Slagging characteristics caused by alkali and alkaline earth metals during municipal solid waste and sewage sludge co-incineration

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ABSTRACT

Municipal solid waste (MSW) and sewage sludge co-incineration is developing into a new method for sludge treatment. However, waste and sludge containing high levels of alkali and alkaline earth metals (AAEMs) will likely cause slagging, corrosion and deterioration of materials during incineration. The occurrence of AAEMs is studied through extraction experiments. Additionally, the surface microstructure and composition of samples are analyzed by SEM-EDS. XRF and XRD are used to analyze the content and crystalline phases of AAEMs. The experimental results indicate that slagging samples are characterized by high amounts of Ca, Na, K, Cl, and S elements. The samples contain numerous irregular particles due to the condensation and nucleation of AAEMs. The extraction experiments and XRD analyses indicate that the insoluble AAEMs are primarily Ca-diopside and gehlenite and Na and K-aluminosilicates in the furnace. The ammonium acetate-soluble Ca consists mainly of sulfates, and the water-soluble Na and K consist of alkali chlorides in the superheaters. In the reaction tower, AAEMs mainly exist as carbonates and the slagging mechanisms are caused by soda manufacture process. The transformation and deposition of AAEMs enhance the slagging and reduce the heat transfer efficiency. The release of AAEMs can be effectively decreased through using sludge granulation technology during MSW and sludge co-incineration, and the furnace running time is extended.

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1. Introduction

In recent years, municipal solid waste (MSW) and sewage sludge co-incineration for energy generation has been used as an efficient method for the harmless treatment of sludge [1–3]. The thermal conversion of waste can realize the reduction, harmlessness and resource utilization of waste, which are of great significance for alleviating the problems of environmental pollution and energy shortage as a result of rapid economic development in China [4–6]. However, the main problem of MSW and sewage sludge co-incineration is that the addition of sludge will increase the yield of ash containing high concentration of chlorine, sulfur, as well as alkali and alkaline earth metals (AAEMs), which will reduce the melting point of ash and enhance the slagging characteristics of ash [7,8]. However, most of previous studies [8–11] mainly focuses on

the pollution cause by heavy metals and ignores the influence of AAEMs on incineration process. In wastes, all kinds of plastics, kitchen waste, building materials and sewage sludge may create high amounts of AAEMs, which will cause deposition, slagging, corrosion, and deterioration of materials during incineration [12,13]. The energy efficiency is also reduced due to formation of hard and voluminous deposits on the surfaces of heat-exchange facilities [14,15]. This results in reducing the stable running time, increasing operational hazards and decreasing economic benefit.

During incineration, some alkali/alkaline metals can react with silicon aluminum oxides to form relatively high melting point compounds [16,17]. In addition, Ca, Na and K are generally released as CaCl_2 , NaCl and KCl [18,19], and alkali/alkaline metal sulfates are produced in the presence of sulfur in effluent gas [20,21]. These sulfates are more stable than chlorides. Alkali/alkaline metal chlorides and sulfates are inclined to deposit on the surface of facilities [22–24], which can cause corrosion of facilities. At present, the behavior of AAEMs has been studied to some extent during pure MSW incineration. Yu et al. [25] studied the solid residues

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originating from CFB combustion of MSW through a detailed physical and chemical characterization and found that the major compounds in the bottom ashes and fly ashes were CaCO_3 , CaCl_2 , CaSO_4 , NaCl and KCl . Tortosa et al. [26] reported that ash rich in NaCl and KCl could decrease the ash melting point, plant efficiency and availability by evaluating the validity of thermal analysis methods to characterize the fusion of biomass and waste ashes. Lebel et al. [27] confirmed that the sulfates formed by Na , K and Ca were the main corrosion deposits via simultaneous simulation of the temperature gradient at the flue-gas/tube interface, and the velocities of flue-gas and ash in a laboratory-scale corrosion pilot. Brossard et al. [28] also reported that combustion of municipal waste would generate highly corrosive gases, such as HCl , SO_2 , NaCl , KCl , and heavy metals chlorides. However, few studies can systematically report the migration and deposition of AAEMs from furnace to reaction tower and slagging phenomenon caused by AAEMs during MSW and sewage sludge co-incineration. Compared with conventional MSW, sludge contains higher concentrations of Cl and S , in addition to Ca , Na and K [16,29], which can promote the release of AAEMs [18,30,31], and then enhance the slagging and corrosion phenomena [32,33].

Because of the complex composition of the wastes, it is difficult to directly study the migration of AAEMs and the slagging phenomenon caused by AAEMs under laboratory conditions. Lin et al. [34] tried to simulate the procedure of co-incineration of sewage sludge with MSW in a full-scale grate furnace incinerator. They found that the simulation results can reflect the actual operating conditions, and also prove the reliability of the mathematical and physical model. Based on the FactSage thermodynamic calculation package and databases, Poole, et al. [35] predicted the equilibrium composition of the solid, liquid and gaseous products from municipal solid waste incineration. They thought an increase in alkali content is predicted to increase the amount of gaseous species involving alkali metals and the amount of slag is also increased. Otsuka [32] also conducted a thermodynamic equilibrium calculation to understand the effects of tube wall temperature, flue gas temperature, and waste chemistry on the type and amount of vapor-condensed “corrosive” salts and found that chlorine, sulfur, sodium, potassium, and calcium contents in waste affected the deposition formation.

