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Speciation Evolutions of Heavy Metals during the Sewage Sludge Incineration in a Laboratory Scale Incinerator

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With the growing application of sludge incineration, the thermal behavior of heavy metals during this process is increasingly a concern. This work was conducted to determine the speciation evolutions of heavy metals during sewage sludge incineration on a laboratory scale. It was found that the acid-soluble fraction of Zn was more inclined to volatilize. As for Pb and Cr, the volatilization of residual fractions and oxidizable fractions dominated, respectively. For Cu without moisture and Ni, the speciation evolutions were by the way of inner transformation. The speciation redistributions of Zn, Pb, Cr, and Cu (40% and 80% moisture) were mainly controlled by the initial volatilization. The speciation evolutions were controlled by the volatilization tendencies of different fractions and were possibly influenced by the reactions with an ash matrix. In addition, most likely, moisture promoted the formation of the acid-soluble fraction of Cu, and some residual fractions of Zn, Pb, and Cr were from hydrolyzation.

1. Introduction

The disposal of municipal sewage sludge is a growing concern throughout the world and in developing countries particularly.[1] As one kind of biosolid, the disposal of wastewater treatment plant (WWTP) sludge is also a growing environmental problem. Especially in Shanghai, it is expected that the annual output of dry WWTP sludge in 2010 will reach over 320 000 tons. It has been a concern for a long time that municipal sewage sludge contains many potentially toxic contaminants such as heavy metals, complex organic pollutants, and pathogens, thus making disposal problematic.

To face this disposal problem, there are three major options currently available, including application to agricultural land, landfill, and incineration.[2] In the European Community, incineration has been increasingly adopted in recent years, and it accounted for about 40% of all the sludge disposal routes in 2005.[3] Because sludge incineration combines several advantages, such as reducing sludge volume significantly, thermally destroying toxic organic constituents, and recovering calorific value, a growing interest is now being directed toward sludge incineration processes.[3]

Though sludge incineration possesses some preponderance, heavy metals in this process are still an issue. The behavior of heavy metals during sludge incineration has been studied by many researchers.[4−8] Corella and Toledo[5] and Van de Velden et al.[7] investigated partitioning during the combustion of sewage sludge. In particular, Toledo et al.[8] studied the influence of temperature and chlorine content and concluded that partitioning of the heavy metals was mainly governed by the diffusion kinetics inside the ash and by the reactions with the ash matrix. On the other hand, interest in speciation evolutions of heavy metals during the sludge disposal process has increased in recent years. Liu et al.[9] reported the evolution of heavy metal speciation in the course of an aerobic composting, and Wong and Selvam[10] discussed the effect of co-composting sewage sludge with lime on heavy metal speciation. However, few studies are available about the chemical speciation transformation of heavy metals during the incineration process. Thus, there should be focus on speciation evolutions during sludge incineration.

Consequently, in this work, Cu, Zn, Pb, Ni, Cd, and Cr were selected as the target heavy metal elements to evaluate their speciation evolutions during the sludge incineration. It is expected that the combined analysis of both heavy metal volatilization and speciation distribution can help to explain the possible mechanisms of chemical speciation transit.

2. Materials and Methods

2.1. Samples and Chemicals. The dewatered sewage sludge was collected from Shanghai Longhua WWTP, the properties of which are shown in Table 1. The proximate analysis was conducted using the ASTM 5142 standard. The moisture content (MC) of the raw sludge was around 80.2 wt %, and the volatile portion accounted for 50.01 wt % (dry basis). The ultimate analysis of the dried samples was carried

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(9) Liu, Y.-S.; Ma, L.-L.; Li, Y.-Q.; Zheng, L.-T. *Chemosphere* **2007**, *67*, 1025–1032.
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Table 1. Properties of Longhua WWTP Sludge

proximate analysis (wt %)			ultimate analysis (wt %)^{db}					
moisture[a]	volatile$_{ad}$	ash$_{ad}$	C	H	N	S	O	Cl
80.2%	50.01%	32.2%	49.87	6.31	5.23	2.32	24.92	0.01

[a] On raw sludge basis; X_{ad}, on air-dried basis; X^{db}, on dry basis.

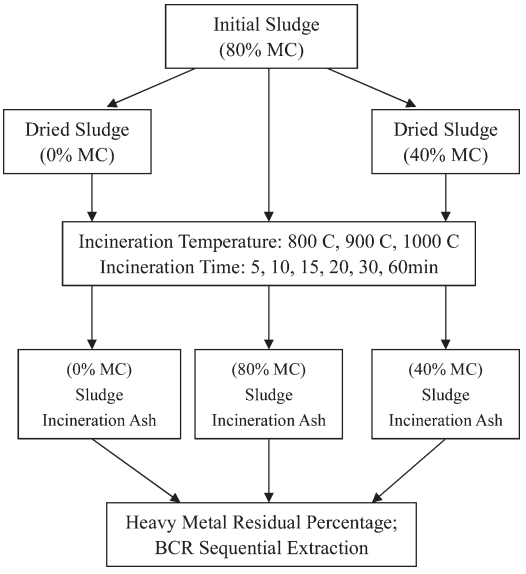


Figure 1. Study method scheme.

out with a CHNS/O elementary analyzer (Euro Vectoe EA3000). The carbon content of sludge was about 50 wt %, and the chlorine content was only 0.01 wt %.

The raw sludge was fully blended by a paddle stirrer to make it evenly distributed. The sludge samples (0% and 40% MC) were produced by drying raw sludge (80% MC) at 105 °C for 24 h and 15 min, respectively.

