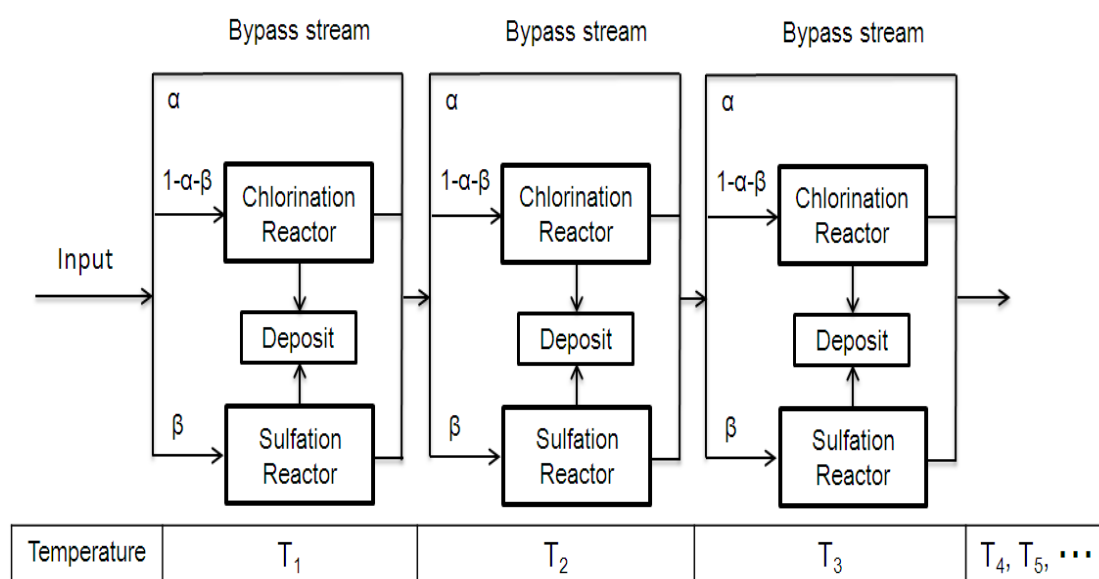


Fig. 2-2. Schematic of a thermodynamic pseudo-equilibrium model on the condensation of metallic vapors during flue gas cooling.

## 2.3. Results and Discussion

### 2.3.1 Condensation of Pb and Zn vapors without particulates in flue gas

The condensation of metallic vapors in cooling section was first examined under the blank condition (without particulates) at three atmospheres: 1) O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and HCl; 2) O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, HCl and SO<sub>2</sub>; and 3) O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, HCl, SO<sub>2</sub> and H<sub>2</sub>O. A quantity of 0.2% HCl was introduced continuously into inner tube for the vaporization of Pb or Zn loaded in TiO<sub>2</sub> while only CO<sub>2</sub> and N<sub>2</sub> were introduced into the outer tube.

The Pb vapor was condensed above 823 K whereas Zn compound vapors condensed below 823 K, as demonstrated in Fig.2-3. XRD analysis indicates the dominance of chlorides for Pb and Zn in the deposits, substantiating the preferential vaporization of two metals from inner tube as chlorides rather than oxides since the metallic chlorides possess higher saturation vapor pressure than oxides. The different condensation temperature of these two chlorides in the cooling section is due to their different boiling point, 1223 K for  $\text{PbCl}_2$  versus 1029 K for  $\text{ZnCl}_2$ . With respect to the metallic vapors escaped from flue gas cooling section, the concentration of Pb in the impinger was lower than the detection limit of AAS whereas about 4% of Zn was found in the impinge solution, reflecting the ease for the  $\text{ZnCl}_2$  to be released out of stack in comparison to  $\text{PbCl}_2$  during MSW incineration.

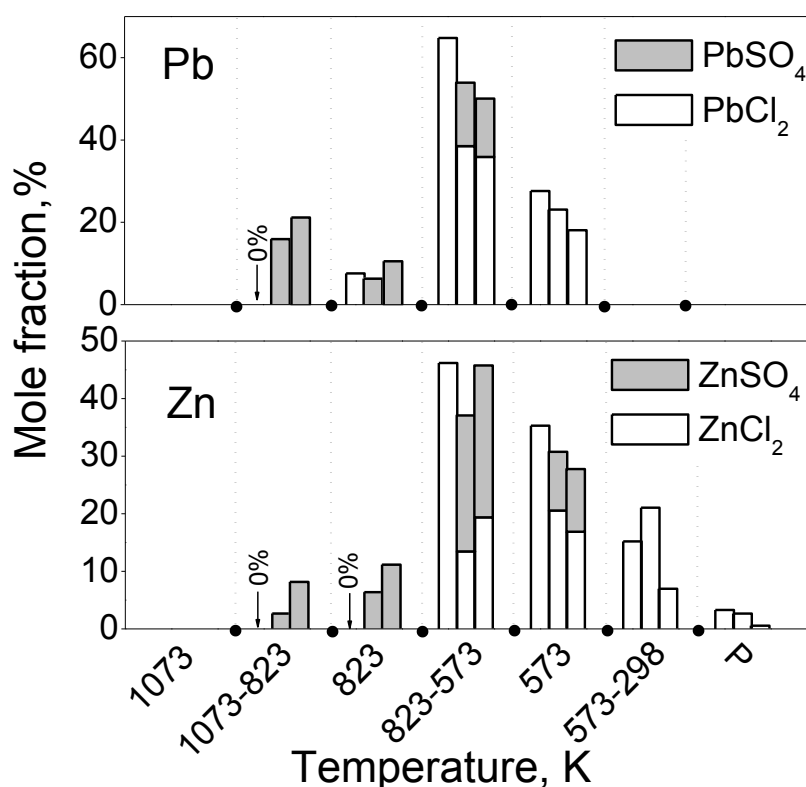


Fig.2-3. Condensation of Pb and Zn vapors without particulates in flue gas under different conditions. The three columns from left to right for each temperature respectively represent 0%  $\text{SO}_2$ , 0.2%  $\text{SO}_2$  and 0.2%  $\text{SO}_2$  plus 8%  $\text{H}_2\text{O}$ . P denotes impinger.

The gas component and composition in the inner tube were fixed as the same as

the above experiments, introducing 2000ppm SO<sub>2</sub> from outer tube resulted in the shift of the condensation of Pb and Zn vapors to the temperature range of 1073-823 K, due to the formation of PbSO<sub>4</sub> and ZnSO<sub>4</sub> through sulfation. The higher boiling point of sulfates of Pb and Zn than chlorides leads to a preferential condensation at high temperature upon flue gas cooling. Doping 0.2% SO<sub>2</sub> and 8% H<sub>2</sub>O together increased the condensation fraction of Pb and Zn sulfates above 823 K. It indicates the sulfation of chlorides is promoted by the addition of H<sub>2</sub>O through reaction (I) [22]. Here, M denotes Pb or Zn.



## 2.3.2. Interaction of Pb and Zn with particulates in flue gas

### 2.3.2.1. Interaction of Pb and Zn vapors in HCl/N<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub> atmosphere

The presence of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> or CaO in flue gas is influential on the fate of Pb and Zn compound vapors, as demonstrated in Fig.2-4. Pb vapor was captured by Al<sub>2</sub>O<sub>3</sub> while Zn vapor was captured by three particulates at 1073 K through comparing the distribution of metals with that in blank condition. In terms of XPS analysis, a new species of Pb was found to be retained in Al<sub>2</sub>O<sub>3</sub>, which bears a formula of PbO·xAl<sub>2</sub>O<sub>3</sub> with uncertain *x* value. The detailed structure cannot be explored because the peak positions for different *x* values are too close to differentiate. It was therefore termed Pb-Al-O hereafter. The Zn-bearing compounds retaining in Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO at 1073K are ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO, respectively, indicative of potential chemical reactions of Zn vapor with inorganic particulates. In contrast, the chemical reaction of Pb vapor with CaO and Fe<sub>2</sub>O<sub>3</sub> is negligible since of the same Pb species with that in blank condition. Such observations are consistent with the results of previous study [14,15].

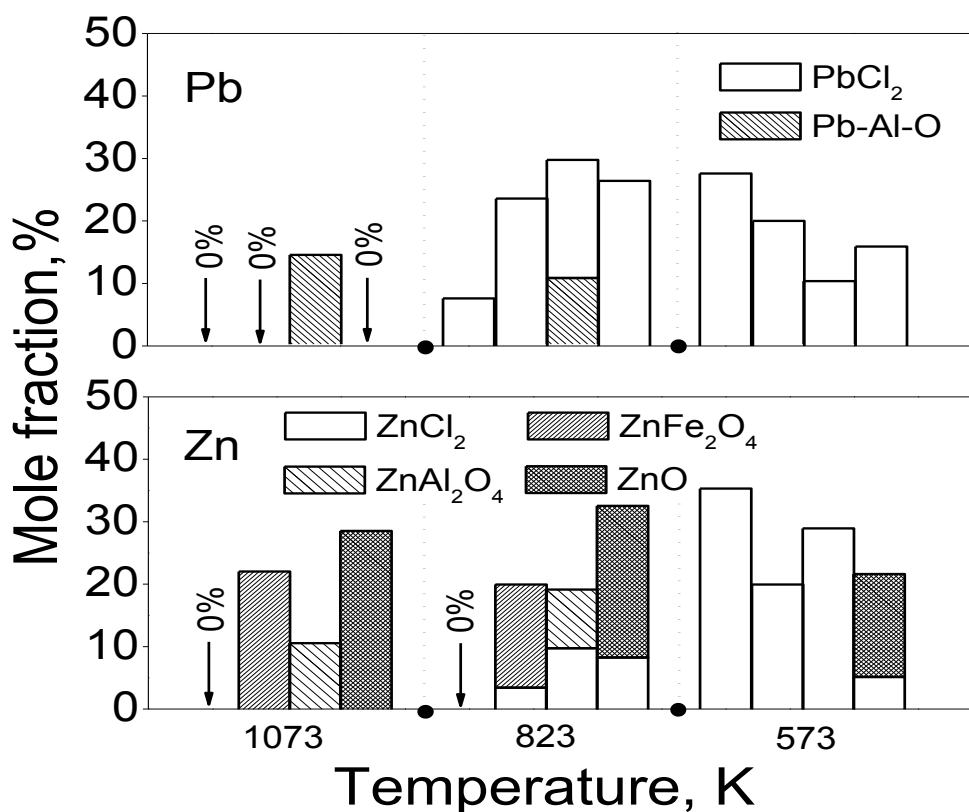


Fig.2-4. Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl /N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

### 2.3.2.2 Influence of SO<sub>2</sub> and steam on the interaction of Pb and Zn with particulates

The influence of SO<sub>2</sub> in flue gas on the interaction of Pb and Zn vapors with particulates is prominent, as demonstrated in Fig.2-5. Apart from Pb-Al-O retained in Al<sub>2</sub>O<sub>3</sub> at 1073 K and 823 K, the PbSO<sub>4</sub> was found remaining at 1073 K when 0.2% SO<sub>2</sub> is present in the flue gas. Since the presence of particulates in flue gas potentially shift the Knudsen number of metallic vapor and hence its diffusivity in carrier gas [23], the resulting sulfate vapor is subjected to collision and then agglomerate into larger cluster, which readily condense on particulates. Similar results can be observed for Zn. Apart from the Zn-bearing species of ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO respectively existed in Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO, ZnSO<sub>4</sub> was observed on three particulates at 1073 K.

Doping 8% H<sub>2</sub>O and 0.2% SO<sub>2</sub> together into flue gas caused little changes to the distribution of Pb and Zn-bearing species over the three temperature ranges relative to the results in Fig. 2-5 for only 0.2% SO<sub>2</sub> in flue gas. The condensation fraction of each species was, however, altered greatly. As shown in Fig.2-6, approximately 14% and 10% PbSO<sub>4</sub> were captured by Fe<sub>2</sub>O<sub>3</sub> and CaO respectively at 1073 K, in comparison to about 10% in Fe<sub>2</sub>O<sub>3</sub> and 7% in CaO without steam in flue gas. This is a clear sign of the promoting influence of steam on the retention of PbSO<sub>4</sub> vapor on particulates. The collision probability of sulfate vapors was improved since of the higher partial pressure of PbSO<sub>4</sub> vapor produced at high temperature due to the promotion effect of steam on the formation of sulfates, which favored the capture of PbSO<sub>4</sub> vapor by particulates. On the other hand, the fractions of Pb-Al-O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO were also increased noticeably, reflecting the reaction between Pb and Zn vapors and particulates were accelerated by steam addition.

