Comprehensive Evaluation of the Control Efficiency of Heavy-Metal Emissions during Two-Step Thermal Treatment of Sewage Sludge

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ABSTRACT: Recycling the phosphorus in sludge by incineration has received great interest at home and abroad. However, heavy metals (HMs) is a restrictive factor for SS thermal treatment. In this study, a comprehensive evaluation method was adopted to evaluate the comprehensive control efficiency of HM emissions during two-step thermal treatment (incineration−calcination). The effects of temperature, calcination time, and additives (CaO and NaCl) on leaching rates, stabilized rates, and comprehensive control efficiency of HM emissions were investigated. Results showed that comprehensive control efficiency increased significantly with an increase of temperature because of the transformation of chemical speciation from a leachable to a more stable combined form. Additives CaO and NaCl promoted the volatilization of HMs and reduced the comprehensive control efficiency. The highest comprehensive control efficiency of HM emissions was 78% when the incineration temperature reached 950 °C. Furthermore, a comparison was made between leaching rates, stabilized rates, and a comprehensive evaluation method. The results were inconsistent when leaching rates and stabilized rates were adopted. In contrast, when the comprehensive evaluation method was used, the results were coordinated and unique. This work can provide a promising approach for the evaluation of control efficiency of HM emissions during the process of thermal treatment of sludge.

1. INTRODUCTION

A large quantity of sewage sludge (SS) is generated during wastewater treatment process worldwide. The annual production of sludge in China reached 36.26 million tons by the end of 2017 (moisture content of 80%). As a byproduct, SS generally contains elements needed for plant growth. For example, SS has been considered as the largest secondary phosphorus resource. As a significant component of cell, phosphorus is an irreplaceable resource, and the most important source of phosphorus is phosphate rock, which is a limited nonrenewable resource. Phosphate rock resources play an extremely important role in global food production and phosphorus chemical industry. It was listed as one of the 20 minerals that cannot meet the needs of national economic development after 2010 in China. So, recycling the phosphorus in sludge by incineration has received great interest at home and abroad.

Our research team aimed to recover phosphorus from sludge through two-step thermochemical treatment: incinerating the sludge completely destroys organic pollutants, enriching the levels of phosphorus and heavy metals (HMs) in the sludge ash for the first step. This is followed by calcination of phosphorus-enriched sewage sludge ash, which removes heavy metals while ensuring a high stabilized rate of phosphorus. In addition, there are many other recycling technologies; however, there are many other hazardous substances in SS, such as heavy metals (HMs), pathogens (e.g., Salmonella spp.), and persistent organic pollutants (POPs), causing serious threats to the environment and ecosystem. The kinds of HMs mainly depend on the sources of sludge, usually including Cu, Zn, Pb, As, Ni, Cr, Cd, and Hg. The main forms of HMs are ion-exchange state, carbonate binding state, iron−manganese oxide state, organic binding state, and residual state. Unlike organic pollutants and others, HMs are difficult to remove in normal circumstances and is a problem needed to be concerned. More importantly, they do not pose risk to environmental health but can also accumulate throughout the food chain. As a result, this may threaten human health, thus limiting the direct SS application.

The safe treatment technology of HMs mainly includes curing and stabilization, especially chemical stabilization technology, asphalt technology, cement solidification tech-
technology, sintering,9 and melting technology. When it comes to the technologies for monitoring of HM emission, leaching and stabilized rates of single trace metals were mainly examined and were applied by many studies.10 However, practical applications for evaluating different metals had produced inconsistent results.11 In some cases, the results even led to paradoxical conclusions. Therefore, it is necessary to find distinct methods and establish different criteria for the comprehensive evaluation of control efficiency of HM emissions.

Until now, the most relevant study for assessing the hazards from HMs is in the fields of river sediments, oceans, and soil.12 Common methods for describing disasters include the pollution load index,13 fuzzy subset theory, comprehensive pollution index, geographic accumulation index,14 excess after-regression analysis, risk assessment code,15 face map, and the secondary-stage enrichment factor.15 Potential ecological risk index (RI)16 is one of the most commonly used methods for assessing the degree of HM toxicity. However, these developed evaluation methods were not coordinated or unique. Based on the literature data, the overall pollution toxicity index (OPTI) and a comprehensive evaluation method for HM emissions are proposed.17 These methods were applied to evaluate the comprehensive control efficiency of HM emissions during two-step thermal treatment of SS for the first time.