All the chemicals used in this study, including HF, HNO_3, $HClO_4$, HAc, $NH_2OH \cdot HCl$, H_2O_2, and NH_4Ac, were of analytical grade, purchased from Sinopharm Group Chemical Reagent Co.

2.2. BCR Sequential Extraction Procedure. The BCR sequential extraction procedure (the Community Bureau of Reference, now the European Union "Measurement and Testing Programme") was used to harmonize the methodology used in the sequential extraction schemes for determining metals in environmental solid samples.

In this paper, a modified BCR sequential extraction procedure was used. The heavy metal speciation is classified into four species: the acid-soluble fraction (AS), soluble and exchangeable or associated with carbonated phases; the reducible fraction (RED), associated with Fe and Mn oxides; the oxidizable fraction (OX), usually bound to organic matter; and the residual fraction (RES), the metals of which do not show a potential high risk to the environment with most occluded in the crystalline structures. The detailed steps were described by Rauret et al.[11]

The recovery rate, which is the ratio of the sequential extracted metal amount to the total metal amount, mainly ranged around 100% ± 10%. So it was satisfactory for analysis.

2.3. Experimental Methods. The study scheme is shown in Figure 1. The sludge samples (0%, 40%, 80% MC) were incinerated at 800, 900, and 1000 °C. The residence time was 5, 10, 15, 20, 30, and 60 min, respectively. Their corresponding incineration ashes were then digested to obtain the residual heavy metal amount. The heavy metal residual percentage (RP) is the ratio of the residual amount to the initial amount.

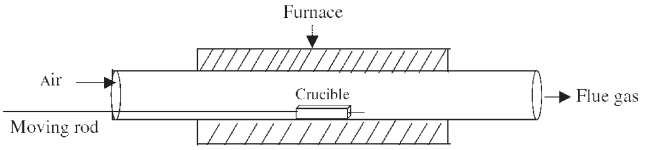


Figure 2. Schematic diagram of the laboratory scale incinerator.

Table 2. Concentration of Heavy Metals in Longhua WWTP Sludge and Comparison with Maximum Permitted Content Used for Soil (GB 4284-84; mg/kg dry matter)[a]

		maximum permitted content used for soil	
element	heavy metal content	(PH < 6.5)	(PH > 6.5)
Cu	9587.35 ± 585.93	250	500
Zn	1472.65 ± 264.78	500	1000
Pb	80.88 ± 19.71	300	1000
Cr	677.46 ± 81.20	5	20
Ni	56.38 ± 11.13	100	200
Cd	43.45 ± 10.01	600	1000

[a] The concentration is the mean ± standard deviation in mg/kg (four replicates).

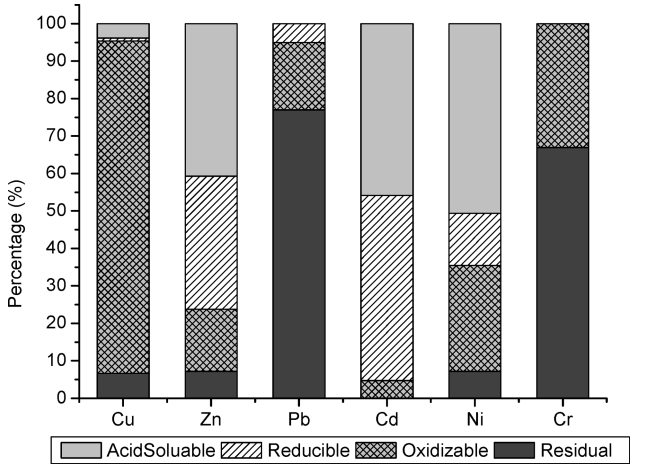


Figure 3. Heavy metal speciation of Longhua WWTP sludge.

The experiment was conducted in a laboratory tubular furnace reactor, which was used to simulate the grate incinerator.[12] The ceramic crucible was used as the sludge container and the transport carrier in the furnace. The incineration process was carried out as a batch experiment: the crucible containing 3 g of sludge (particles smaller than 10 mm were used) was manually pushed to the highest temperature zone and kept for the given residence time. Then, the sample was pulled out in a reverse way with a constant rate at a given time. The furnace scheme is shown in Figure 2.

All analysis was performed on three parallel samples with blanks throughout the complete procedure, following the U. S. E.P.A. approved QA/QC system. The data are presented by average value.

2.3.1. Specimen Preparation of Different Speciation Fractions. In order to understand the speciation evolution during the

(11) Rauret, G.; López-Sánchez, J. F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. *J. Environ. Monitor.* **1999**, *1*, 57–61.

(12) Jorg, W.; Stucki, S. *Chem. Eng. Technol.* **1999**, *22*, 209–222.

Table 3. Heavy Metal Residual Percentage in Different Speciation Matrices after Incineration

specimen	remained speciation	incineration temperature	residual percentage (%) Cu	Zn	Pb	Cr
B0	AS+RED+OX+RES(Raw Sludge)	800 °C	99.31	60.78	60.98	60.08
		900 °C	100.43	53.96	22.74	53.51
		1000 °C	95.41	19.67	16.00	48.31
B1	RED+OX+RES(After BCR step 1)	800 °C	99.82	86.52	63.03	62.85
		900 °C	100.08	83.03	23.91	55.75
		1000 °C	99.00	52.70	18.87	47.91
B2	OX+RES(After BCR step 2)	800 °C	98.80	88.93	67.85	67.13
		900 °C	99.57	83.50	29.23	58.04
		1000 °C	100.08	78.16	19.88	52.91
B3	RES(After BCR step 3)	800 °C	100.15	100.28	79.52	95.18
		900 °C	99.87	95.91	47.96	91.09
		1000 °C	100.03	91.92	32.08	88.13

sludge incineration, different speciation fractions were specially prepared from different BCR steps. They included four specimens: B0, the remaining sludge after BCR step 1 (RED, OX, and RES contained); B1, the remaining sludge after BCR step 2 (OX and RES contained); B3, the remaining sludge after BCR step 3 (only RES contained); and B4, the initial sludge sample (AS, RED, OX, and RES contained). These four specimens were incinerated at 800, 900, and 1000 °C for 30 min. Then, the RPs were calculated.