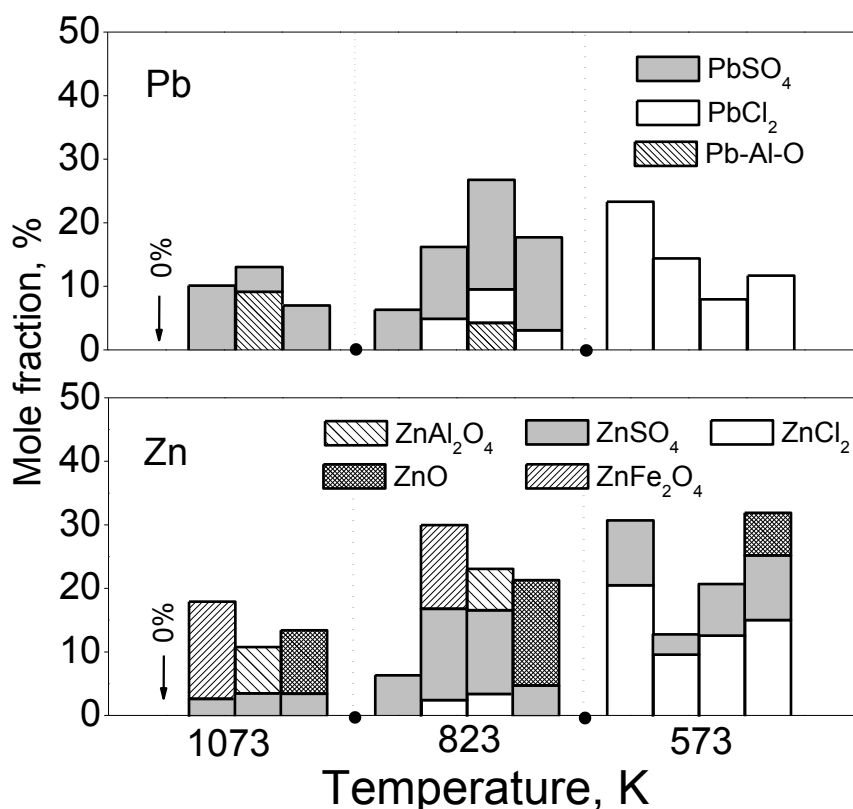


Fig.2-5. Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl/SO<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

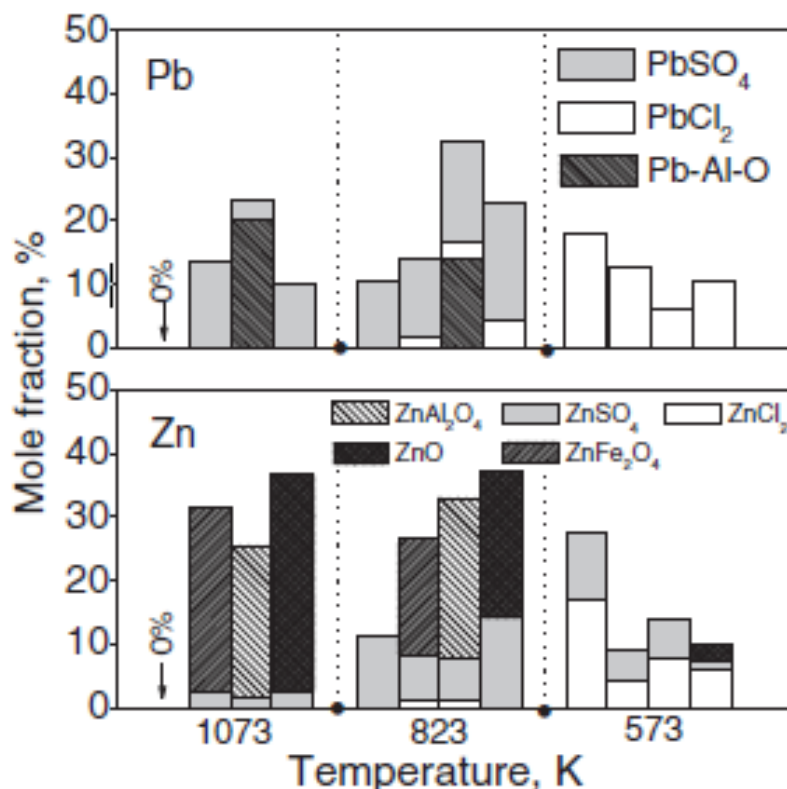


Fig.2-6. Pb and Zn compounds at 1073K, 823K and 573K with particulates in flue gas under HCl/SO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The four columns from left to right for each temperature respectively represent blank condition, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.

### 2.3.3 Interaction mechanisms of Pb and Zn vapors with particulates

The fate of metallic vapors upon flue gas cooling was influenced by the interaction with preexisting particulates including chemical reaction and heterogeneous nucleation [24]. The formation of Pb-Al-O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO is undoubtedly attributed to the former mechanism, which are highly dependent on flue gas composition. Doping 0.2% SO<sub>2</sub> into flue gas retarded the reaction of metallic vapors and particulates, which was substantiated by the experimental observation that the total condensation fraction of Pb- and Zn- bearing species was reduced in spite of the particulates type, as shown in Fig.2-7. The formation of Pb- and Zn- bearing species is mainly attributed to the reaction of particulates with metallic chlorides rather than sulfates. Otherwise, the total fraction of resulting Pb- and Zn- bearing species should be the same as that under the condition of no SO<sub>2</sub> in



flue gas. Nevertheless, the above explanation is not the exclusive reason for the decrease of ZnO with the introduction of SO<sub>2</sub> into flue gas, since the transformation of CaO into CaSO<sub>4</sub> is expected to prevent the reaction of ZnCl<sub>2</sub> vapors with calcium.

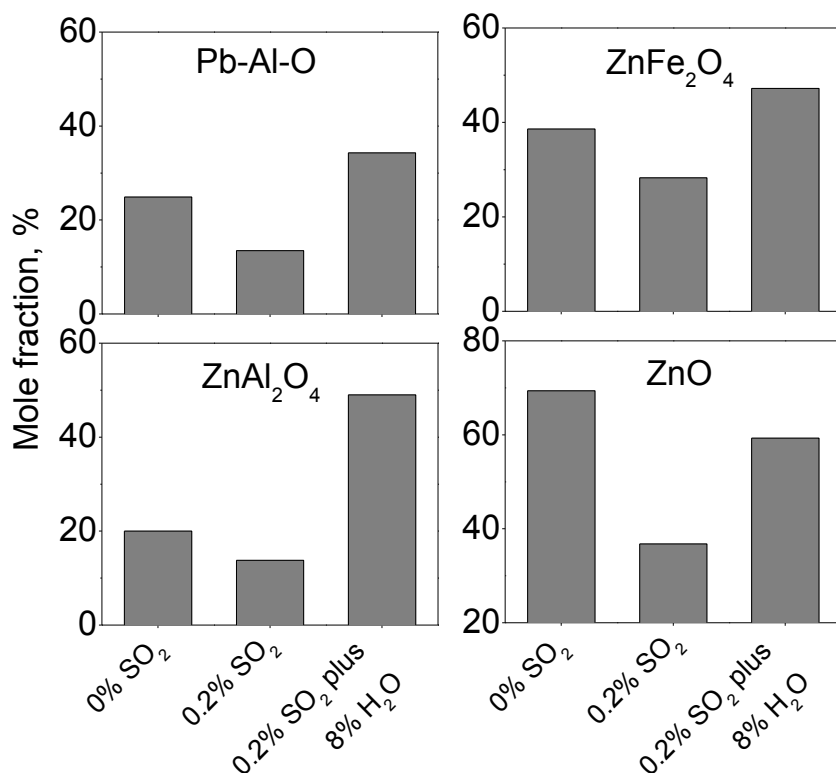


Fig.2-7. Total fraction of Pb-Al-O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO retained in particulates under different flue gas composition.

To confirm this hypothesis, CaSO<sub>4</sub> was used and placed in the cooling section in HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. As described in Fig.2-8, the distribution of Zn-bearing species was altered remarkably. Here, it should be noted that the effects of the surface performance of CaO and CaSO<sub>4</sub> on chemical reactions can be ruled out since of the comparable BET surface area of the two calcium compounds, 2.733 m<sup>2</sup>/g of CaO and 2.571 m<sup>2</sup>/g of CaSO<sub>4</sub>. Approximately 5% ZnO was detected on CaSO<sub>4</sub> at 1073 K, relative to about 30% ZnO on CaO, clearly suggesting that the formation of ZnO is caused by the reaction between ZnCl<sub>2</sub> and CaO rather than CaSO<sub>4</sub>. Doping 8% H<sub>2</sub>O and 0.2% SO<sub>2</sub> together into flue gas promoted the reaction of metallic vapors with particulates compared to the condition of 0.2% SO<sub>2</sub> in flue gas, as shown in Fig. 8. The possible reactions of Pb and Zn vapors with particulates, as demonstrated in table 2-2, are thermodynamically available. The addition of steam facilitates the right side

of these reactions and in turn increases the formation of Pb-Al-O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO. Regarding the formation of ZnO at 573 K, apart from the reaction of ZnCl<sub>2</sub> with CaO, the reaction of ZnCl<sub>2</sub> with Ca(OH)<sub>2</sub> derived from the hydration of CaO is another possible contributor. This reaction is also available in thermodynamics.

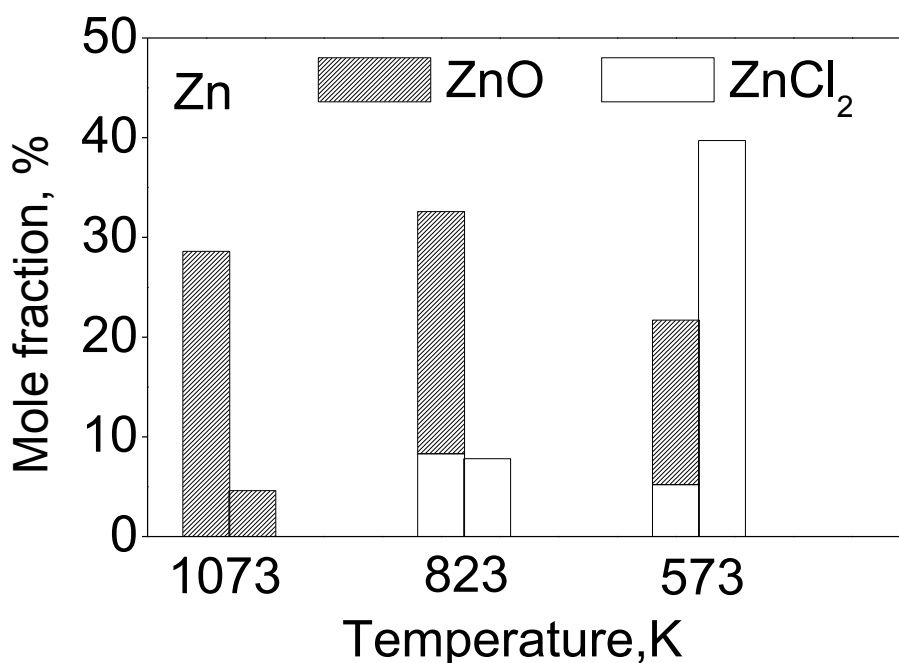


Fig.2-8. Zn compounds at 1073K, 823K and 573K with CaO (left column) and CaSO<sub>4</sub> (right column) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere.

Table 2-2. Possible reactions of PbCl<sub>2</sub> and ZnCl<sub>2</sub> vapors with particulates and their Delta G under different temperature.

Reactions	Delta G, kJ/mol		
	1073	823 K	573 K
$PbCl_2(g) + xAl_2O_3(s) + H_2O(g) \rightarrow PbO \bullet xAl_2O_3(s) + 2HCl(g)$	-90.52	-128.64	-166.14
$ZnCl_2(g) + Fe_2O_3(s) + H_2O(g) \rightarrow ZnFe_2O_4(s) + 2HCl(g)$	-70.09	-78.47	-87.23
$ZnCl_2(g) + Al_2O_3(s) + H_2O(g) \rightarrow ZnAl_2O_4(s) + 2HCl(g)$	-36.51	-48.18	-60.34
$2ZnCl_2(g) + CaO(s) + H_2O(g) \rightarrow 2ZnO(s) + CaCl_2(s) + 2HCl(g)$	-63.76	-107.33	-153.99

Apart from the effect of chemical reaction between metallic vapors and particulates, the nucleation is another route affecting the fate of metallic vapors. The pre-existing particulates in flue gas are expected to act as nuclei and potentially trigger the condensation of metallic vapors. The pseudo-equilibrium thermodynamic model was first used to predict the condensation of metallic vapors in HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> atmosphere. The modeling result for a  $\alpha$  value of zero denotes a state for all the species to reach equilibrium instantly. The deposition fraction predicted by the model is far higher than that observed in experimental results, as illustrated in Fig. 2-9, reflecting the important influence of super-cooling on the condensation of the metallic vapors. The resulting saturated metal vapors diffused downwards through the high-temperature cooling zone as their original gaseous state, and preferential deposited at low temperatures. The  $\alpha$  values of 0.4 for Pb and 0.35 for Zn were found to fit the blank experimental results well. When the particulates of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO were present in flue gas, a satisfactory fitting can be obtained when the  $\alpha$  values were set at 0.2 for Fe<sub>2</sub>O<sub>3</sub>/CaO and 0.25 for Al<sub>2</sub>O<sub>3</sub>, indicating the offset of super-cooling of metallic vapors by pre-existing particulates. The preexisting particulates in flue gas promote the condensation of metallic vapors through heterogeneous nucleation, which was substantiated by the fact that the condensation fraction of PbCl<sub>2</sub> and ZnCl<sub>2</sub> was increased as the particulates were present in flue gas in comparison to the results under blank conditions (see Fig.2-4). The formation of sulfates also have a potential to affect the condensation of metallic vapors upon flue gas cooling since sulfate possesses higher condensation temperature than chlorides, as mentioned above.