A two-step thermal treatment (incineration—calcination) of sludge was performed in a horizontal tube furnace system. The purpose of this research was to investigate the effects of temperature, calcination time, and additives (CaO and NaCl) on leaching rates, stabilized rates, and comprehensive control efficiency of HM emissions. A comparison was made between leaching rates, stabilized rates, and comprehensive evaluation method. First, the total amounts of HMs (Cu, Zn, Cr, Pb, Ni, Cd) and leaching characteristics of sludge after thermal treatment were analyzed using the triacid digestion method and the TCLP procedure, respectively. Second, overall pollution toxicity index (OPTI) and comprehensive evaluation method were adopted to evaluate the overall toxicity control efficiency of HMs. Therefore, this work was intended to develop an integrated evaluation method with uniqueness and accuracy when it was used to select HM control technology.

### 2. MATERIAL AND METHODS

#### 2.1. Material

Dewatered domestic sludge samples were obtained from a sludge treatment plant in Shenyang, Liaoning Province, China. They were naturally dried in the laboratory at room temperature for 2 weeks, ground using an abrasive machine, and sieved with a 100 mesh (0.15 mm) sieve. Then, they were dried to a constant weight at 105 °C in an oven and stored in a desiccator for future tests. The content of moisture in sludge was 3.86%. Proximate analysis, ultimate analysis, and heavy-metal contents of sludge are presented in Table 1.

| M | A | FC | V | ultimate analysis (a dry%) |
|---|---|----|---|---------------------------|
| 3.860 | 33.700 | 5.960 | 57.110 | 39.405 | 5.122 | 7.096 | 2.334 | 12.343 |
| 96.4 | 12.1 | 215.7 | 2544.5 | 297.2 | 46.4 | 82.1 | 853.8 |

### 2.2. Experiment Setup

The two-step thermal treatment consisted of incineration and calcination. In the first step, sludge was incinerated to obtain the sludge ash, and the co-enrichment of phosphorus and HMs was realized by adding CaO. In the second step, the sludge ash gained in the first step was calcinated by adding NaCl, and then the removal of HMs was realized with very little phosphorus volatilization. A horizontal tube furnace system was used to carry out the experiments. The furnace reactor consisted of an alundum tube with length and diameter of 1 m and 40 mm, respectively. The temperature range of this system was 200–1800 °C. The incineration—calcination process was performed in this horizontal tubular furnace system. The airflow rate and the heating rate were set to 100 mL min⁻¹ and 10 °C min⁻¹, respectively. In each experiment, the mass of the raw sludge or sludge ash was 10 g, and it was taken to the furnace center when the temperature of the furnace reached the desired value. The sludge ash was obtained in the first step (750 °C, 2% CaO). When the setting time was achieved, the heating process was stopped. After the horizontal tubular furnace was cooled to room temperature, the sample was taken out and stored in a desiccator for subsequent testing. In each experiment, two bottles containing 10% H₂O₂ and 5% HNO₃ (by volume), respectively, were used to absorb the HMs in flue gas according to the EPA method 29. The exhaust gas was collected in the absorption device (deionized water, 10% H₂O₂ solution, 5% HNO₃, 4% KMnO₄ and 10% H₂SO₄ solution, silica gel desiccant). The experimental matrix is shown in Table 2.

#### 2.3. Analysis of HMs

To analyze the heavy-metal contents of sludge or bottom ash, 100 mg of sludge or bottom ash was digested in mixed-acid solution (5 mL of HNO₃, 2 mL of hydrofluoric acid, 5 mL of HClO₄, and 1 mL H₃BO₃) in a system of microwave digestion (MDS-6G, PerkinElmer), and then the digestion solution was diluted to 50 mL with deionized water. Finally, all of the above samples were analyzed by Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima-ICP8300, PerkinElmer) to gain the contents of HMs.