2.3.2. Simplified Symbols Used for Analysis. The symbols of RP curves are expressed simply. The 0, 40, and 80 represent 0%, 40%, and 80% MC. The 800, 900, and 1000 represent 800, 900, and 1000 °C. For example, "40−800" means that the sludge (40% MC) was incinerated at 800 °C.

As for the BCR analysis section, the symbols of speciation columns are expressed briefly as well, including the parameters of incineration temperature and residence time. The 8, 9, and 1 represent 800, 900, and 1000 °C. The 5, 10, 15, 20, 30, and 60 represent 5, 10, 15, 20, 30, and 60 min, respectively. For instance, "8−5" means "sludge incinerated at 800 °C for 5 min", and "1−5" represents "sludge incinerated at 1000 °C for 5 min". Moreover, speciations are also described simply. For example, four speciation types of Cu are shown by Cu-AS, Cu-RED, Cu-OX, and Cu-RES.

2.4. Analysis of Heavy Metal Content. The sludge samples, incineration ashes, and all residual fractions were digested in a multiacid total digestion system ($HF-HNO_3-HClO_4$) in cleaned PTFE vessels. Then, the completed digestion solution was transferred into calibrated flask through a 0.45 μm filter and diluted to the mark with deionized water. Like a digestion solution, the supernatants of the previous three sequential extraction steps were pretreated in this way before being determined.

Inductively coupled plasma emission spectrometry (PerkinElmer Optima 2000) was used to measure the dissolved Cu, Zn, Pb, Cr, Ni, and Cd.

3. Results and Discussion

3.1. Heavy Metal Characterizations of Raw Sludge. The constituents and contents of heavy metals in Longhua WWTP sludge are listed in Table 2. According to the maximum permissible limits proposed for agricultural use (GB 4284−84), the concentrations of Cu, Zn, and Cr exceeded the standard limit values for both acid and alkaline soil.

As seen in Figure 3, heavy metal speciations are presented by percentage columns. For Cu, the OX fraction occupied almost 90% of the total, indicating that copper can be preferentially combined with organic matter.[13] Zn and Cd were mainly distributed between the AS and RED fractions, while Pb and Cr were concentrated in the RES form, the percentages of which were 77% and 68%, respectively. In the case of Ni, the speciation was dominated by AS and OX fractions. The initial heavy metal speciation distribution is a very important reference for tracking the speciation evolutions in the process of sludge incineration.

3.2. Speciation Evolutions of Heavy Metals during the Sludge Incineration. To clearly understand the evolution trends of different speciation fractions, different specimens were specially designed and made. These samples were incinerated at different temperatures to track the volatilization behavior of heavy metals. Thus, the approximate volatilization ratios of heavy metals as a function of temperature in AS, RED, OX, and RES fractions could be calculated.

3.2.1. Volatilization Character of Heavy Metals with Different Speciation Fractions. In Table 3, the RPs of Cu, Zn, Pb, and Cr in different speciation fractions are listed, excluding Ni and Cd. These two metals are excluded because the RP was approximately 100% for Ni and 0% for Cd, which can be observed in Figure 4.

On the basis of the RPs listed in Table 3, the volatilization proportions of heavy metals in different fractions were calculated and listed in Table 4. For instance, after the incineration at 1000 °C, the RPs of Zn in B3 and B2 were 91.92% and 78.16%, respectively, showing the volatilization percentages of Zn−B3 (Zn-RES) and Zn−B2 (Zn-OX-RES) as 8.08% and 21.84%, respectively. Supposing there was no interaction between OX and RES during the incineration, the volatilization proportion of Zn-OX was 13.76% at 1000 °C, which was calculated by the difference between 21.84% and 8.08%. Similarly, the volatilization proportion of Zn-RED could be calculated by the deduction between Zn−B1 (Zn-RED-OX-RES) and Zn−B2 (Zn-OX-RES). The volatilization proportion of Zn-AS was obtained in the same way.

From Table 4, the volatilization tendencies of heavy metals in different speciation fractions are given by the following expressions.

$$\text{Zn-AS} > \text{Zn-OX} > \text{Zn-RED} \approx \text{Zn-RES (except 1000 °C)} \quad (1)$$

$$\text{Cu-AS} > \text{Cu-RED} > \text{Cu-OX} = \text{Cu-RES (at 1000 °C)} \quad (2)$$

$$\text{Pb-RES} > \text{Pb-OX} > \text{Pb-RED} > \text{Pb-AS} \quad (3)$$

$$\text{Cr-OX} > \text{Cr-RES} > \text{Cr-RED} = \text{Cr-AS} \quad (4)$$

For Zn, Zn-AS was most inclined to volatilize at three incineration temperatures. Especially at 1000 °C, besides

(13) Luo, Y.-M.; Christe, P. *J. Environ. Qual.* **1998**, *27*, 335–342.