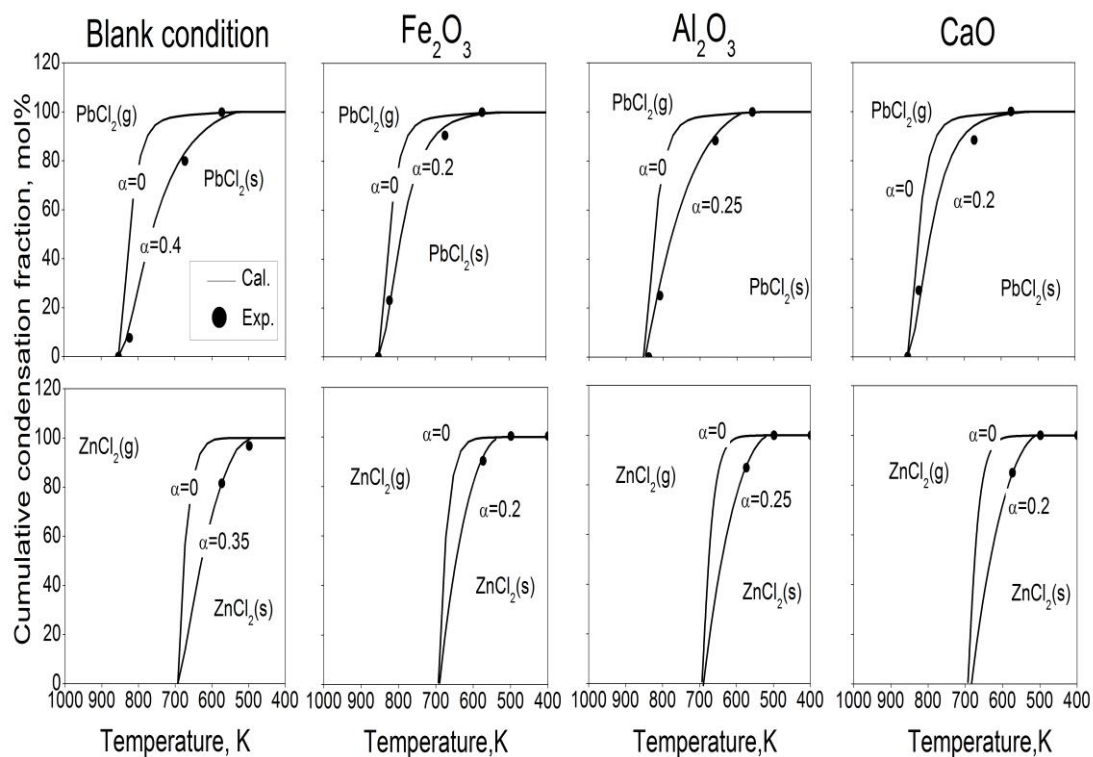


Fig 2-9. Comparison of model calculation with experimental results in HCl/N<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub> atmosphere.

In this model, the shift of  $\beta$  value denotes to the changes of sulfation rates in the flue gas cooling section. Assuming the super-saturation fraction,  $\alpha$ , is constant regardless of flue gas composition when the particulates are present in flue gas. Model results in Fig. 2-10 indicate that the  $\beta$  value was increased with the presence of particulates in flue gas, reflecting the sulfation of metallic vapors was promoted by the particulates. The retention of sulfate in particulates through collision and agglomeration at 1073 K potentially reduce the partial pressure of the sulfates vapors of Pb and Zn relative to that in blank condition, which is in favor of the right side of the reaction (1).

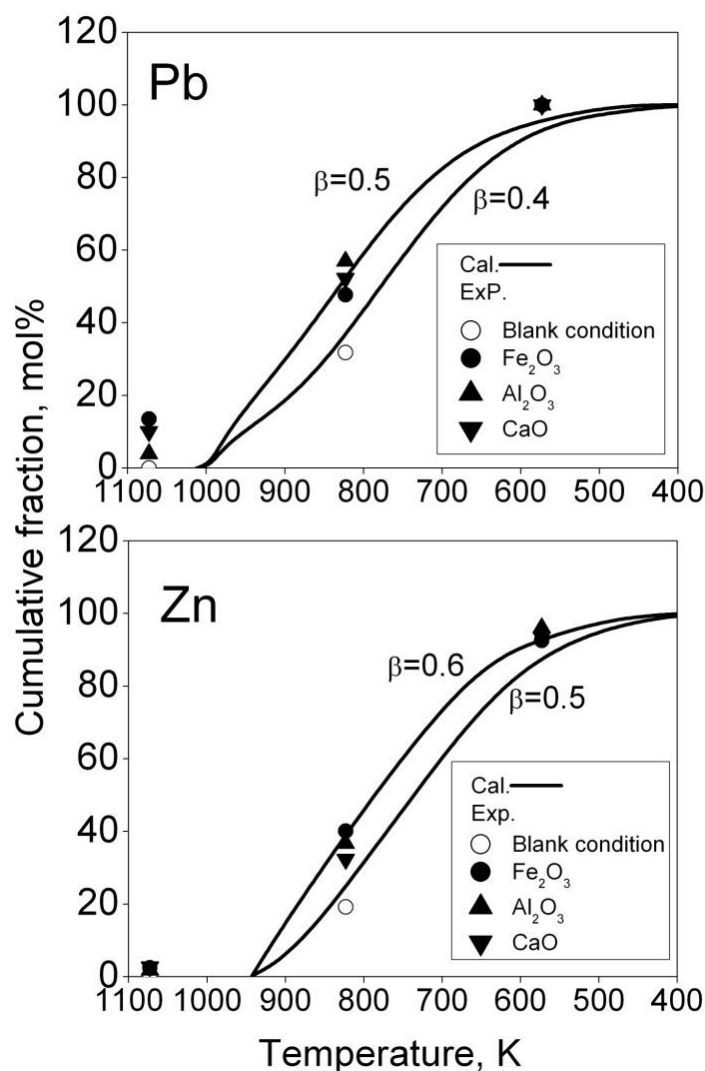


Fig. 2-10. Comparison of model calculation with experimental results in the present of  $\text{SO}_2$  and steam in flue gas.

Following above discussion, the existence of particulates in flue gas has proven influential in the transformation of Pb and Zn species upon flue gas cooling. Two metallic chlorides,  $\text{PbCl}_2$  and  $\text{ZnCl}_2$ , which is notorious for toxicity propensity and corrosion in MSW incineration, can be controlled through adjusting incineration process parameters. As summarized in table 2-3, the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , as well as inorganic particulates in flue gas is favorable to increase the ratio of sulfate/chloride. Therefore, adjusting  $\text{SO}_2$  and  $\text{H}_2\text{O}$  concentration in flue gas and the composition of inorganic particulates via carefully monitoring the feedstock waste materials is a promising method to prevent the formation chlorides.

Table 2-3 Total mole ratio of sulfate/chloride of Pb and Zn in the deposits at 1073 K, 823 K and 573 K.

	Condition	Blank	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO
Pb	0.2% SO <sub>2</sub>	0.3	1.1	1.6	1.3
	0.2%SO <sub>2</sub> Plus 8%H <sub>2</sub> O	0.9	1.8	2.2	1.8
Zn	0.2% SO <sub>2</sub>	0.7	1.6	1.4	1.1
	0.2%SO <sub>2</sub> Plus 8%H <sub>2</sub> O	1.3	2.5	1.7	2.8

## 2.4. Conclusions

The influence of particulates in flue gas on the fate of Pb and Zn vapors and their dependence on the variation of flue gas composition were experimentally investigated in a laboratory-scale rotary kiln reactor coupled with a multi-cooling zone. A thermodynamic pseudo-equilibrium model was employed to explain the condensation mechanism of metallic vapors. The following conclusions are obtained:

- 1) With the absence of inorganic particulates in flue gas, Pb and Zn condensed as PbCl<sub>2</sub> and ZnCl<sub>2</sub> with the absence of SO<sub>2</sub> and steam in flue gas. With the presence of SO<sub>2</sub> in flue gas, Pb and Zn preferentially deposited as sulfates above 823 K due to sulfation reaction, which was further promoted by the addition of steam.
- 2) The presence of Al<sub>2</sub>O<sub>3</sub> particles in flue gas helped the capture of Pb vapor to form Pb-Al-O at the temperature above 823 K through chemical reaction. Zn vapor preferentially retained the particulates of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO as ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO above 823 K, respectively. These reactions preferentially occurred between inorganic particulates and metallic chlorides, which were further promoted by the presence of steam in flue gas.
- 3) The condensation of metallic vapors upon flue gas cooling is influenced by super-cooling, which however can be greatly compensated by the presence of inorganic particulates. The ratio of sulfate/chloride in the deposits is increased in

the presence of particulates in flue gas and thereby the formation of chloride is inhibited.

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## **Chapter 3**

# **Condensation behavior of heavy metal vapors upon flue gas cooling in oxy-fuel versus air combustion**

### **3.1 Introduction**

Trace element emission is one of the major environmental concerns for pulverized and fluidized bed coal fired power stations. In pulverized coal combustion, the trace elements in a fuel usually undergo complicated chemical and physical transformations, and a fraction is eventually emitted to the atmosphere as dust or metallic vapors[1-2]. Due to the adverse health effects of the emitted trace elements[3], it is desirable to understand the emission of trace elements from coal-fired power stations. Lead and zinc during coal combustion vaporization from flame zone, subsequently condensing during flue gas cooling through nucleation. Both experimental observations and thermodynamic equilibrium prediction have confirmed that the chlorine concentration in MSW is one key factor affecting the vaporization of lead and zinc[4-7]. Being one of the leading options for next-generation low-emission clean coal technologies, oxy-fuel combustion has been investigated by numerous studies in the past decades. It has been clarified that oxy-fuel combustion differs from air-firing in heat transfer[8], ignition[9], combustion characteristics[10], char combustion characteristics and pollutant formation[11-12].

Crosiet et al. [13] found that trace elements measured in the flue gas stream upstream of a fabric filter were almost exactly the same whether coal was fired in air-firing or oxy-fuel mode. However, Suriyawong et al.[14] have point out that ash particles in the ultrafine and submicron size regimes are enriched in toxic heavy metals, and efficient removal of these particles from combustion exhaust flow is extremely important in  $O_2/CO_2$  and  $O_2/N_2$  environments. Sheng et al.[15] studied a Chinese lignite and found that the mass fraction of very fine particles smaller than  $\sim 0.1\mu m$  formed in  $O_2/CO_2$  combustion was higher while that of the particles between 0.1 and  $0.5\mu m$  was lower than those formed in  $O_2/N_2$  combustion at a same oxygen concentration. No apparent shift of the submicron mode center was observed when the gas environment is changed. The study of Li et al.[16] in a 25 kW down-fired pulverized furnace suggested that the  $PM_{10}$  and  $PM_1$  amounts were larger under oxy-fuel mode than in the air-firing condition for a Chinese lignite. However, a generalized conclusion regarding the PM emission upon coal combustion from air to oxy-firing has not yet been achieved.

Extensive research on the toxic elements transformation behaviors in pulverized coal combustion system reported that the behaviors of toxic elements are determined by the coal composition, combustion atmosphere, physic-chemical characteristic and combustion technology [17-20] In most cases, the presence of gaseous chlorine may shift the distribution of trace elements such as Pb and Cd towards more volatile chlorides, thus promoting the vaporization.[18,19] After being vaporized from the fuel, the trace elements may undergo reactions both with the ash particles and the gaseous species in the flue gas.[20] Apart from gas components, the ultrafine particulates containing the refractory elements are also supposedly dominant in flue gas. Their existence has the potential to alter the condensation propensity of Pb and Zn compound vapors through complex chemical reactions and/or heterogeneous nucleation. Zinc retained in waste combustion bottom ash and fly ash has been found to partially combine with Si and Al.

The effect of gas properties and temperature gradient in the cooling section of the

boiler is crucial in determining the formation of  $PM_{10}$  for metal condensation.  $PM_{10}$  refers to the ultrafine particulates smaller than  $1 \mu m$  in aerodynamic diameter. Varghese and Gangamma[21] reported the modeling results of aerosol formation and growth in a laminar flow aerosol generator. Lewis number ( $Le$ ), the ratio of thermal diffusivity to mass diffusivity, was reported to be one of the principal parameters to predict the effect of cooling rate and transport properties of a vapor-carrier gas system on homogeneous particle formation on a rapid cooling of the vapor-carrier gas mixture. The high  $Le$  system ( $Le = 10$ ) results in the formation of nearly monodispersed aerosols and the low  $Le$  system with  $Le$  equal to around 1 results in highly polydispersed aerosols. In light of this, it is apparent that the heat and mass transfer properties of a vapor-carrier gas system is influential on the deposition of metallic vapors to wall and the final ash particle size distribution.

To understand the  $PM_{10}$  formation based on vaporization-condensation mechanism in air-firing and oxy-fuel combustion, It is essential to investigate the differences of condensation behavior of metallic vapors and the influence of flue gas cooling rate, flue gas composition, co-existence of multi-elements and the reaction between trace elements and fly ash particulates in air and oxy-fuel conditions,. The typical  $Le$  of an exhaust gas for air combustion approximates 1 at 800 K. On the other hand,  $Le$  of flue gas for oxy-fuel combustion is around 0.83 due to the higher thermal capacity of  $CO_2$  than  $N_2$ , and the lower mass diffusivity of  $O_2$  in  $CO_2$  than in  $N_2$ . As a result, condensation of the vapor in oxy-fuel condition has the potential to result in higher polydispersed fine particles after the growth.[21] To prove such a hypothesis, the experiments have been carried on a unique horizontal reactor that has been employed by our previous work[22-26]. Cheng confirmed that the pre-existing  $PbSO_4$  particles were found to pose noticeable influence on the condensation distribution of other metal vapors via heterogeneous condensation and the conventional thermodynamics equilibrium software cannot appropriately predict the experimental results very well[22-23]; Jiao developed a thermodynamic pseudo-equilibrium model to predict trace elements condensation behaviors[24-25]; Song compared the characteristics of

condensation particles size, shape and average diameter between air and oxy-fuel conditions.[26] As the continuation of our previous works, this paper aims to clarify the influence of flue gas and fly ash compositions on the condensation behavior of Pb and Zn vapors under air-firing and oxy-fuel conditions, so as to reveal any probable influence of Lewis number on fine/ultra-fine particulate formation. To the best knowledge of the authors, the quantitative evaluation of flue gas cooling on the condensation of metallic vapors has not yet been touched in the research field on coal oxy-fuel combustion.