#### 2.4. Leaching and Stabilized Rates

The leaching test of sludge or bottom ash under different experimental conditions was performed according to EPA method 1311 to obtain the leaching characteristics of the sample.

\[
\text{leaching rate} = \frac{(C_1 \times V)}{(C_2 \times M)}
\]

\[
\text{stabilized rate} = \frac{(C_2 \times M_j)}{(C_b \times M_b)}
\]

Cᵢ indicates the consistency of HMs in the leaching solution, mg L⁻¹; V indicates the volume of leaching solution, mL; C₂ indicates the mass consistency of HMs in the leaching sample, mg kg⁻¹; M indicates the mass of leaching sample used in the TCLP procedure, g; C_b indicates the mass consistency of HMs of the sample before incineration or calcination, mg kg⁻¹; M_b indicates the mass of the sample before incineration or calcination, g; and V indicates the volume of leaching solution, mL.
indicates the mass of the sample before incineration or calcination, \( g_i \); \( C_i \) indicates the mass consistency of HMs of the sample after incineration or calcination, mg kg\(^{-1}\); and \( M_i \) indicates the mass of the sample after incineration or calcination, g.

### 2.5. Comprehensive Evaluation Methods.

This study adopted a novel method to evaluate the comprehensive control efficiency of HM emissions. It was proposed in our previous studies (the overall pollution toxicity index (OPTI) of HMs and comprehensive evaluation method).\(^{17} \) It was the first time to apply it to the two-step thermal treatment of sludge. The comprehensive control efficiency (\( \eta \)) can be defined as follows.

\[
\eta = \frac{1 - \frac{\sum_{i=1}^{n} K_i OPTI_i}{OPTI_w + \sum_{j=1}^{m} A_j OPTI_A}} \times 100\%
\]  

(3)

where \( W \) is the hazardous waste, OPTI\(_{w}\) is the overall pollution toxicity index of the HMs in the hazardous waste, \( R_p \) is the product obtained after the technical treatment of hazardous waste, \( n \) is the product’s number, \( K_i \) is the mass percentage of \( R_p \), OPTI\(_L\) is the overall pollution toxicity index of HMs in \( R_p \), \( A_j \) is the type of additive used during the technical treatment process, and \( m \) is the additive’s number. \( K_i \) and OPTI\(_A\) are the mass percentage and overall pollution toxicity index of HMs in \( A_j \), respectively.

The key to this method is the calculation of the overall pollution toxicity index of heavy metals, which indicates their potential risk to the environment and considers the following parameters:

- The quantity reflects the impact of heavy metals on the environment. The hazards of multiple heavy metals should be higher than that caused by a single or several heavy metals.
- The intensity directly reflects the impact of heavy metals on the environment. The higher the concentration of heavy metals, the greater the pollution intensity. The heavy-metal pollution intensity (\( C_i \)) can be calculated as follows

\[
C_i = C_k - C_k^0
\]  

(4)

where \( k \) is the type of heavy metal used, \( C_k \) is the concentration of the heavy metal, and \( C_k^0 \) is the reference value for the concentration of heavy metals according to Table 3. Generally, the background value of heavy metals is that found in the topsoil before industrialization.

### Table 2. Experimental Matrix

| experimental condition | no. | CaO (%) | NaCl (%) | time(min) |
|------------------------|-----|---------|----------|-----------|
| First Step: Incineration |     |         |          |           |
| 750 °C                  | 1   | 0       | 65       |           |
| 850 °C                  | 2   | 2       | 65       |           |
|                        | 3   | 4       | 65       |           |
|                        | 4   | 6       | 65       |           |
| 950 °C                  | 5   | 0       | 65       |           |
|                        | 6   | 2       | 65       |           |
|                        | 7   | 4       | 65       |           |
|                        | 8   | 6       | 65       |           |
|                        | 9   | 0       | 65       |           |
|                        | 10  | 2       | 65       |           |
|                        | 11  | 4       | 65       |           |
|                        | 12  | 6       | 65       |           |
| Second Step: Calcination |    |         |          |           |
| 950 °C                  | 13  |         | 30       |           |
| 1050 °C                 | 14  |         | 30       |           |
| 1100 °C                 | 15  |         | 30       |           |
| 1050 °C                 | 16  |         | 20       |           |
| 1050 °C                 | 17  |         | 10       |           |
| 1050 °C                 | 18  |         | 40       |           |
| 1100 °C                 | 19  | 5       | 30       |           |
| 1100 °C                 | 20  | 10      | 30       |           |
| 1100 °C                 | 21  | 15      | 30       |           |