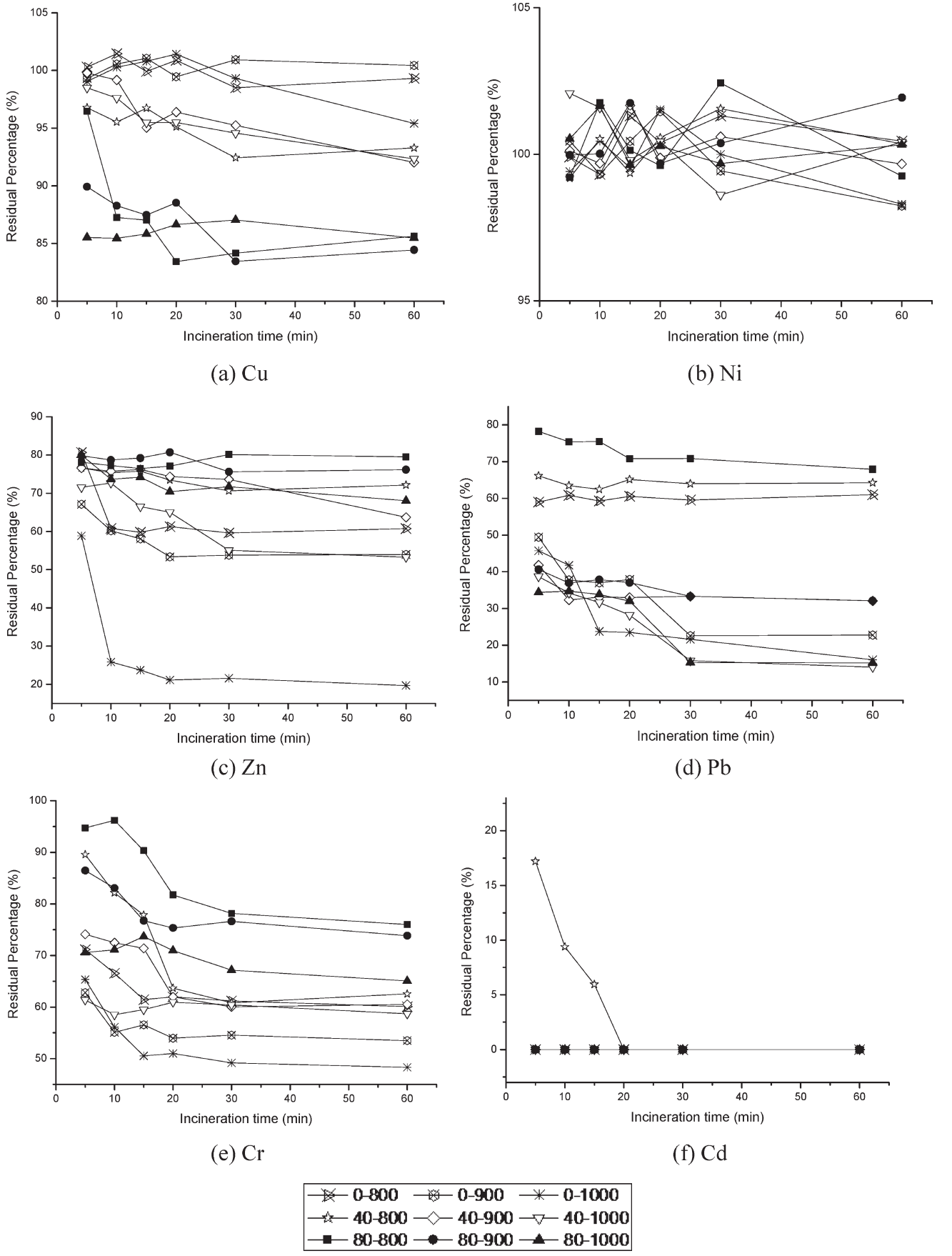


Figure 4. Residual percentage of heavy metals during sludge incineration.

Zn-AS, the volatility of Zn-RED and Zn-RES increased as well.

For Cu, only a bit of Cu-AS volatilized at 1000 °C, the proportion of which was 3.59%.

Table 4. Estimated Volatilization Proportion of Heavy Metals in Different BCR Fracions after Sludge Incineration

element	incineration temperature	total volatilization percentage[a] (%)	estimated volatilization proportion (%)			
			AS	RED	OX	RES
Cu	800 °C	1.2	0	0	1.2	0
	900 °C	0.43	0	0	0.3	0.13
	1000 °C	4.59	3.59	1.0	0	0
Zn	800 °C	39.22	25.74	2.41	11.07	0
	900 °C	46.04	29.07	0.47	12.41	4.09
	1000 °C	80.33	33.03	25.46	13.76	8.08
Pb	800 °C	36.97	0	4.82	11.67	20.48
	900 °C	76.09	0	5.32	18.73	52.04
	1000 °C	81.13	0	1.01	12.2	67.92
Cr	800 °C	32.87	0	0	28.05	4.82
	900 °C	41.96	0	0	33.05	8.91
	1000 °C	47.09	0	0	35.22	11.87

[a] Total volatilization percentage is equal to the sum of estimated volatilization proportion in each fraction.

Table 5. Overall Characters of Speciation Evolutions of Different Heavy Metals

HM	evolution types	evolution trends				possible mechanisms
		AS	RED	OX	RES	
Cu[a]	inner transition	increases initially and then decreases gradually	increases initially and then decreases gradually	decreases significantly	increases gradually	1. loss of volatile 2. influenced by ash matrix 3. controlled by the volatilization tendencies of different fractions
Ni		decreases obviously	decreases gradually	decreases gradually		
Cu[b]		increases initially and then decreases gradually	increases initially and then decreases gradually	decreases significantly	increases gradually	1. loss of volatile 2. influenced by ash matrix
Pb	initial volatilization	no change	decreases	decreases obviously		3. lower boiling points 4. controlled by the volatilization tendencies of different fractions 5. hydrolyzation
Zn		decreases obviously	decreases gradually	decreases gradually	increases significantly	
Cr		no change	some appear	decreases obviously		
Cd[c]		disappears gradually	disappears lastly	disappears gradually	no change	lower boling points

[a] 0% MC. [b] 40% and 80% MC. [c] 40% MC.