## **3.2 Experimental**

### **3.2.1 Experimental setup and conditions**

The experimental apparatus and analyzed method are the same as in our previous papers[23-25]. The apparatus made from quartz glass and has two parts, a vaporization section with a constant temperature at 1223K and a cooling section from 1223 K to 400 K. The vaporization section consists of double tube. A gas with known concentration of HCl, O<sub>2</sub> and N<sub>2</sub> is fed to the inner tube, which is chloride volatility process of Pb and/or Zn materials. The rotation of the inner tube causes the chloride vapor to come in contact with the gas in order to achieve a constant rate of vaporization. The flue gas from the inner tube mixed with the gas in the outer tube with N<sub>2</sub> and CO<sub>2</sub> and/or SO<sub>2</sub>, H<sub>2</sub>O flows into the cooling section. The average concentration of each metal in flue gas was 100 ppm Pb and 43 ppm Zn. Table 3-1 shows the gas composition of these experiments. As the table shows, the balance gas (N<sub>2</sub> and CO<sub>2</sub>) mixed with oxygen was used to simulate the varying air-firing and oxy-fuel conditions. Two series of experiments have been conducted in this paper; single mode for the introduction of a single metal into the reactor, and mixture mode for the co-feeding of both two metals into the system. Three quartz filters were set at different temperatures to capture condensed substance of the inorganic vapors in the

cooling section.

**Table 3-1** Gas composition of the feeding

Gas species	Air-firing condition [vol.%]	Oxy-fuel condition [vol.%]
HCl	0.2	0.2
O <sub>2</sub>	5	5
SO <sub>2</sub>	0, 0.1	0, 0.1
H <sub>2</sub> O	0, 5, 10	0, 5, 10
CO <sub>2</sub>	12	Balance
N <sub>2</sub>	Balance	0

The experiments were conducted under both air-firing and oxy-fuel conditions. Figure 3-1 shows the temperature profile of the cooling section for both two series of experimental conditions. The temperature profile of oxy-fuel condition was observed to be slightly higher than that of air-firing condition, due to the higher thermal heat capacity of CO<sub>2</sub> than N<sub>2</sub>. The average cooling rate and residence time of the gas with metallic vapors during the cooling section is about 125 K/s and about 1.5 s, respectively.

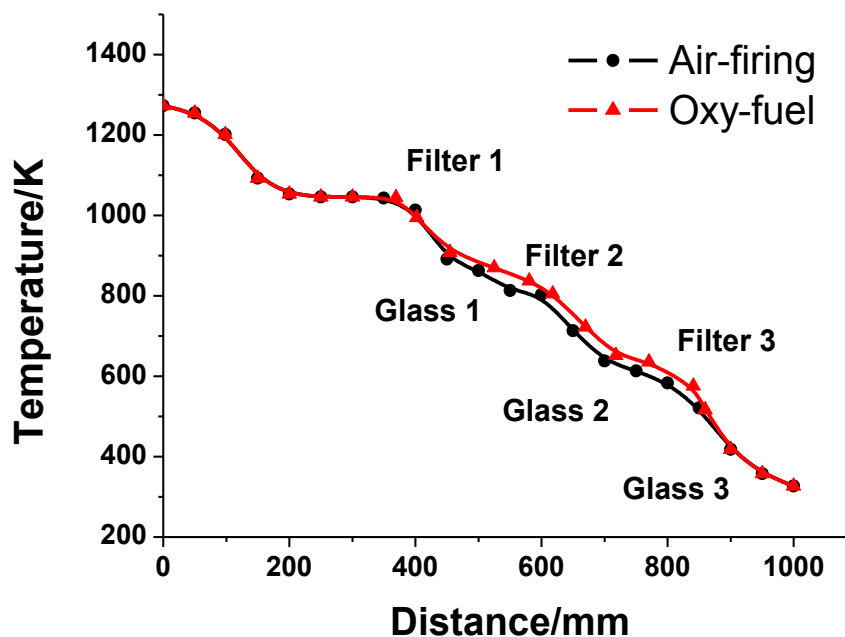


Figure 3-1 Temperature profile of cooling zone in a reactor

The active  $\text{Al}_2\text{O}_3$  with diameter of 1-2 *mm* and  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  with diameter of 10-150  $\mu\text{m}$  were tested in the cooling section. For each run, 0.5 g inorganic particulates were put on each cooling stage where a silica thimble filters was located for flue gas to pass through. The quartz wool was used to disperse the particulates as uniformly as possible. Two impingers containing 1M  $\text{HNO}_3$  were installed downstream the cooling section to capture the non-condensable Pb and Zn vapors.

X-ray diffraction (XRD, Rigaku RINT) was employed for determining the crystalline species in deposits. The concentrations of metals and anions of the deposit were quantified using atomic absorption spectrophotometer (AAS, Shimadzu AA-6200) and ion chromatography (IC, Shimadzu) with a CDD-6A conductivity detector, respectively. The results from replication experiment indicated a minor error less than 5% in this experiment. Metallic species retained in inorganic particulates were subjected to X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-3300) characterization using Mg  $K\alpha$  (1253.6 *eV*) as the excitation source. *C1s* energy of carbon atom (284.6 *eV*) was used to calibrate the binding energy of other atoms. The Pb and Zn-bearing species retained in particulates were determined and quantified through the comparison of the binding energy of of Pb ( $4f_{7/2}$ ) and Zn ( $2p_{3/2}$ ) with that of a series of standard samples. The reproducibility error of the experiments was less than 5%.

### 3.2.2 Thermodynamic pseudo-equilibrium model

The thermodynamic pseudo-equilibrium model and calculating method have been described in our previous work[25]. The variable of  $\alpha$  in the model is the ratio of bypass stream to the metal vapor flow. This value gives the explanation of the deviation from the equilibrium of the condensation of metal vapor species in a certain cooling stage. The variable of  $\beta$  in this model is employed to evaluate the rate of overall sulfation reaction in the process of flue gas cooling in the presence of  $\text{SO}_2$  with/without  $\text{H}_2\text{O}$ .

The schematic of the model with two reactors including chlorination reactor and sulfation reactor is demonstrated in Figure 3-2. The flue gas quenching rate is influential in terms of the deposition of a metal vapor species at a given temperature. A rapid cooling of flue gas, namely super-cooling, has the potential to cause supersaturation of a vapor with little being deposited. Therefore, a variable,  $\alpha$ , was introduced in the model to describe the proportion of a metal vapor which does not condense on a certain cooling stage and thus reflect the effect of supercooling on the condensation of metal vapor species. The value of  $\alpha$  was optimized by curve-fitting the experimental results for the condition of HCl/O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub>, which was further applied to the other conditions with SO<sub>2</sub> and/or steam entering the outer tube.

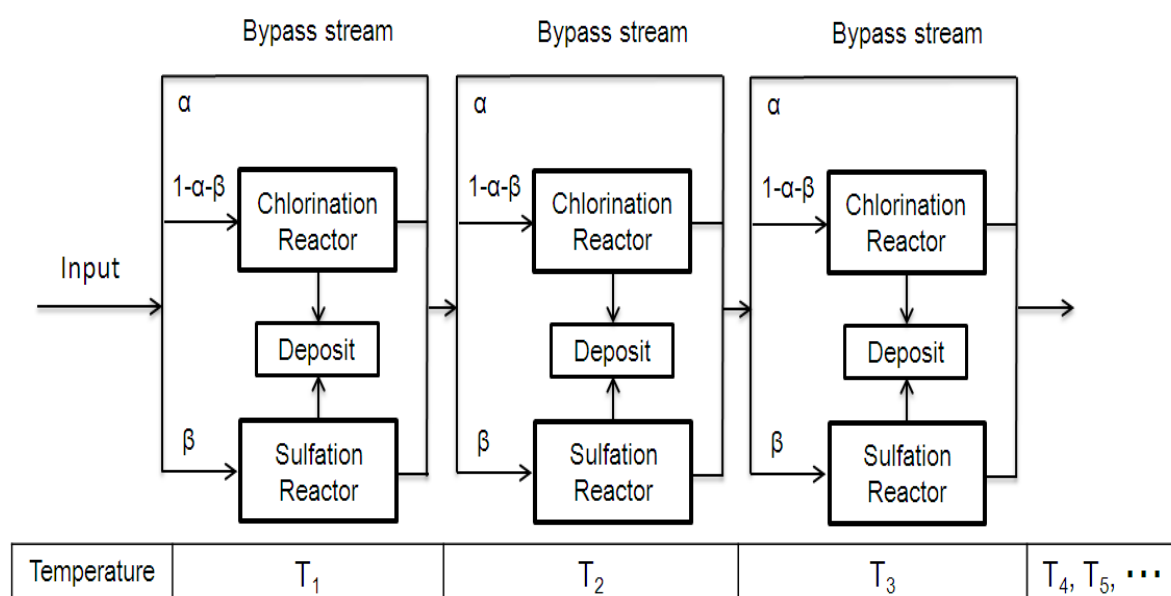


Figure 3- 3 Schematic of a thermodynamic pseudo-equilibrium model on the condensation of metallic compound vapors during flue gas cooling.

The chemical reaction rate also plays role on the distribution of metal species with the present of SO<sub>2</sub> in flue gas. A very short residence time in the cooling section is expected to limit the chemical reaction extent. Therefore, another variable,  $\beta$ , was employed to evaluate the extent of overall sulfation reaction in the process of flue gas cooling when SO<sub>2</sub> and/or H<sub>2</sub>O were introduced into flue gas. It denotes the proportion of a heavy metal vapors sulfated in the present of SO<sub>2</sub> at the sulfation reactor.



Accordingly, the remaining metal vapor species,  $1-\alpha-\beta$ , refers to those condensed without sulfates flowed into chlorination reactor. Clearly, as  $\beta$  is close to  $1-\alpha$ , the sulfation of metal vapors approach equilibrium. The value of  $\beta$  was obtained by curve-fitting the experimental results. The shift of  $\beta$  and  $1-\alpha-\beta$  under different conditions indicates a competition reaction of metal vapor species between sulfation and chlorination.

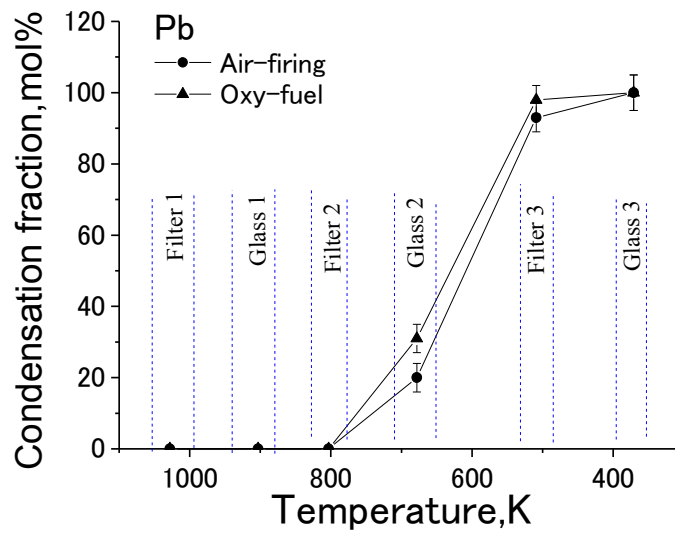
The flue gas compositions and the amount of inorganic vapors determined under an experiment were used as input for the modeling. The output includes the metal species in both gas and solid phases. A wide temperature span from 1273 to 373 K with an interval of 50 K at atmospheric pressure was simulated.

### **3.3 Results and Discussion**

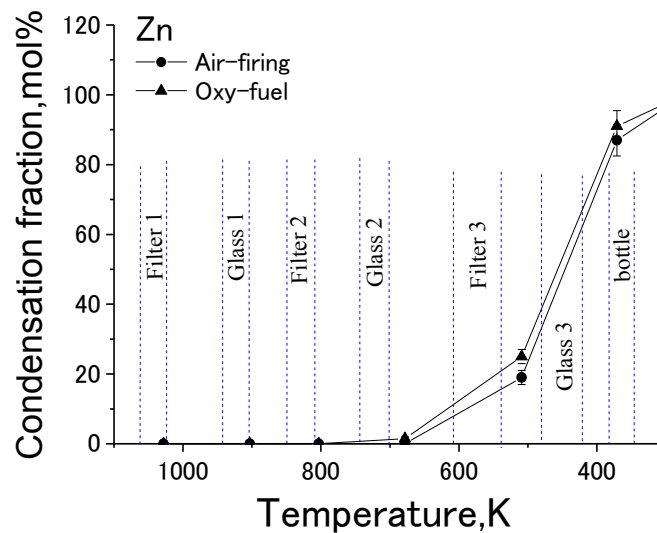
#### **3.3.1 Condensation behavior of Pb and Zn vapors in single mode without particulates**

##### **3.3.1.1 Influence of HCl**

Figure 3-3 shows deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl under the single mode. For each metal, its vapor was condensed entirely in the cooling section. However, the initial condensation temperatures for the two metals are different. The condensation temperature of  $\text{PbCl}_2$  is about 800 K and that of  $\text{ZnCl}_2$  is about 670K. Moreover, it is found that there is a little difference of the deposition behaviors between air-firing and oxy-fuel conditions. The condensation fraction of either Pb or Zn at the temperature range from 700 to 400K is slightly higher in oxy-fuel condition than in air-firing condition.