### Table 3. Reference Values and Toxicity Factors of Heavy Metals

| heavy metal | Ni | Cd | Cr | Pb | Cu | Zn |
|-------------|----|----|----|----|----|----|
| \( C_k \) (mg kg\(^{-1}\)) | 27 | 0.10 | 61 | 26 | 23 | 74 |
| \( T_l \) | 5  | 30 | 2  | 5  | 5  | 1  |

Toxicity reflects the toxicity of heavy metals and the sensitivity of organisms toward these heavy metals. Hakanson’s potential toxic response factor (\( T_l \)) can indicate toxicity. The \( T_l \) values of several heavy metals are shown in Table 3.

Stability reflects the releasability of different forms of heavy metals, and it can be determined by leaching characteristics. Only heavy metals released into the environment can cause ecological risks. Heavy metals are usually dissolved in water before they endanger the ecological environment. Therefore, the leaching rate (\( L_k \)) can be defined as characterizing the stability of heavy metals

\[
L_k = \frac{m_k^1}{m_k^0} \times 100\%
\]  

(5)

where \( k \) is the type of heavy metal considered, \( m_k^1 \) is the mass of heavy metals in the leaching solution, and \( m_k^0 \) is the mass of heavy metals in the leached sample. Using these four parameters, the overall pollution toxicity index (OPTI) of heavy metals can be calculated as follows

\[
OPTI = \sum_{k=1}^{s} T_l^k C_k^1 L_k^l
\]  

(6)

where \( s \) is the amount of heavy metals.

The comprehensive control efficiency (\( \eta \)) of heavy metals in the stabilization process such as sludge incineration and calcination shows the degree of reduction of heavy-metal hazards and accurately describes the harmlessness of heavy metals. In this study, after incineration and calcination, most of the heavy metals remain in the slag; the remaining heavy metals volatilize to the gas phase and require additional treatment. Therefore, the comprehensive control efficiency (\( \eta \)) of heavy metals during sludge incineration and calcination can be expressed as follows

\[
\eta = \left(1 - \frac{K_{slag}OPTI_{slag} - K_{gas}OPTI_{gas}}{OPTI_{ash}}\right)
\]  

(7)

OPTI\(_{ash}\) can be calculated by

\[
OPTI_{ash} = \sum_{k=1}^{s} T_l^k C_k^1 \times L_k^l
\]  

(8)

where \( C_k^1 \), \( T_l^k \), \( L_k^l \) are pollution intensity and leaching rate of heavy metals in fly ash, respectively. OPTI\(_{slag}\) can be calculated by
With an increase of incineration temperature, leaching rates of As, Cd, and Mn decreased significantly, especially that of As decreased from 56.7 to 28.3%. This phenomenon is attributed to the fact that the residual fraction and the oxidizable fraction of HMs increased gradually, and acid-soluble fraction gradually decreased, resulting in a decrease of leaching rates of HMs. Figure 1 also shows that leaching rates of As and Cd were higher than those of other HMs at the same temperature. The leaching rates of Cr and Pb were the lowest. When the incineration temperature reached 950 °C, the leaching rates of As, Cd, Mn, Cu, Zn, Ni, Pb, and Cr were approximately 28.3, 10.9, 1.5, 2.8, 4.2, 1.4, 0.1, and 0.02%, respectively. In general, bioactivity and leaching toxicity of HMs decreased to follow the order of acid-soluble fraction > reducible fraction > oxidizable fraction > residual fraction. The acid-soluble fraction is also called the exchangeable fraction, which mainly includes HMs that are in ionic form or combine with carbonate. HMs that combine with iron and hydroxides or manganese oxides are the major reducible fraction. Acid-soluble fraction and reducible fraction, especially the former, are considered as the most loosely combined phases. HMs are more likely to be released from this fraction, therefore posing a potential risk to the living creatures and ecosystem. Another aspect, the oxidizable fraction means the HMs combine with stable silicate or sulfides, HMs are difficult to be released from this fraction under normal conditions. The residual fraction is considered as the most stable fraction of HMs and does not pose a potential threat to living creatures and the ecosystem. Therefore, different forms and combinations of HMs cause differences in leaching rates of HMs.