Table 6. Physical Properties of Metals and Their Compounds[a]

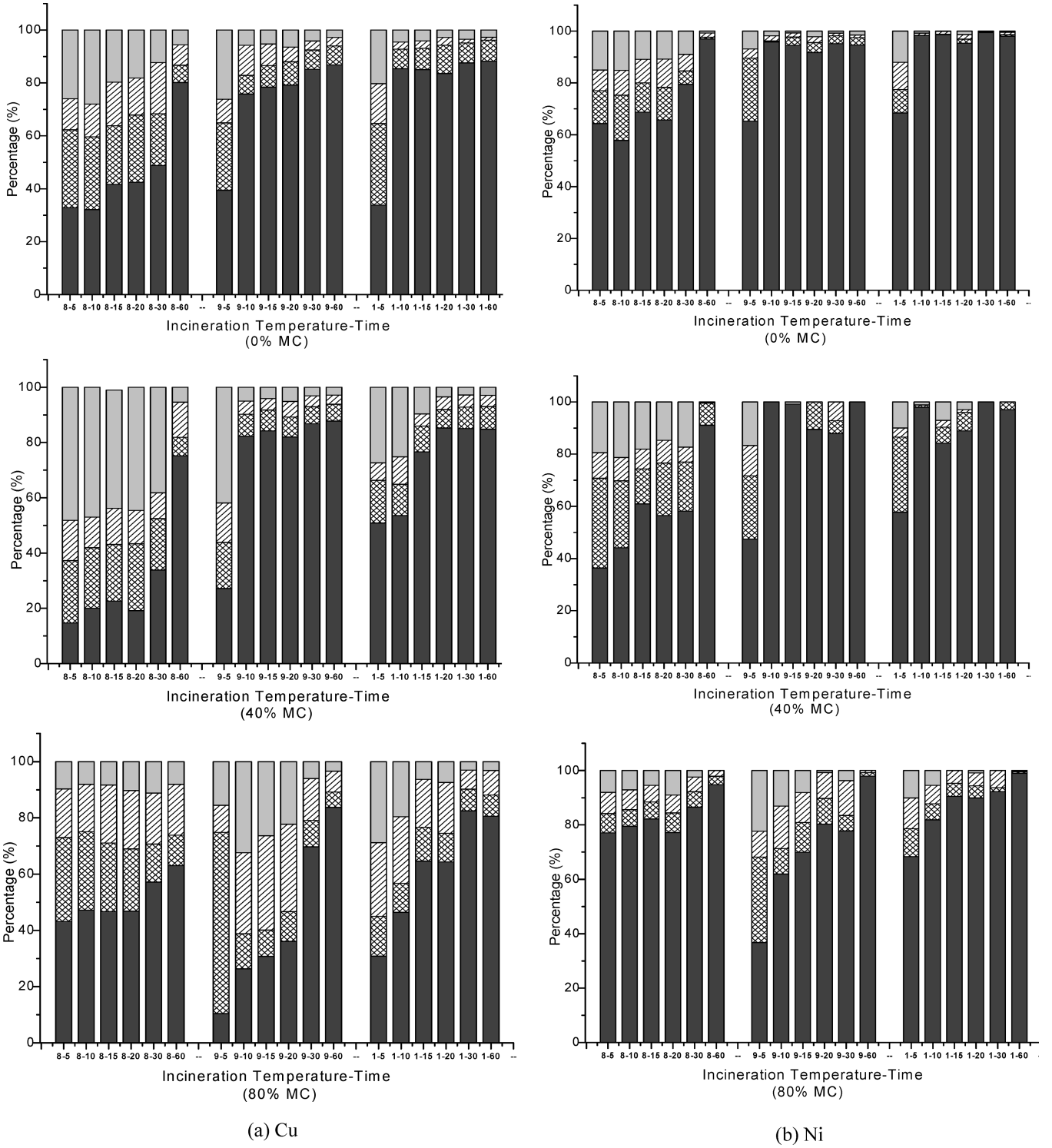
element	metallic		oxides		chlorides		sulfates		sulfides	
	MP (°C)	BP (°C)	MP (°C)	BP (°C)	MP (°C)	BP (°C)	MP (°C)	BP (°C)	MP (°C)	BP (°C)
Zn	419.53	907	1974	1800 subl	290	732	680 dec		1700	subl
Pb	327.46	1749	887	1470	501	951	1087		1113	
Cu	1084.6	2562	1227		598	993	560 dec		trans 507	
Cd	321.07	767		1559 sp	568	964	1000		≈1480	
Ni	1455	2913	1957		1031	985 sp	840 dec		976	
Cr(III)	1907	2671	2320	≈3000	1152	1300 dec	dec >700			

[a] MP, melting point; BP, boiling point; subl, sublimes; sp, sublimation point; dec, decomposes; trans, transition, transformation.

In the case of Pb and Cr, OX and RES fractions dominated the volatilization. Pb-RES volatilized most, the proportion of which was 67.92% at 1000 °C. On the contrary, Cr-OX volatilized more than Cr-RES.

For some heavy metals which are inclined to volatize at high temperatures, the thermal stability of different fractions can be various, mainly depending on their bonding ability with diffrent substances. At lower incineration temperature such as 800 °C, RES fractions are thermally more stable, except for Pb. And, with a rise in temperature, the volatilization is enhanced; even the RES fraction has higher volatilization.