(a) Pb



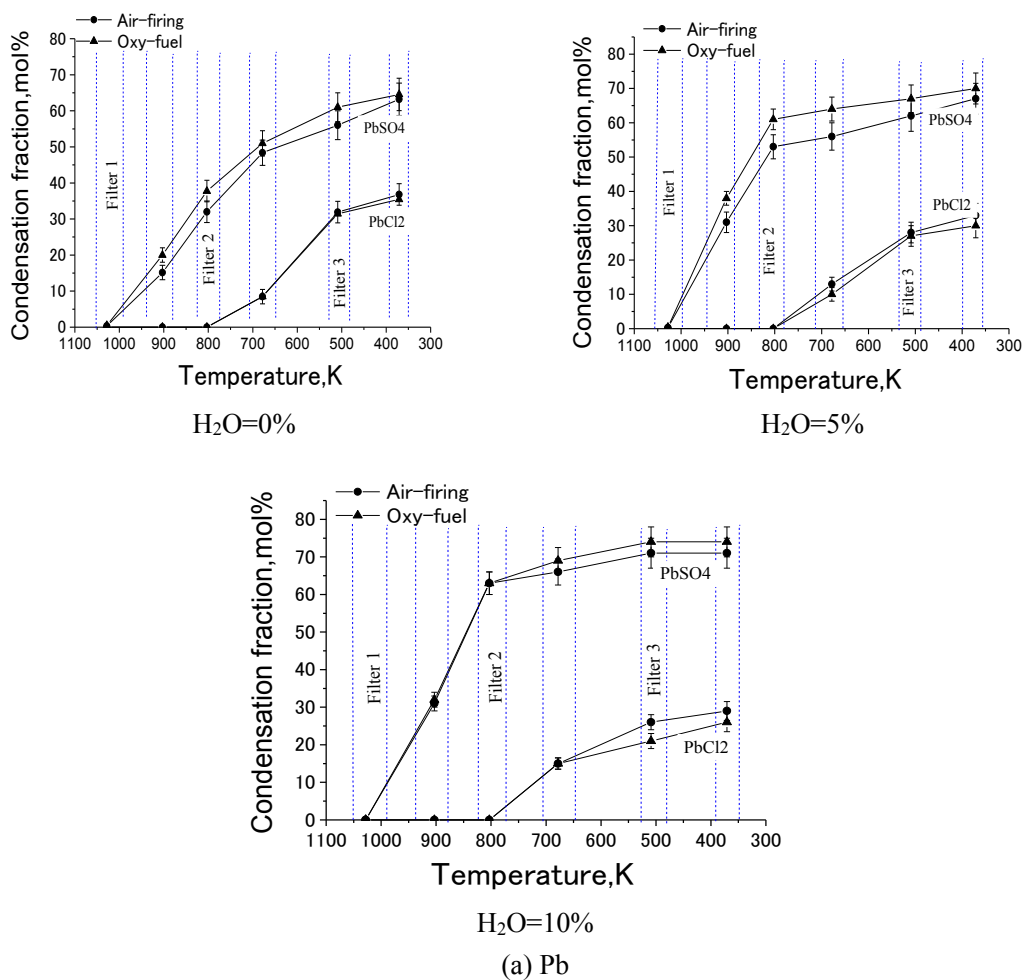
(b) Zn

Figure 3-3 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl under single mode

### 3.3.1.2 Influence of HCl/SO<sub>2</sub>/H<sub>2</sub>O

Due to increase in the amount of metal sulfates at high temperature zone and reduction in chloride in the low temperature zone in cooling section, introducing SO<sub>2</sub> into flue gas is supposed to promote the amount of condensation Pb at the temperature

above 900 K while Zn condensed at the temperature above 800 K. simultaneously, increasing steam can also cause a noticeable shift of the deposition of these metals. These hypothesis were confirmed in Figure 3-4. The condensation fraction of Pb and Zn have been increased to 20% and 6% at 1023–673 K, respectively, indicating the synergic influence of H<sub>2</sub>O and SO<sub>2</sub> on the formation of sulfate with high dew point, which reflect the promoting effect of steam on the sulfation according to reaction (2), where M refers to the metals.



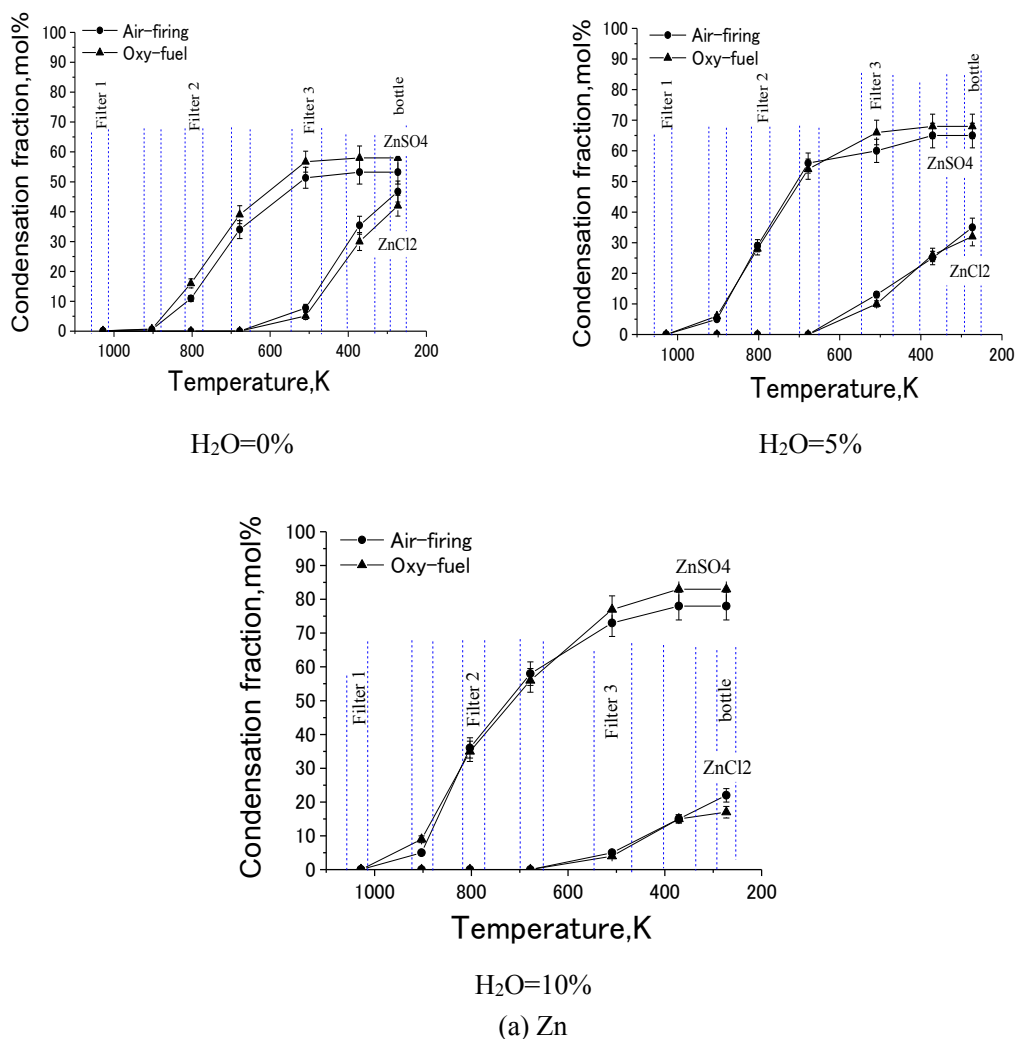
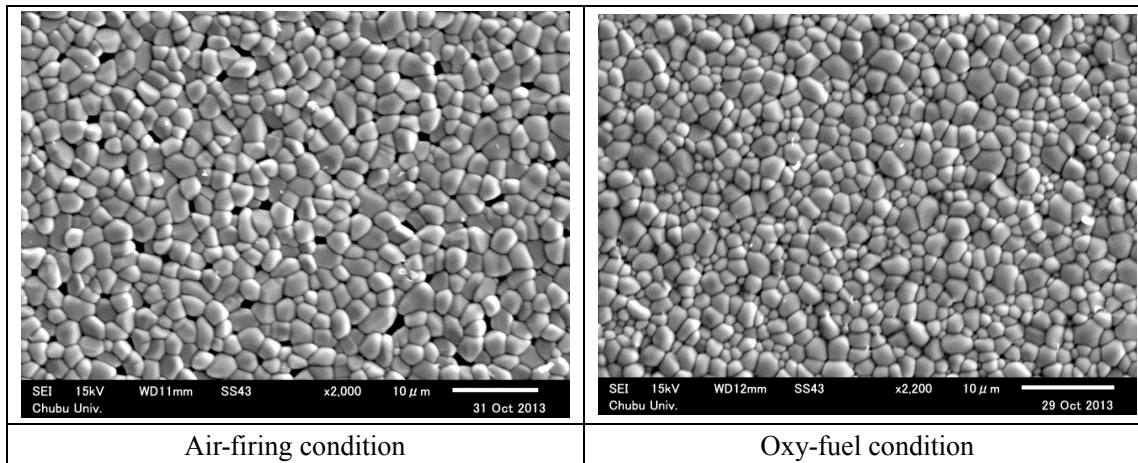


Figure 3-4 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single mode

In these reactions, the partial pressure of CO<sub>2</sub> exerts no impact on the formation of SO<sub>3</sub> except the potential effect of being the third body as a collision molecule. However, for each flue gas condition, the condensation fractions of Pb and Zn are slightly higher in oxy-fuel condition than the respective results in air-firing condition. The typical Le of an exhaust gas for air-firing condition is higher than that for oxy-fuel condition. Therefore, for the same oxygen concentration in the furnace, oxy-firing is supposed to generate a gradual temperature gradient on the cross-section of the tubular reactor, since less heat is transferred from center of reactor tube back to wall. In contrast, the same volume flow rate between N<sub>2</sub> and CO<sub>2</sub> but a larger molecular weight of CO<sub>2</sub> than N<sub>2</sub> means the mass flux of CO<sub>2</sub> is larger than N<sub>2</sub> in the

reactor, which in turn incurs a higher convective heat transfer from gas to particles and enhance its primary nucleation. Consequently, the primarily nucleated particles will act as seed to escalate the nucleation rate, which in turn quickly deplete the metallic vapor and suppress the new particle formation. [21] In the end, the particle temperature and that of flue gas will reach close to each other in the steady state. The nucleation rate of particles will correspondingly slow down and even cease. Such a non-uniform nucleation is believed to be the principal cause for the high polydispersed aerosols after the growth and the enhanced sulfation reactions of Pb and Zn at higher temperature zone.

Figure 3-5 shows SEM picture of deposit at 803 K with 1000 ppm SO<sub>2</sub> for Pb under both air-firing and oxy-fuel conditions. Although the shape of deposit particles is almost similar, there is more small size of particles formed under oxy-fuel condition. The peak size of Pb deposit is 1.8 μm for oxy-fuel and 4.5 μm for air-firing condition. In addition, the higher polydispersed fine particles were found for condensation of the vapor in oxy-fuel condition.



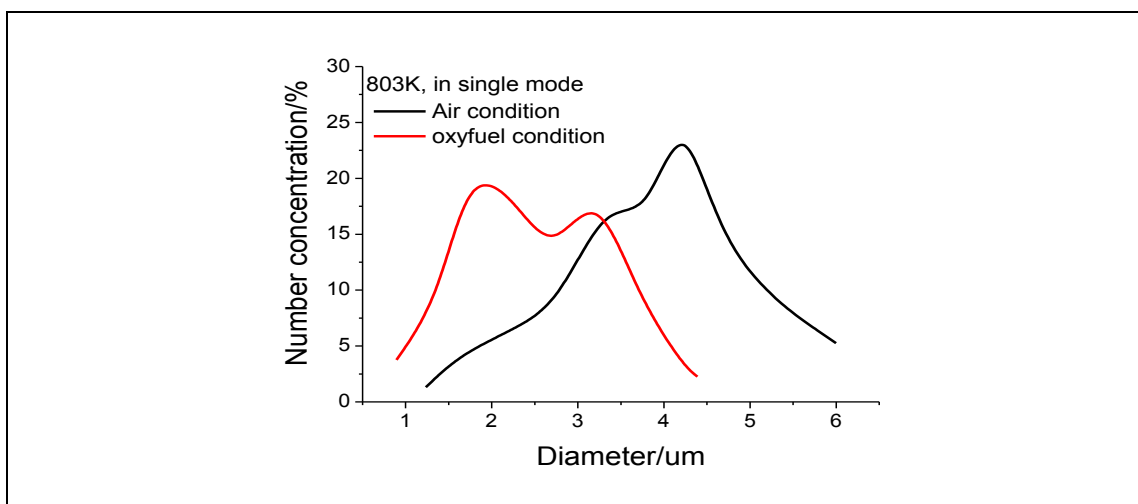


Figure 3-5 SEM picture of deposit and particle size distribution at 803K in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub> under single mode

### 3.3.2 Condensation behavior of Pb and Zn vapors in mixture mode

#### 3.3.2.1 Influence of HCl

Figure 3-6 shows deposition distribution of metallic vapors in air-firing and oxy-fuel conditions with HCl under mixture mode. In a mixture mode of Pb and Zn fed together in the reactor tube, there are insignificant differences of the deposition fraction of each metal between air-firing and oxy-fuel conditions. However, the condensation fraction of either Pb or Zn in the mixture mode (Fig. 3-6) is higher than the respective result in the single mode (Fig. 3-4) at the temperature range from 700 to 400K. The fine particles generated by homogeneous nucleation and subsequent non-uniform nucleation in cooling zone may alter the Knudsen number, diffusivity and collision probability of metallic vapor in a carrier gas[27].