3.2. Influence of Additive (CaO) on Leaching Rates of HMs during Incineration. The leaching rates of HMs with different additions of CaO are shown in Figure 2. The leaching rate of Ni was low, which was consistent with the results obtained by other studies or our previous study.19 The addition of CaO had a great influence on the leaching rates of As, Cd, Cu, and Mn. When the temperature was 750 and 850 °C, with the increasing proportion of CaO, the leaching rates of As and Cd decreased gradually, which showed a linear change. When the temperature was 750 and 850 °C, with the increasing proportion of CaO, the leaching rates of As and Cd decreased gradually. However, the effects of CaO on the leaching rates of other HMs were not consistent. When the temperature reached 950 °C, there was no regular change of the leaching rates of all HMs. It was not only proving the inconsistency of leaching rates but also the necessity of proposing a new method to evaluate the control efficiency of HM emissions. According to Figure 2, it can also be seen that under the same addition of CaO, with an increase of temperature, the leaching rates of HMs continuously decreased, which was consistent with the discussion above. Generally speaking, the interaction between the active center of CaO and HMs depended on the chemical nature of the HMs. Distribution of these active sites was not uniform, and a competition of the HMs for the active sites was selective, therefore resulting in a difference in the leaching rates of HMs.

3.3. Effect of Incineration Temperature on Stabilized Rates of HMs during Incineration. Figure 3 shows that temperature had a great influence on the stabilized rates of HMs during incineration, which was similar to other studies,20 while higher incineration temperatures resulted in increase of the volatilization of HMs due to easier formation of volatile trace-metal oxide. The stabilized rate of Cr was between 56
and 75%, while that of Cd was around 30%. The maximum stabilized rates for Cu (96%) and Mn (92%) were obtained when the incineration temperature was 850 °C. As the temperature increased, the stabilized rate of Zn increased from 37 to 62%. Vogel et al.\textsuperscript{21} have found that Zn$_2$SiO$_4$ or ZnAl$_2$O$_4$ can be formed during high-temperature thermal treatment, which inhibits the volatilization of ZnO and increased the stabilized rate of Zn. This was the major reason for the change in the stabilized rate of Zn. The stabilized rate of Cd increased obviously as temperature increased and was about 32% when the temperature was 950 °C. Because of the high volatility of Pb, the stabilized rate decreased to 39% when the temperature reached 950 °C. Complete oxidation of HMs will be promoted when the incineration temperature increased, which would fix HMs in the slag more and reduce the potential threat to humans.\textsuperscript{22}

### 3.4. Influence of Additive (CaO) on the Stabilized Rates of HMs during Incineration.

The stabilized rates of HMs under different additions of CaO are shown in Figure 4. At 750 °C, with an increase of CaO, the stabilized rates of As, Cd, Cr, Mn, and Cu increased gradually, while the stabilized rates of Pb and Zn decreased slightly. When the temperature reached 850 °C, with increasing CaO, there was no notable change in the stabilized rates of HMs. However, the stabilized rate of As increased initially and decreased afterward, reaching its maximum value on the addition of CaO. When the temperature reaches 950 °C and the ratio of CaO was 6%, stabilized rates of some HMs increased slightly. According to Figure 4 and the discussion above, when the addition of CaO was 4%, it could better fix HMs in the bottom slag during the
process of incineration, which was consistent with the literature data.23

3.5. Comprehensive Evaluation of the Control Efficiency of HM Emissions during Incineration. Figure 5 shows the comprehensive control efficiency of HM emissions during sludge incineration. With an increase in incineration temperature, the comprehensive control efficiency of HMs generally exhibited a consistent change and increased gradually. This was because HMs were easy to form their oxides during the thermal process, which can be transformed

Figure 4. Influence of additive (CaO) on the stabilized rates of HMs during incineration: (a) incineration temperature 750 °C; (b) incineration temperature 850 °C; (c) incineration temperature 950 °C.