3.2.2. Heavy Metal Speciation Evolutions during the Sludge Incineration. By the combined analysis of volatilization and speciation redistribution, the speciation evolutions of heavy metals can be classified into two types. The overall evolution characters are listed in Table 5 and will be explained in detail in the following sections.



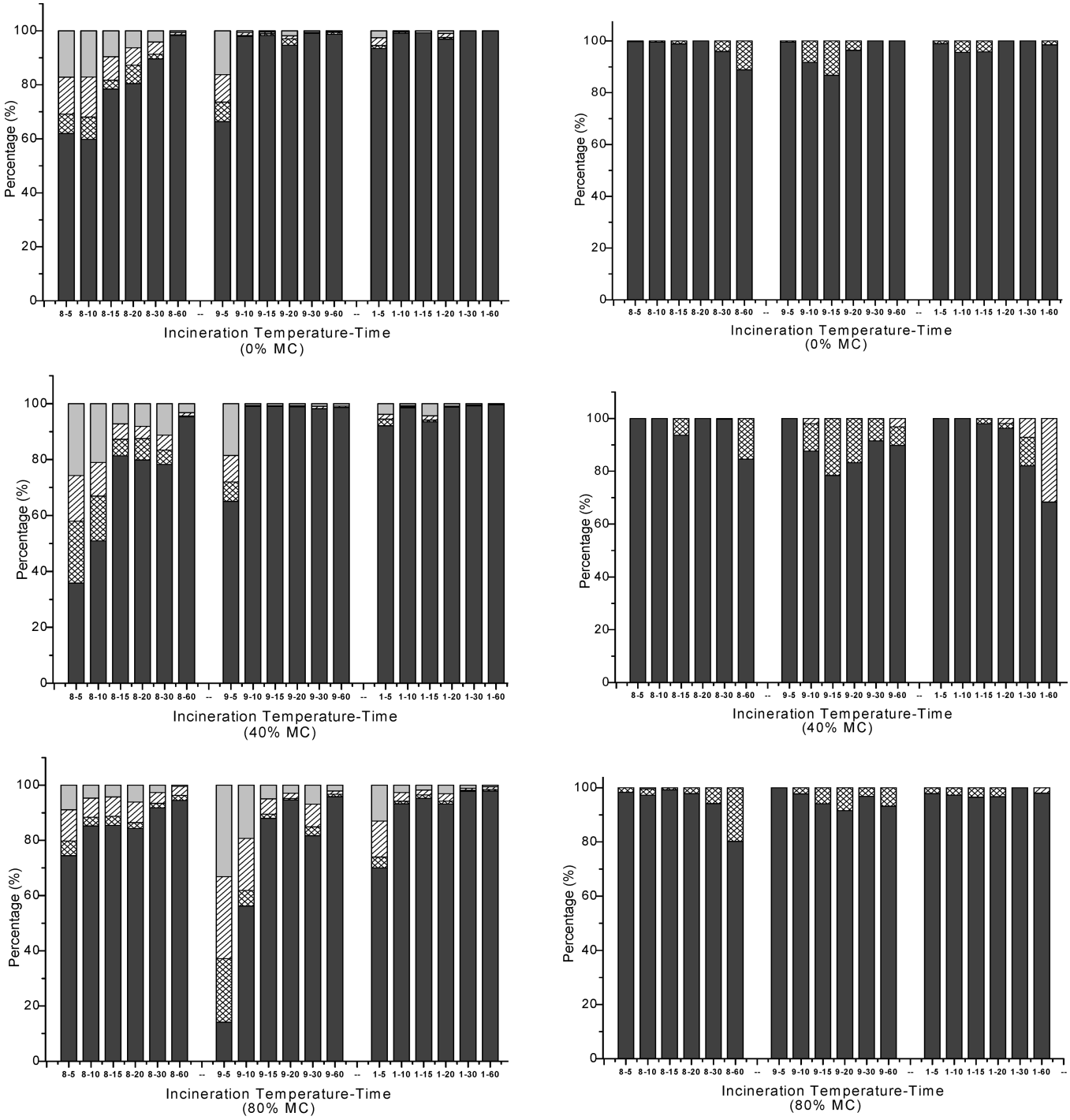
(a) Cu (b) Ni

Figure 5. Continued

3.2.2.1. Speciation Evolutions Controlled by the Inner Transition. The speciation evolutions of Cu and Ni were dominated by the inner speciation transition. This resulted because almost the entire initial totals of Cu (0% MC) and Ni remained during the incineration, which is shown in Figure 4a and b. Besides the factor of boiling points shown in Table 6, heavy metals such as Ni can be trapped or reacted with the mineral constituents of the ash and then retained.[5]

3.2.2.1.1. Cu (0% MC). In Figure 5a, compared with the initial speciation distribution in Figure 3, the OX fraction decreased significantly after 5 min from the initial 90% to 30%. Simultaneously, large quantities of AS and RES fractions appeared. It is known that the OX fraction includes metal sulfides and metals that are complexed or peptized by the natural organic substances.[14] The raw sludge used in this study contained over 50% volatile material (on dry basis), which was mainly composed of organic matter. Thus, after

(14) Fuentes, A.; Lloréns, M.; Sáez, J.; Aguilar, M. I.; Ortuño, J. F.; Meseguer, V. F. *J. Hazard. Mater*. **2004**, *108*, 161–169.



(c) Zn (d) Pb

Figure 5. Continued

the incineration for 5 min, the majority of volatiles in the raw sludge were lost remarkably. Therefore, the decrease of Cu-OX was mainly due to the decomposition of organic substances.