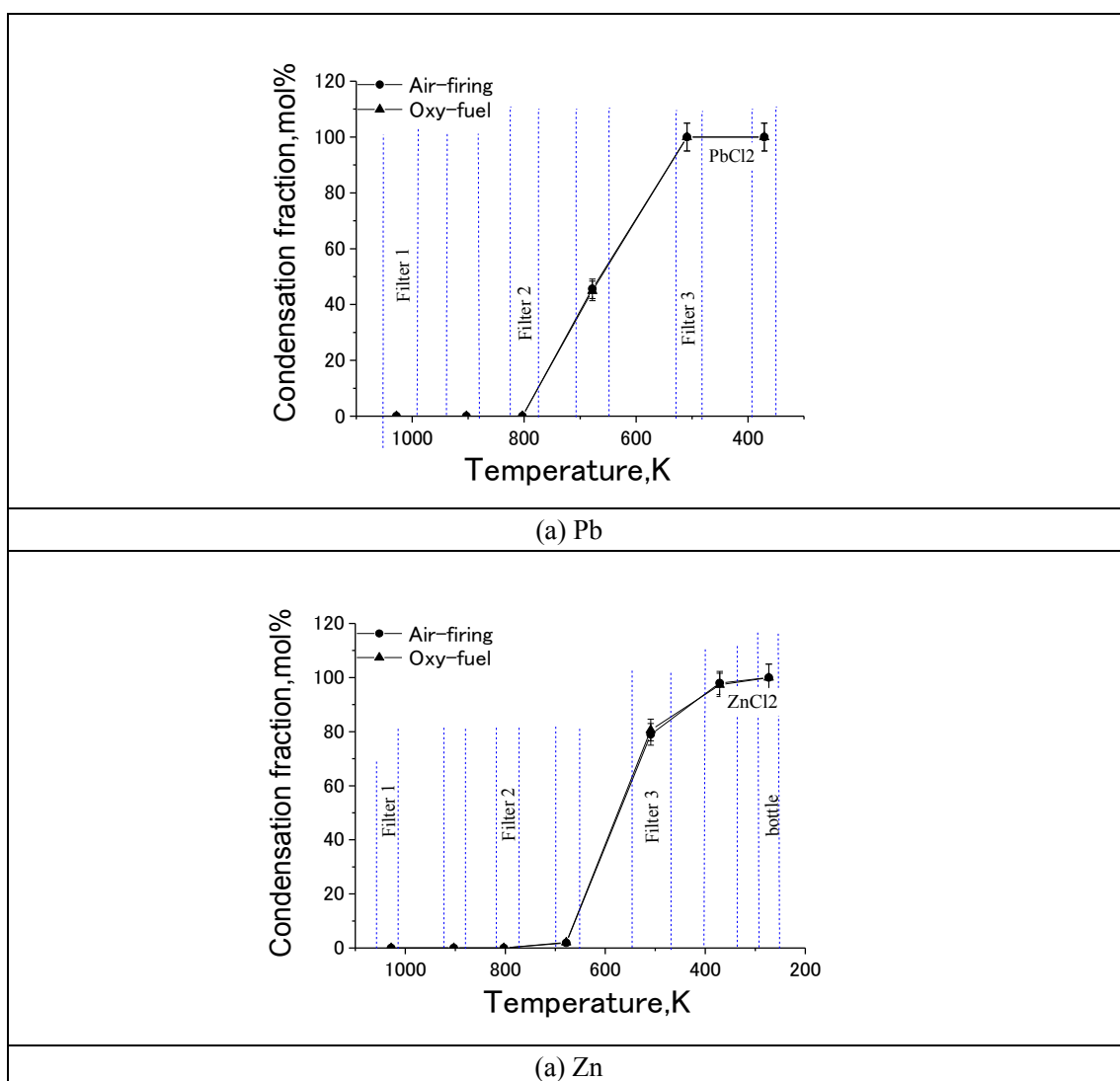
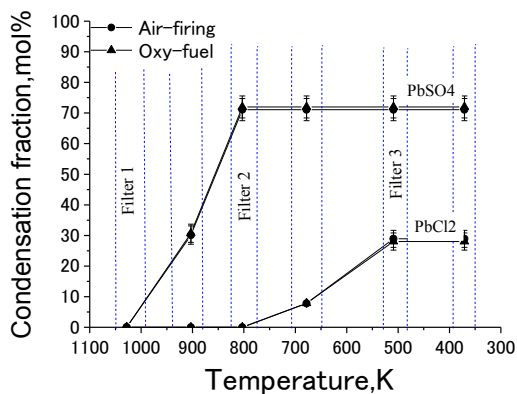
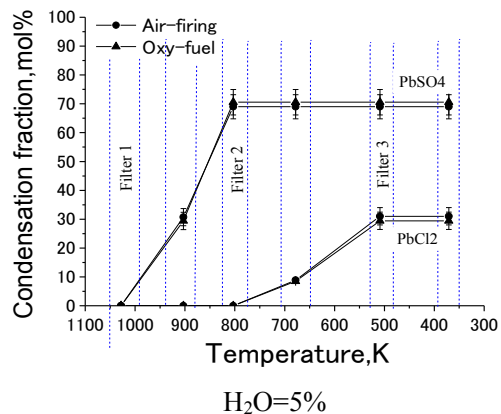
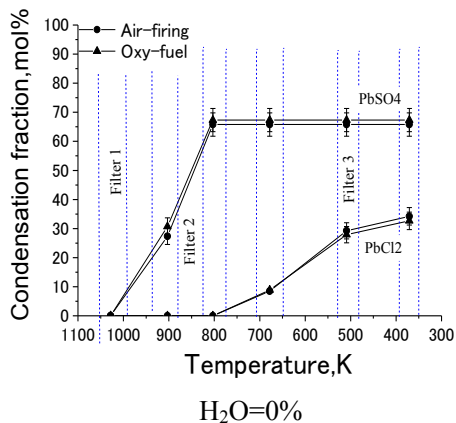


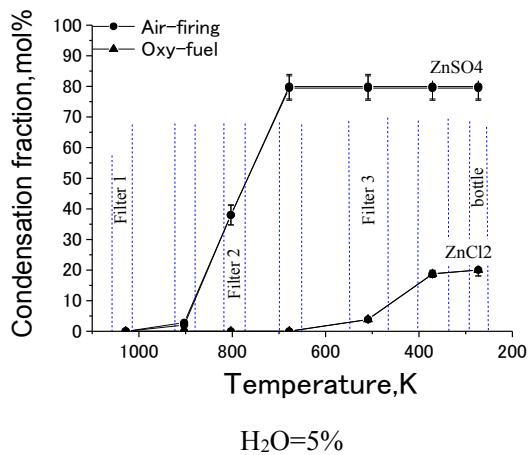
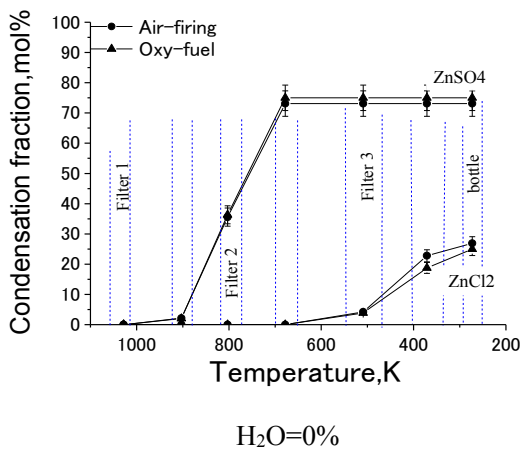
Figure 3-6 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl under mixture mode

### 3.3.2.2 Influence of HCl/SO<sub>2</sub>/H<sub>2</sub>O

Figure 3-7 shows the deposition distribution of metallic vapors in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under mixture mode. In mixture modes with HCl/SO<sub>2</sub>/H<sub>2</sub>O together in flue gas, there is insignificant discrepancy between two combustion modes in terms of the deposition fraction of either Pb or Zn. However, the condensation fraction of either PbSO<sub>4</sub> or ZnSO<sub>4</sub> is higher in the mixture modes (Figure 3-7) than that in the single mode (Figure 3-4) at the temperature range from 700 to 400 K, having the same tendency as section 3.3.1.2.



H<sub>2</sub>O=10%  
(a) Pb





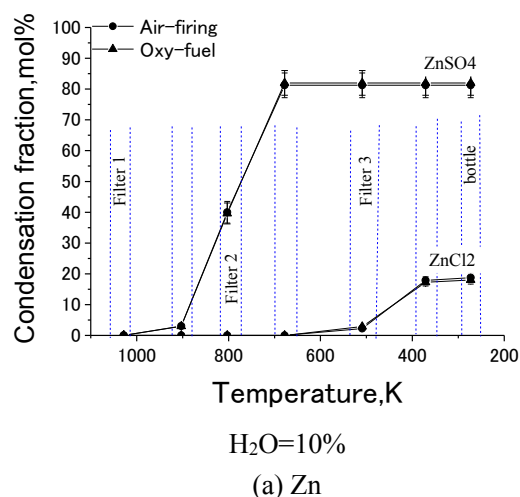


Figure 3-7 Deposition distribution of metal vapors in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under mixture mode

### 3.3.3 Condensation mechanism of metal vapor species

In a real combustion process in the boiler, the mechanisms of particles formation via gas-to-solid are complicated. When metal vapor species reach a supersaturating state, the condensation would occur to promote the formation of ultrafine particulates and further grow up by Brownian motion, which is governed by the mechanisms of either homogeneous condensation to form new particles, or heterogeneous condensation. [27-29]

Figures 3-8 (a) and (b) show the typical results of the comparison of model calculation with experimental results in oxy-fuel condition with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single mode. The resulting saturated metal vapors diffused downwards through the high-temperature cooling zone at their original gaseous state, and preferential deposited at low temperatures. Figure 3-8 (a) shows  $\alpha$  values of 0.25 for Pb and 0.3 for Zn in oxy-fuel condition with HCl were found to fit the experimental results. On the other hand, Figure 3-8 (b) shows  $\beta$  values in oxy-fuel condition with HCl/SO<sub>2</sub>/H<sub>2</sub>O. Assuming the super-saturation fraction,  $\alpha$ , is constant regardless of the introduction of SO<sub>2</sub> with/without H<sub>2</sub>O into the outer tube, the model results in Fig. 3-8 (b) show that the  $\beta$  value was improved with the addition of SO<sub>2</sub> and H<sub>2</sub>O. The

modeling results for Pb case indicate  $\beta$  value of 0.4 for introducing 1000 ppm SO<sub>2</sub>, 0.5 for 1000 ppm SO<sub>2</sub> plus 5% H<sub>2</sub>O and 0.55 for 1000 ppm SO<sub>2</sub> plus 10% H<sub>2</sub>O into flue gas, respectively.

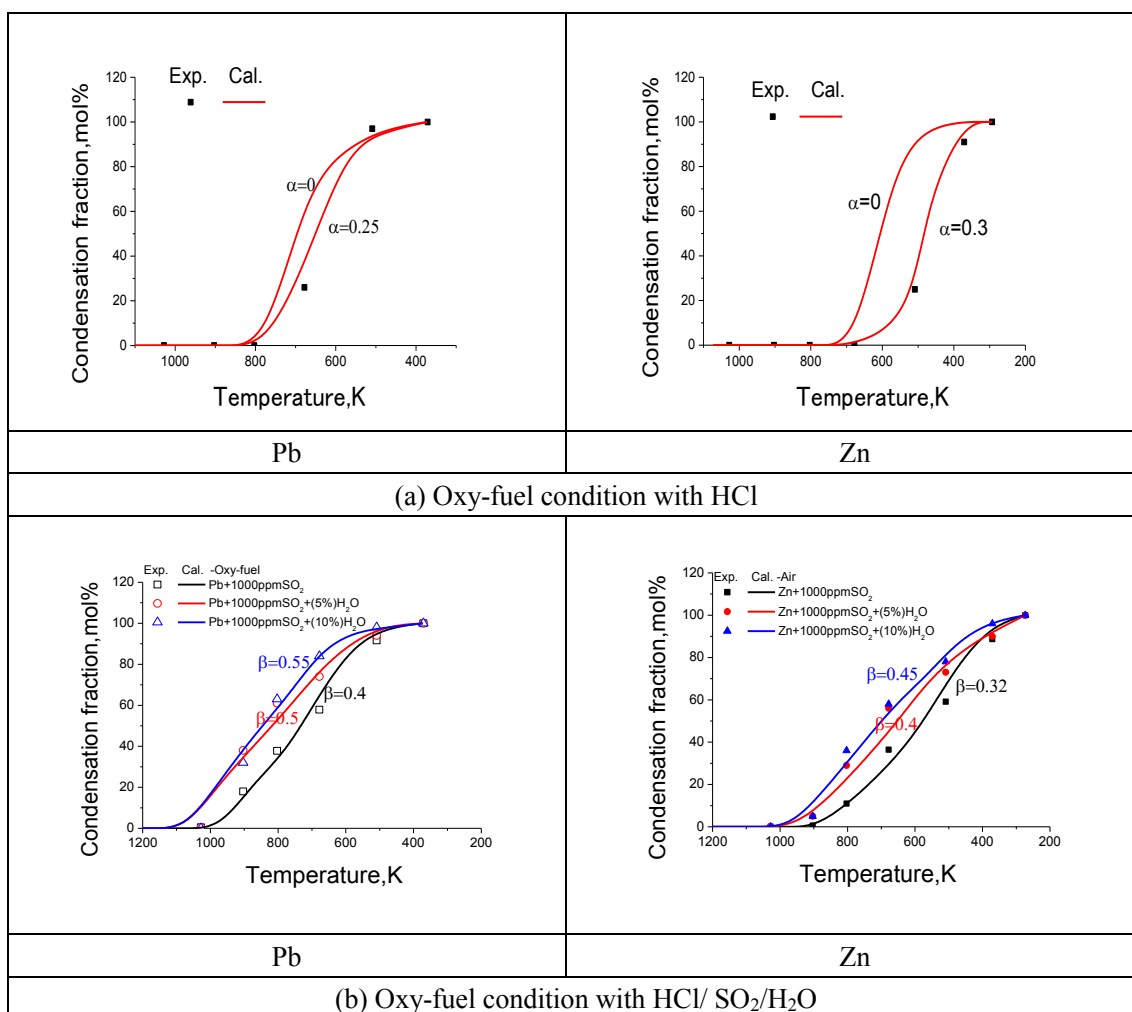


Figure 3-8 Comparison of model calculation with experimental results under single mode.