Figure 5. Comprehensive evaluation of control efficiency of heavy-metal emissions during incineration: (a) effects of temperature and (b) effects of additive.
into the form of high-volatile chlorides and elemental form. However, their oxides may be combined with aluminosilicate at high temperatures. Therefore, HMs will be stabilized in the slag. With an increase of CaO, the comprehensive control efficiency decreased. The addition of CaO could promote the volatilization of HMs. Luan et al. found that the surface of the sludge without CaO was smooth and scaly, while that of sludge with CaO exhibited many regular columnar porous structures. The structure increased the surface area of the sludge particles, so the generated volatile heavy-metal chloride diffuses outward more easily, thereby improving the vitalization of HMs during sludge thermal treatment. Moreover, the effects of calcium on different HMs were different. It could also play a competitive role of HMs to occupy the position and maybe capture HMs, leading to the higher vitalization of HMs. Volatilization of HMs got its peak with a 6% CaO addition; however, it would be further explored whether the volatilization of HMs will increase with increasing addition of CaO in later experiments. In general, the addition of CaO has a great influence on the comprehensive control efficiency of HM emissions.

### 3.6. Effects of Calcination Temperature, Additive (NaCl), and Calcination Time on Leaching Rates of HMs during Calcination.

The effect of calcination temperature on leaching rates of HMs can be seen in Figure 6a. The leaching rate of Cr was low. With an increase of calcination temperature, the leaching rate of Zn increased, and the leaching rates of As and Cd first increased and then decreased. However, the leaching rates of Cu and Mn first decreased and then increased with increasing calcination temperature. Compared with the process of incineration, the leaching rates of HMs decreased obviously. The reason was that with the increase of calcination temperature, the amount of silicate or aluminosilicate compound of some HMs increased gradually during the process of sludge calcination, and HMs were blocked in the crystalline structures. In general, the leaching rates of HMs were not significantly affected by the calcination temperature. The leaching rates of HMs at different NaCl addition conditions are shown in Figure 6b. With the addition of NaCl, the leaching rate of Cr changed linearly, but it was still very low. The leaching rates of As and Cd first decreased and then increased with the increase of NaCl, and those of Zn and Cu increased with increasing NaCl. The leaching rate of Mn first increased and then decreased with an increase of NaCl. Overall, the leaching rates of HMs were kept below 5%. HMs were more transformed into the slag, reducing bioactivity. In general, the leaching rates of various HMs were significantly affected by the amount of chlorinating agents added. Figure 6c shows the effect of calcination time on the leaching rates of HMs. There was no obvious regular change. The leaching rates of various HMs were different because of their different contents and existence forms. With an increase of calcination time, the leaching rate of Cr increased but remained at a low level. The leaching rate of Mn was less affected by calcination time than other HMs.

### 3.7. Effects of Calcination Temperature, Additives (NaCl), and Calcination Time on Stabilized Rates of HMs during Calcination.

The HMs will evaporate when temperature...
atures reach near the boiling point of element or compound, which suggests that the emission of HMs will increase at high calcination temperatures. From Figure 7a, it could be seen that the stabilized rates of HMs decreased gradually with increasing calcination temperature. This was because temperature was the decisive factor for SS during calcination treatment. Within the temperature range of 900–1100 °C, removal of HMs increased with increasing temperature, with Zn being more evident. For Pb, As, and Cd, the reason was the three elements were mainly present as chlorides and oxides in the sludge and reached their boiling points at 900–1000 °C; therefore, large amounts of them were volatilized.