After the organic substances volatilized, the decomposed Cu-OX redistributed the speciation. Some soluble Cu ions and elemental Cu possibly appeared and could be classified into Cu-AS and Cu-RES, respectively. With the incineration time increasing, Cu-AS might be oxidized into CuO gradually, and Cu could also be trapped in the ash matrix, which contributed to the increase of the RES fraction.

3.2.2.1.2. Ni. In Figure 5b, Ni-AS decreased obviously from the initial 50%, while Ni-RES increased gradually. Eventually, similar to Cu (0% MC), the RES fraction dominated the distribution.

3.2.2.2. Speciation Evolutions Mainly Controlled by the Initial Volatilization. In Figure 4, the RPs of Zn, Pb, Cu, Cr, and Cd are close to the retention percentage ranges obtained by Miller.[15] Although, the ranges are a bit different from

(15) Miller, B. B.; Kandiyoti, R.; Dugwell, D. R. *Energy Fuels* **2002**, *16*, 956–963.

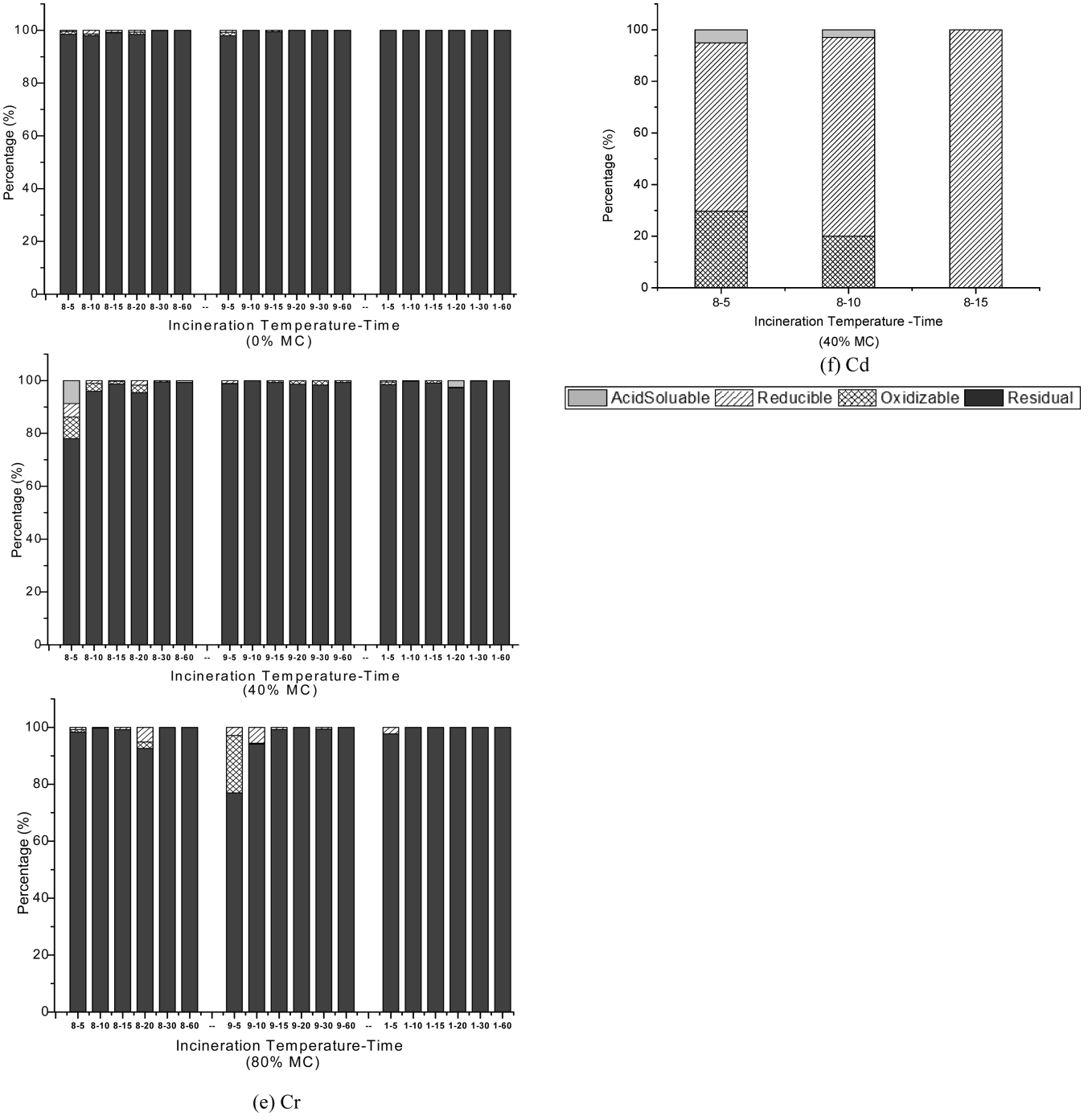


Figure 5. Speciation evolutions of heavy metals during incineration of sludge with different MC.

Toledo's results, except for Pb and Cd, which showed that the average partitioning percentage of each heavy metal in bottom ash was around 36%.[8] The difference is possibly due to the different operational conditions between a laboratory scale and a pilot plant scale. However, for Cd and Pb, the results are similar, in which both are significantly present in the vapor phase, and Pb has an intermediate behavior between Cd and the other heavy metals such as Zn.[8] Additionally, Abanades et al.[16,17] indicated that Cd and Pb need at least 10 min to diffuse out of an ash particle, and the average time for Cd is about 20 min, which corresponds to the results shown in Figure 4.

Crucially, Figure 4 shows that Zn, Pb, Cr, Cu (40% and 80% MC), and Cd (40% MC) volatilized mainly before 30 min. So, the speciation evolutions of these heavy metals were primarily controlled by the initial volatilization. After 30 min, almost no volatilization occurred, meaning that the evolutions were dominated by the inner fraction transformation.