This is clear that the overall sulfation rate for Pb upon the addition of SO<sub>2</sub> and H<sub>2</sub>O to flue gas was improved. Figure 3-9 shows the comparison of  $\alpha$  value in air-firing and oxy-fuel conditions with HCl under single and mixture modes. It is observed that  $\alpha$  value becomes lower in oxy-fuel condition than in air-firing condition under single mode, which suggests that the particle conversion of gas-to-solid in flue gas cooling section is promoted by the slow heat transfer for oxy-fuel condition. In addition,  $\alpha$  value under mixture mode of Pb and Zn vapors are much smaller than those under single mode. This result indicated that it is much faster to reach an equilibrium state for the species under the mixture mode. Figure 3-10 shows the

comparison of  $\alpha$  and  $\beta$  values in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single and mixture modes. On the assumption that the super-saturation fraction,  $\alpha$ , is not to change in the regardless of the introduction of H<sub>2</sub>O into the outer tube, the  $\beta$  values of mixture mode are higher than those of single mode. Especially, the  $\beta$  values of Zn in air-firing and oxy-fuel conditions are varied from 0.32 to 0.45 with H<sub>2</sub>O under single mode, while those of Pb in air-firing and oxy-fuel conditions are varied from 0.45 to 0.55 with H<sub>2</sub>O under mixture mode. So the compounds of Pb condensate first and then the compounds of Zn will condensate with Pb in heterogeneous crystallization, which caused the  $\beta$  values of Zn to change significantly with increasing H<sub>2</sub>O concentration in flue gas. The heterogeneous crystallization is interaction, it also can promote the condensation of Pb.

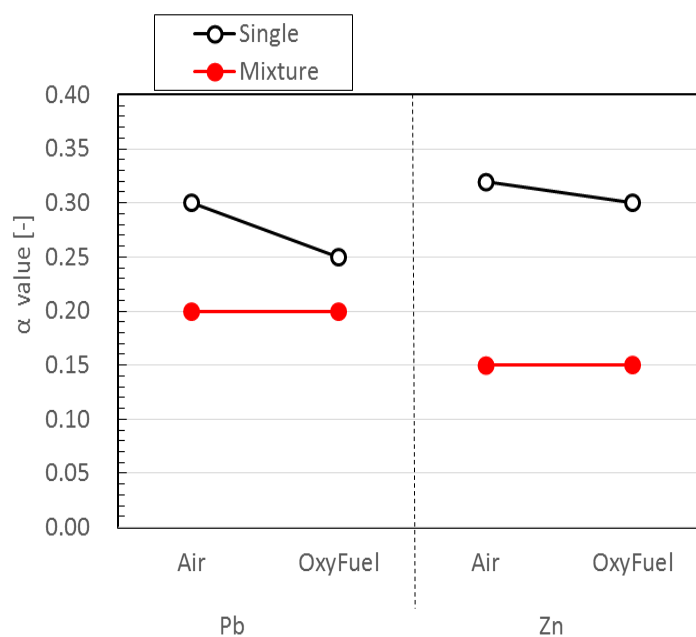
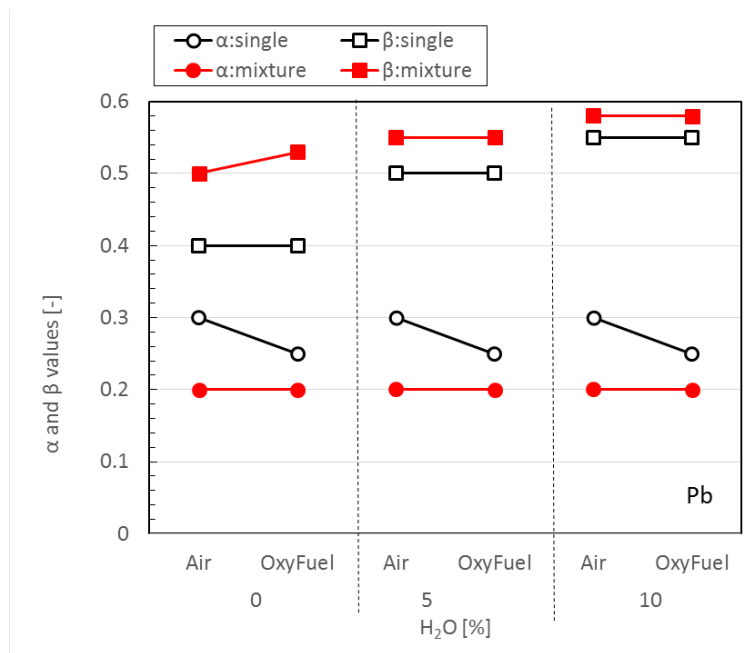
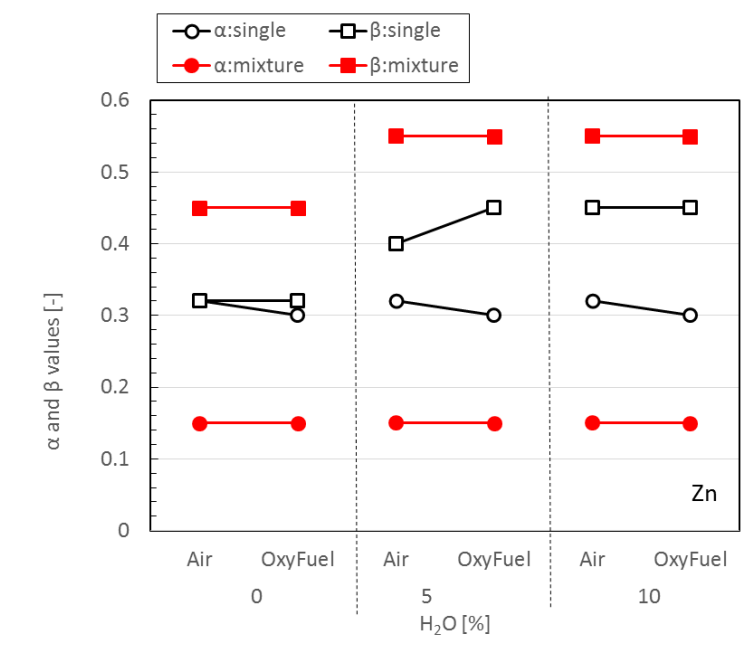


Figure 3-9 Comparison of  $\alpha$  values in air-firing and oxy-fuel conditions with HCl under single and mixture modes



(a) Pb



(b) Zn

Figure 3-10 Comparison of  $\alpha$  and  $\beta$  values in air-firing and oxy-fuel conditions with HCl/SO<sub>2</sub>/H<sub>2</sub>O under single and mixture modes

### 3.3.4 Condensation of Pb and Zn vapors with particulates in air and oxy-fuel conditions

In order to investigate the influence of fly ash on heavy metal condensation in air

and oxyfuel combustion, three compounds of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  were employed and placed individually in flue gas cooling section to simulate inorganic particulates. Figure 3-11 shows the condensation of Pb and Zn with particulates in air and oxy-fuel condition. As mentioned as chapter 2, the species of condensation is not changed. The presence of  $\text{Al}_2\text{O}_3$  particles in flue gas helped the capture of Pb vapor to form Pb-Al-O at the temperature above 823 K through chemical reaction. Zn vapor preferentially retained the particulates of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  as  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnO}$  above 823 K, respectively. Injected the three compounds in the reactor tube, there are insignificant differences of the deposition fraction of each metal between air-firing and oxy-fuel conditions. However, after injecting  $\text{CaO}$ , the condensation fraction of Zn in air condition is higher than in oxy-fuel condition.

As mentioned, in single modes with  $\text{HCl}/\text{SO}_2/\text{H}_2\text{O}$  together in flue gas, there is insignificant discrepancy between two combustion modes in terms of the deposition fraction of either Pb or Zn with three compounds. In the actual flue gas, there are many heavy metals simultaneous presence, while the results indicated that Pb just can react to  $\text{Al}_2\text{O}_3$ , for simulate the actual condition, the mixture mode experiment just was carried out with  $\text{Al}_2\text{O}_3$  in air and oxyfuel condition. Figure 3-12 shows the results of Condensation of Pb and Zn vapors with particulates in flue gas of 0.2% $\text{HCl}$ , 0.1% $\text{SO}_2$ , 5% $\text{O}_2$ , 10% $\text{H}_2\text{O}$  under mixture mode. It indicated that the differences of the deposition fraction of each metal between air-firing and oxy-fuel conditions are insignificant differences. Comparing with single mode, the condensation fraction of Pb-Al-O and  $\text{ZnAl}_2\text{O}_4$  is a little lower, which may be caused by the competition of Pb and Zn reaction to  $\text{Al}_2\text{O}_3$  and heterogeneous which promote the formation of solid  $\text{PbSO}_4$  and  $\text{ZnSO}_4$  and then the solid covered the surface of  $\text{Al}_2\text{O}_3$  to prevent the reaction of  $\text{PbCl}_2$  and  $\text{ZnCl}_2$  with  $\text{Al}_2\text{O}_3$ .

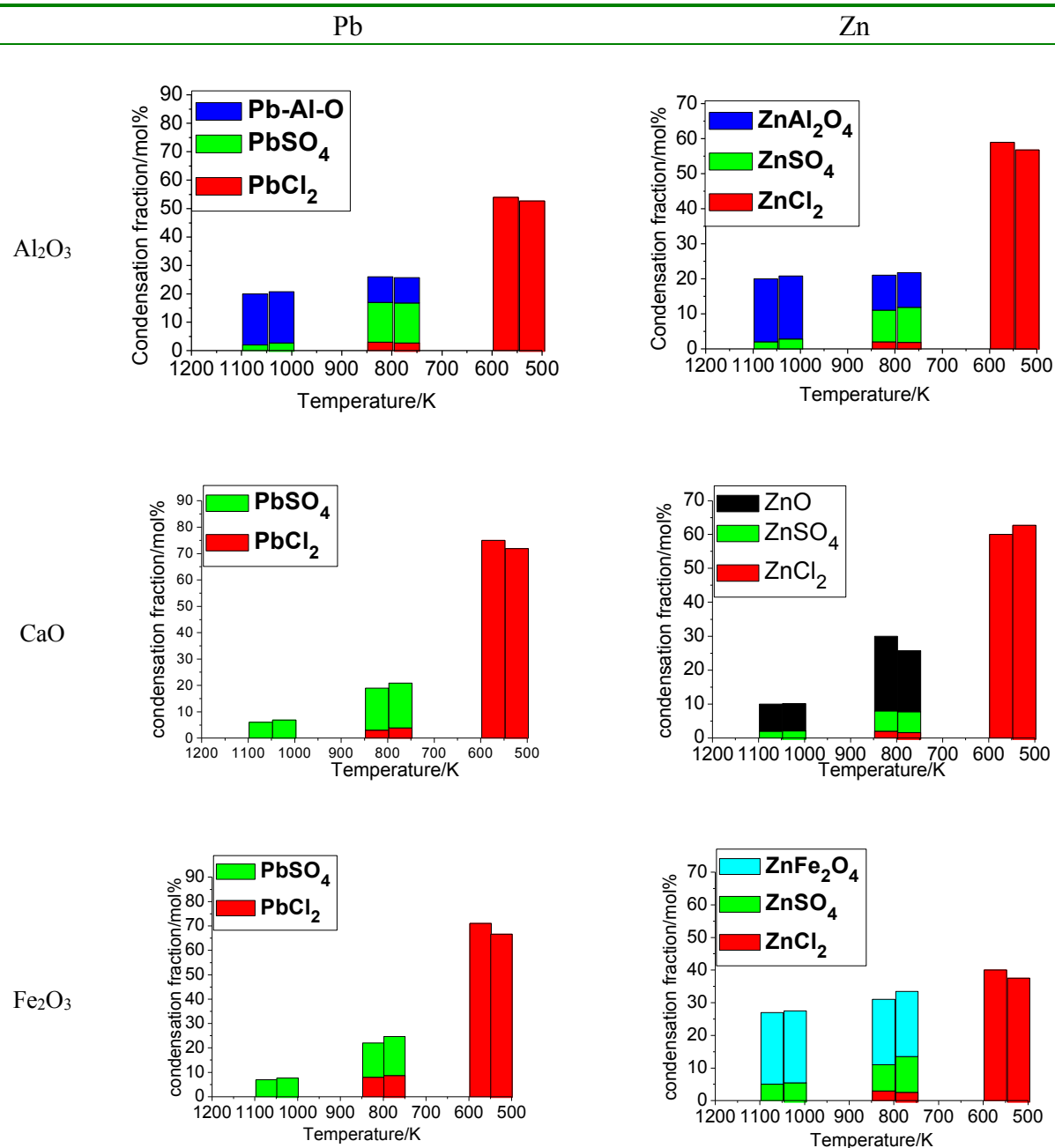


Figure 3-11 Condensation of Pb and Zn vapors with particulates in flue gas under 0.2%HCl, 0.1%SO<sub>2</sub>, 5%O<sub>2</sub>, 10%H<sub>2</sub>O under single mode. In each picture, the left columns represents air condition, the right column represents oxy-fuel condition.

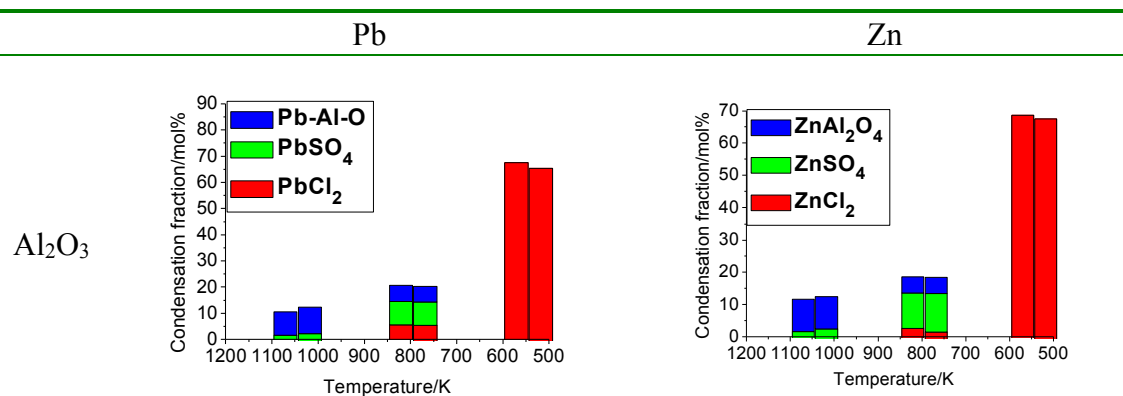
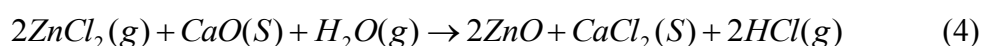


Figure 3-12 Condensation of Pb and Zn vapors with particulates in flue gas of 0.2%HCl, 0.1%SO<sub>2</sub>, 5%O<sub>2</sub>, 10%H<sub>2</sub>O under mixture mode. In each picture, the left columns represents air condition, the right column represents oxy-fuel condition.