Calcination temperature had a significant effect during the process of volatilization of HMs. In general, high calcination temperature could improve vaporization of HMs via increasing vapor pressure and promoted sludge particle combustion. At a high calcination temperature, the vaporization rate of HMs is controlled by particle combustion. However, the influence of calcination temperature on the volatilization of HMs is still a complex process. It was still needing a lot of experimentations to explore specific reaction process and removal mechanism. According to Figure 7b, stabilized rates of HMs in slag decreased with increasing amount of NaCl during the process of calcination. The reason was that heavy-metal chlorides have a higher vapor pressure, and the participation of Cl in thermal treatment of sludge delays the condensation of metal compounds, thereby exacerbating volatilization of HMs. From Figure 7b, it can also see that the trends of decrease of Zn and Pb were more obvious than those of As and Cd; this was because that the gaseous HCl was produced by an intermediate mechanism in the removal of HMs (WO) by an inorganic chlorinating agent (MClx), which was different from the removal effect of Cl2 on HMs. HCl was more favorable for the removal of Zn and Pb, therefore causing a large amount of volatilizing of Zn and Pb. Figure 7c shows the changes in stabilized rates of HMs in the slag with increasing calcination time. As the calcination time increased, the stabilized rates of Cd and Zn decreased by 22 and 31%, respectively, while the stabilized rates of As and Pb did not present a regular change.

3.8. Comprehensive Evaluation of Control Efficiency of HM Emissions during Calcination. Figure 8 shows that calcination time had a great influence on the comprehensive control efficiency of HM emissions. When the calcination time was 20, 30, and 40 min, the comprehensive control efficiencies of HM emissions were 43, 53, and 59%, respectively. Therefore, we can conclude that an appropriate calcination time should be used to achieve a higher comprehensive control efficiency. The volatilization of HMs in the waste will be promoted during the process of high-temperature thermal treatment by adding an appropriate content of chlorine to the waste system. From Figure 8, it can be seen that the comprehensive control efficiency gradually decreased and was lower with the addition of NaCl, which can be explained by the angle of mass transfer. The removal of HMs from sludge slag...
was a complex, thermochemical process involving related chemical reactions and heat and mass transfer processes. Heavy-metal compounds in sludge ash reacted with the chlorinating agent to form volatile heavy-metal chlorides. Under high-temperature conditions, the generated heavy-metal chloride volatilizes and diffuses to porous sludge ash particles, which improved the heavy-metal removal rate. When the ratio of NaCl was 5%, the comprehensive control efficiency reached its highest value (27%). On the one hand, the function of chlorides to volatilization of HMs relied on their ability to release chlorine radicals; on the other hand, the chlorine binding ability with heavy metals is also important. According to a previous study,33,36 volatilization of HMs has a strong positive relationship with the addition of chlorides during the process of calcination, and HMs were supposed to be oxides at the conceived temperature. Besides, during the process of calcination, Cl was easily transformed into HCl and other forms, including Cl, Cl₂, ClO, and HOCl.33 From the above discussion, it can see that the addition of chlorides showed a positive relationship with the volatilization of HMs. Figure 8 also indicates that with increasing calcination temperature, the comprehensive control efficiency gradually decreased. When the calcination temperature was 1100 and 1050 °C, the comprehensive control efficiencies were 20 and 53%, respectively. When the temperature was 950 °C, the highest comprehensive control efficiency (67%) was achieved. Therefore, an appropriate calcination temperature can achieve a higher comprehensive control efficiency of HM emissions.

### 4. CONCLUSIONS

A new comprehensive evaluation method of HMs control efficiency was adopted in this paper. Application of this method in the incineration and calcination of sludge showed that the comprehensive control efficiency of the incineration process was much better than that of the calcination process. This study demonstrated that compared to the evaluation standards of HM control efficiency: leaching rates and stabilized rates, this method is unique and accurate for different HMs, and it also has consistency when it was used to evaluate the superiority of different operating conditions. Therefore, it could be used in the technology selection and optimization of HM control accurately. Further work on the application of this method will be the evaluation of comprehensive control efficiency of HMs in municipal solid waste incineration.

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#### Notes

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