3.2.2.2.1. Zn. In Figure 5c, after the incineration for 5 min at 800 °C, the Zn-AS's of the 0%, 40%, and 80% MC sludges were reduced to 17%, 25%, and 9%, respectively, from the initial 40%. Particularly, when incinerated at 1000 °C for

(16) Abanades, S.; Flamant, G.; Gauthier, D. *Combust. Flame* **2000**, *134*, 315–326.
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5 min, the AS fractions decreased to the minimum. As discussed in section 3.2.1, Zn-AS volatilized more, which was mainly due to the low boiling points of Zn-AS, such as $ZnCl_2$ with a boiling point of 732 °C. Additionally, some Zn-RED and Zn-OX fractions volatilized. Due to the initial volatilization of these Zn fractions, the RES percentages became higher correspondingly. Zn-RES could also be a result of the reactions with the ash matrix to form mixed oxides such as $ZnFe_2O_4$, $ZnAl_2O_4$, $ZnCr_2O_4$, and Zn_2SiO_4.[8,18]

3.2.2.2.2. Cu (40% and 80% MC). As shown in Figures 4a and 5a, the RPs of Cu and the percentages of Cu-AS decreased simultaneously. Also, as discussed in section 3.2.1, the volatilization was mainly from Cu-AS, so the speciation evolutions of Cu were accompanied by the volatilization of Cu-AS. The initial increase of Cu-AS was due to both soluble Cu ions from the decomposition of Cu-OX and chlorides of Cu produced by moisture promotion. In Figure 4a, the results show that a higher MC can reduce the RPs of Cu. Hence, the presence of moisture can promote the formation of more volatile forms from metallic and oxide forms, e.g., from metallic copper to its chloride,[19] such as copper chlorides, which are presented by Cu-AS. Also, in Table 6 it can be seen that the boiling point of chlorides of Cu is much lower, which makes them prone to volatilization. With the residence time increasing, the volatilization of Cu-AS made the Cu-RES percentage increase, leading to the speciation redistributed.

Correspondingly, by comparing the speciation evolution of Cu (40% MC) with that of Cu (0% MC) at 800 °C, it was found that more Cu-AS appeared in the speciation column during the incineration process. Likewise, when incinerating 80% MC sludge at 900 °C, there was obviously more Cu-AS than that with 0% MC sludge. Therefore, it possibly shows the influence of more moisture on the percentage of Cu-AS.

3.2.2.2.3. Pb and Cr. Due to the low boiling points of Pb and the possible formation of volatile CrO_2Cl_2,[18,20,21] the speciation redistribution of Pb and Cr was mainly controlled by its volatilization; their evolutions were similar. As seen in Figure 5d and e, due to the initial decomposition and volatilization, the percentages of OX fractions decreased significantly. Some previous OX fractions quite possibly belonged to RES fractions after decomposition. On the other hand, RED fractions were thermodynamically unstable and tended to be thermally destroyed and volatilized as well. Though, certain amounts of Pb-RES and Cr-RES volatilized as discussed in section 3.2.1, the speciations mostly existed in the RES fraction. These speciations could be presented in the form of solid oxide $Pb_2B_2O_4$ or simple metal Pb.[18] In addition, the higher sulfur content in the raw sludge could inhibit the volatilization of Pb and Cr.[22,23] For instance, at higher temperatures, Pb sulfate was favored over its chloride, raising the dew point.[23]

3.2.2.2.4. Cd. As seen in Figure 4f, only a bit of Cd remained when the 40% MC sludge was incinerated. Correspondingly, as observed in Figure 5f, lots of Cd-AS volatilized, making other speciation fractions higher. At 15 min, Cd-OX and Cd-AS disappeared, while the Cd-RED fraction reached a maximum.

3.2.2.2.5. Impact of Hydrolyzation. Specifically, some RES fractions of Zn, Pb, and Cr were possibly from hydrolyzation. In Figure 4c, d, and e, it can be seen that a higher MC led to higher RPs at the same incineration temperatures. Under a high MC, chlorides of zinc and lead might hydrolyze to form hydroxide, and then they are dewatered to form less volatile oxides,[19] such as PbO and ZnO. These final oxides belong to the RES fraction. As for Cr, it is active under high temperatures and could react with halogen directly, resulting in the formation of haloid. The valence of formed Cr compounds is usually three, such as in $CrCl_3$. Hence, Cr(III) ions hydrolyze and are dewatered to Cr oxides. The newly formed oxides can be extracted as a RES fraction as well.

4. Conclusions

This study mainly showed the speciation evolutions of heavy metals during the sewage sludge incineration process as follows:

1. By incinerating specimens with different speciation fractions, it was found that Cu and Zn in the acid-soluble fraction of the sludge were more inclined to volatilize. Organically associated Cr volatilized more than Cr in the residual fraction, while Pb in the residual fraction volatilized more than organically associated Pb.
2. The speciation evolutions of heavy metals in the sewage sludge could be classified into inner transition control and initial volatilization control. For Cu (0% MC) and Ni, the inner speciation transformation occurred. For other heavy metals, the speciation redistributions were mainly controlled by the initial volatilization.
3. The speciation evolutions should follow the volatilization tendencies of different fractions. Also, the evolutions could be influenced by the reactions with the ash matrix.
4. Moisture had some impact on the speciation evolutions of Cu, Zn, Pb, and Cr. The more acid-soluble fraction of Cu was formed due to the promotion of moisture. Some RES fractions of Zn, Pb, and Cr resulted from hydrolyzation.

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