The formation of Pb–Al–O, ZnFe<sub>2</sub>O<sub>4</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and ZnO are highly dependent on flue gas composition and the injected oxides. After injecting CaO, the condensation fraction of ZnO in air condition is higher than in oxy-fuel condition, which is observed in Fig3-11. This may be caused by the reaction 3. The reaction 3 consumed CaO to form CaCO<sub>3</sub>, which can compete with reaction 4 [21], and CaCO<sub>3</sub> may also prevent the formation of ZnO. To confirm this hypothesis, more CaO and CaCO<sub>3</sub> was used and placed in the cooling section in HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O atmosphere. As described in Figure 3-13 and Figure 3-14 in air condition, after injected more CaO the distribution of ZnO was remarkably higher than in oxyfuel condition, because the reaction 3 is easier in oxyfuel condition. Comparing with the results of CaO, there is a little ZnO condensed at the middle temperature, while in higher temperature the condensation fraction of ZnO is almost the same, because in higher temperature, CaCO<sub>3</sub> decomposed to CaO, in middle temperature there is just CaCO<sub>3</sub> which prevented the formation of ZnO. It is clearly suggesting that the formation of ZnO is caused by the reaction between ZnCl<sub>2</sub> and CaO rather than CaCO<sub>3</sub>.



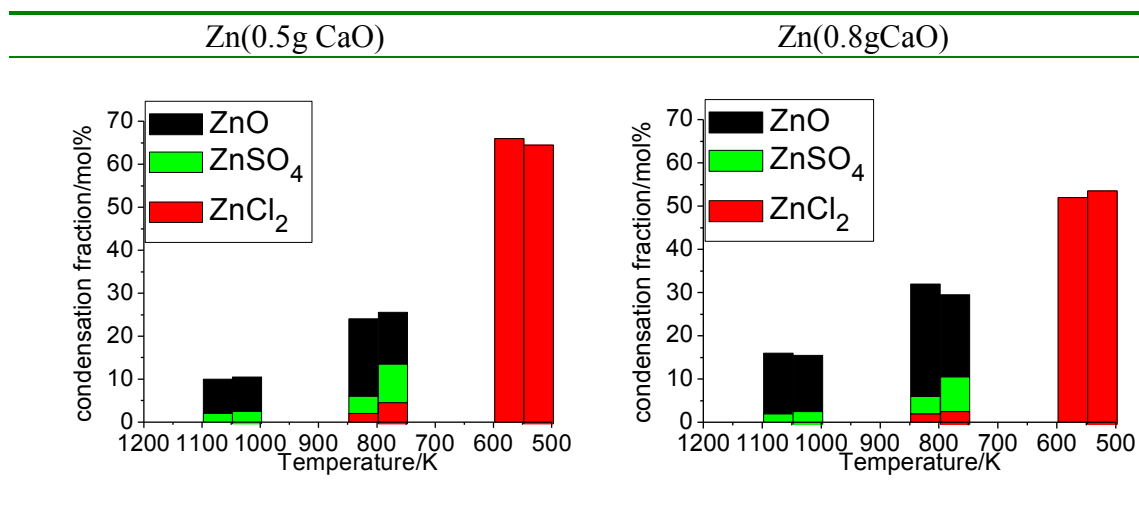


Figure 3-13 Zn compounds at 1073, 823 and 573 K with 0.5g CaO (left) and 0.8g CaO (right) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O atmosphere.

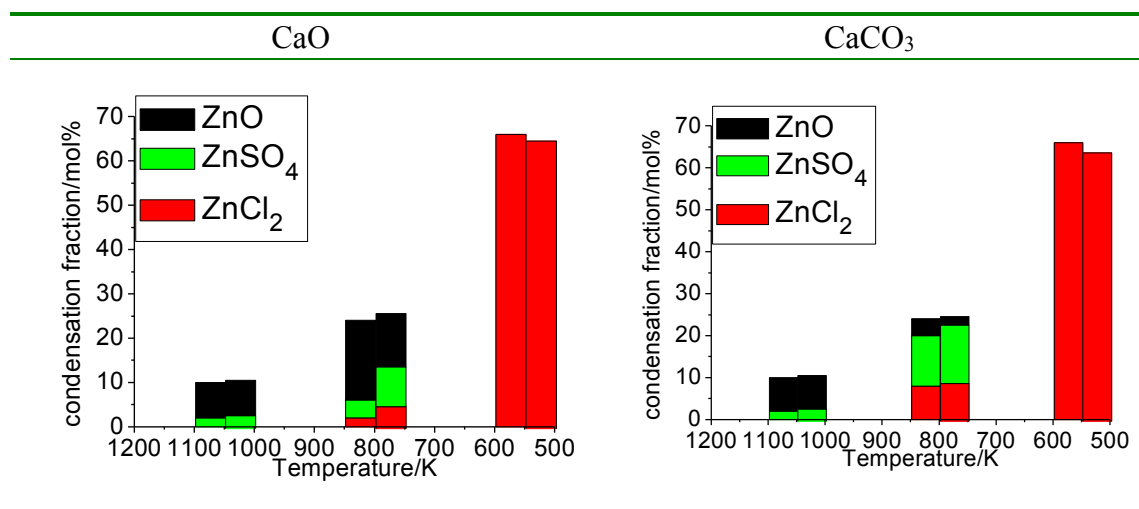


Figure 3-14 Zn compounds at 1073, 823 and 573 K with 0.5g CaO (left) and 0.5g CaCO<sub>3</sub> (right) in flue gas under HCl/N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O atmosphere.

### 3.4 Conclusions

The condensation behavior of Pb and Zn vapors was experimentally investigated under air-firing and oxy-fuel conditions. The condensation mechanisms were also evaluated by a thermodynamic pseudo-equilibrium model. The major conclusions are as follows:



1. The condensation fractions of Pb and Zn are slightly higher in oxy-fuel condition than that the respective results in air-firing under single mode. The typical Le number of an exhaust gas for air-firing condition is higher than that for oxy-fuel condition due to higher thermal capacity of CO<sub>2</sub> compared to N<sub>2</sub> and the lower mass diffusivity of O<sub>2</sub> in CO<sub>2</sub> than in N<sub>2</sub>. The oxy-fuel condition generates a gradual temperature gradient in the cross-section of tubular reactor, since less heat is transferred from wall to center of reactor tube. In contrast, the same volume flow rate between N<sub>2</sub> and CO<sub>2</sub> but a larger molecular weight of CO<sub>2</sub> than N<sub>2</sub> means the mass flux of CO<sub>2</sub> is larger than N<sub>2</sub> in the reactor, so primary nucleation rate will be enhanced in the oxy-fuel case. The primarily nucleated particles will act as seed nuclei that quickly deplete the vapor and suppress the new particle formation. This non-uniform nucleation consequently results in very high polydispersed aerosols after the growth and enhancing the sulfation reactions of Pb and Zn at higher temperature zone.

2. Under mixture mode of Pb and Zn vapors, there are little differences of each deposition fraction of Pb and Zn between air-firing and oxy-fuel conditions. However, the condensation fraction of either Pb or Zn in the mixture mode is higher than that in the single mode at the temperature range from 700 to 400K. The pre-existing particulates in flue gas can act as nuclei to trigger the condensation of the super-saturated metal vapors. The compounds of Pb condensed first, creating the seeds for the compounds of Zn to condense via heterogeneous crystallization, which caused the  $\beta$  values of Zn to change significantly with increasing H<sub>2</sub>O concentration in flue gas.

3. The influence of particulates on the condensation of heavy metallic is insignificant difference between air and oxyfuel condition, while the CaO react with CO<sub>2</sub> to form more CaCO<sub>3</sub> in oxy-fuel condition, which changes the surface reaction to inhibit the formation of ZnO.

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# Chapter 4

## Conclusions and Recommendations

### 4.1 Conclusions

Coal and waste-fired power plants currently provide over 40% of the world's electricity, while the problems of trace elements emission limited the utilization of coal and waste. For understanding the emission behavior of trace elements in air and oxyfuel combustion, the homogeneous nucleation and heterogeneous condensation behavior of trace metals, the influence of HCl, SO<sub>2</sub>, H<sub>2</sub>O and oxide particulates on condensation behavior of trace metals and the differences of condensation behavior of trace metals between traditional combustion and oxy-fuel combustion in flue gas cooling were investigated. The conclusions of each chapter are drawn as follows:

In chapter 2, Three oxides of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO as inorganic particulates were placed individually in flue gas cooling section to mimic pre-existing particulates in flue gas and examine their impact on the fate of Pb and Zn compound vapors. The effect of gaseous components including HCl, SO<sub>2</sub> and H<sub>2</sub>O on the heterogeneous condensation of Pb and Zn compound vapors on particulates grains has also been clarified. The presence of particulates in flue gas exerted remarkable influence on the fate of Pb and Zn compound vapors. Pb compound vapor was found being captured by Al<sub>2</sub>O<sub>3</sub> as Pb-Al-O at the temperature above 823K through chemical reaction, regardless flue gas

composition. Zn preferentially transformed into  $ZnFe_2O_4$ ,  $ZnAl_2O_4$  and  $ZnO$  respectively on the presence of  $Fe_2O_3$ ,  $Al_2O_3$  and  $CaO$  above 823 K. The presence of  $SO_2$  inhibited the chemical reactions of Pb and Zn vapors with particulates. Such an inhibitory effect was however compensated by the introduction of steam to flue gas. The presence of particulates in flue gas promoted the condensation of Pb and Zn compound vapors at higher temperature in comparison to the blank conditions, through heterogeneous nucleation, which in turn offset the effect of super-cooling. Moreover, the formation of sulfate was increased since the presence of particulates in flue gas triggered the condensation of sulfates vapors at high temperature and then reduced its partial pressure in flue gas, facilitating the sulfation reaction. Adjusting the concentrations of  $SO_2$  and  $H_2O$  in flue gas can prevent the formation of chloride of Pb and Zn, which is notorious for its toxicity and corrosion propensity during solid waste incineration.

In chapter 3, Vaporization of Pb and Zn-loaded model compounds has been carried out in a lab-scale rotary kiln reactor to clarify their condensation behavior upon flue gas cooling in both air-firing and oxy-fuel combustion modes. The influence of flue gas impurities including HCl,  $SO_2$  and  $H_2O$  has been examined systematically. For the two metals existing separately in the reactor, namely at single mode, both preferentially condensed as chlorides in the presence of HCl, under air-firing and oxy-fuel conditions.  $SO_2$  and steam in flue gas promote chloride into sulfide at high temperature. It was noticed that the deposition propensities of Pb and Zn vapors under oxy-fuel condition of the single mode were slightly enhanced than that in air-firing condition. This is due to a lower Lewis number of oxy-fuel combustion that is in favor of the formation of highly polydispersed fine particles. However, this discrepancy was diminished in the case that both two metals co-exist as the mixture mode in the reaction system. At the mixture mode from 700 K to 400 K, the condensation fraction of either Pb or Zn was confirmed higher than that in the single mode, due to an enhanced heterogeneous nucleation of Zn vapors on  $PbSO_4$  nuclei.

## 4.2 Recommendations for the future works

Based on this study, some recommendations for the future works are suggested as follows:

- **Condensation behavior of inorganic and organic trace elements in coal and waste combustion**

Current study on this topic only focused on the condensation of metallic vapors in flue gas cooling section. However, in real combustion system, there are inorganic and organic trace elements in coal and waste, their volatilization and condensation behavior are expected to be different in air and oxyfuel combustion. In fly ash there are a lot of inorganic particulates which alter the condensation of metallic vapors through chemical and/or physical reactions. What is more, heavy metal vapors may combine with these inorganic particles to form new stable and less-soluble compounds. These assumptions should be confirmed in future work.

- **Trace elements transformation during oxy-fuel combustion of coal and waste combustion**

In this work, Pb and Zn transformation behavior has been investigated. It has been found that there are some differences between oxy-firing condition and air-firing condition. However, the condensation behavior of As, Se, Hg and so on also need to be further investigated in oxyfuel combustion. Therefore, it is important to clarify their transformation under oxy-firing condition and investigate whether the As-, Se-, Hg-containing species in this new combustion technology can be shifted from toxic compounds to less toxic compounds or not.

- **The control of trace elements emission during oxy-fuel combustion of coal and waste**

An alternative technology for the control of trace elements emission is to prevent

the metal vapors forming during combustion process and minimize the formation of metal vapors at the hot-end of the coal combustion process. According to the possible species of trace elements in fly ash, the use of suitable sorbents to reduce the amount of heavy metal volatilization during combustion or capture volatilized heavy metal vapors through chemical reaction and/or physical adsorption is one of possible methods to control toxic elements emission. As mentioned above, many researchers did the research works about these in air combustion, while the environment of oxyfuel combustion is different between air combustion, it need further research work about the control technology of trace elements emission, especially, when the dirty flue gas containing the impurities of HCl, SO<sub>2</sub> and steam is used to recirculate in oxyfuel condition, these operation problems would be intensified. In terms of this, the control of trace elements emission during oxy-fuel combustion of coal and waste should be investigated in future work.