Although the calculation can better predict the incineration process of waste, the migration and deposition of mineral elements such as AAEMs and how to cause slagging phenomenon are not completely and accurately presented. To fully understand and reveal the actual slagging and corrosion mechanism in facilities, such as furnace, heat exchangers and reaction tower, the release, transformation and deposition paths of AAEMs are indirectly inferred through investigating the occurrence mode and crystal structure of AAEMs in slagging samples at different positions. Accordingly, AAEMs can be categorized into four occurrence modes according to a sequential extraction method [36]: water soluble (deionized water), exchangeable (ammonium acetate), acid soluble (hydrochloric acid) and acid insoluble (aqua regia). The water-soluble alkali metals (NaCl , KCl , and Na_2SO_4 etc.) and acetate-soluble alkaline earth metal (CaSO_4) are usually the main forms that cause the slagging and corrosion [37–40]. The addition of sewage sludge rich in Cl and S into waste will promote the release of AAEMs during MSW incineration. Therefore, there is an urgent need to develop a method for pretreatment of sludge to reduce the release of Cl and S during incineration.

The aim of this paper is to study the release, transformation and deposition paths of AAEMs during MSW and sludge co-incineration and formation mechanisms of slagging samples that are obtained from four different positions: furnace, high-temperature superheater, medium-temperature superheater and reaction tower.

Firstly, scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) and X-ray fluorescence (XRF) are used to analyze the surface microstructures and the content of elements. The occurrence modes of AAEMs and the contents can be determined by chemical extraction methods. The detailed crystalline phases of AAEMs are studied by X-ray diffraction (XRD). Secondly, the release and migration paths of AAEMs are predicted based on the above results. Particularly, the mechanisms of transformation and slagging of AAEMs in the furnace, superheaters and reaction tower are discussed. Finally, during the actual operation of the plant, the paper discusses how sludge granulation affects the release of AAEMs and furnace running time through studying three different waste feeding methods, such as pure waste, waste and sludge, as well as waste and granulated sludge. And the effectiveness and practicality of sludge granulation are evaluated during actual MSW and sewage sludge co-incineration.

2. Experimental section

2.1. Experimental materials

Waste (90%) mixed with sludge (10%) incineration takes place in the combustion chamber on a moving grate (as shown in Fig. 1(a)), which located in Yantai, Shandong, China, which handles 580 tons of MSW, which includes all kinds of plastics (approximately 6.8%), kitchen waste (approximately 33.4%), yard waste (approximately 10.6%), paper (approximately 6.7%), fabric (approximately 4.2%), glass (approximately 2.3%), metals (approximately 2.5%), building materials (approximately 27.4%) and others (approximately 6.1%).

Fig. 1. (a) Schematic of the waste-to-energy facility located in Yantai, Shandong, China: (A) furnace, (B) high-temperature superheater, (C) medium-temperature superheater, and (D) reaction tower. (b) Gas temperature corresponding to the slagging position.

According to the results provided by plant laboratory, the mass fraction of AAEMs is approximately 2.62–4.28%, that of Cl is approximately 0.11–0.35%, and that of S is approximately 0.14–0.43%. Primary air is injected through the grate and secondary air is introduced through the wall of the furnace chamber. The walls of the combustion chamber are made of evaporator tubes (water-wall) producing saturated steam going to the drum. Incineration gases including AAEMs, leave the furnace at a temperature near 1173 K, and go through the waste heat boiler pass, where several types of heat-exchangers are positioned. After that, the flue gas will enter the reaction tower for deacidification. Samples as received from A, B, C and D in Fig. 1(a) are ground to powder and sieved to particle sizes between 60 and 105 μm , named FU, HTS, MTS, and RT, respectively. The samples are dried at 378 K for 2 h and stored as experimental samples. The gas temperatures of the sample positions are shown in Fig. 1(b).

The composition analysis of slagging samples is listed in Table 1. Obviously, slagging samples are characterized by high levels of Ca, Na and K. For example, the Ca content of the high-temperature surface of superheater is approximately 30% and the content is 10% for alkali metals (Na and K). In addition, the Na content in the slagging sample is relatively high in the reaction tower, indicating that a large amount of Na in the flue gas is captured during deacidification. This process will seriously cause alkali corrosion to the equipment and affect the safe operation of facilities.

The sewage sludge treated by waste-to-energy plants mainly comes from domestic wastewater treatment. The physicochemical properties of the sludge feedstock used in this work are shown in Table 2. The sludge is not only rich in AAEMs, but also contains high contents of Cl and S. Sludge addition further aggravates the release of AAEMs, which will cause serious slagging and corrosion of the equipment. This process increases the operational risks of the equipment and reduces the economic benefits.

2.2. Experimental procedures

2.2.1. Chemical extraction experiments

All the sieved slagging samples are dried again in an oven at 378 K in a N_2 atmosphere for 1 h before conducting the experiments. Based on the study of Benson [41] on low-rank coals, a four-step sequential extraction method is employed. Water soluble: 0.5 g slagging samples and 50 ml deionized water are mixed in a 100 ml polyethylene centrifuge tube. Then, the tube is placed in a 333 K water bath at a constant temperature for more than 24 h with centrifugation at 200 rpm/min. The water soluble Ca, Na and K analysis can be determined by the washing solution. The residue is used for the next step. Exchangeable: 50 ml of the 1 mol/L NH_4OAc buffer solution is added to the residue and the above operation is repeated. Acid soluble: the solution used for the residue is 1 mol/L HCl, and the step is the same as that of the exchangeable step. The measured Ca, Na and K are acid soluble. The residue collected from the above step is dried in an oven at 378 K in a N_2 atmosphere for 1 h and then digested by using HNO_3 and HF. Later, the vessel is heated to 493 K and kept at that temperature for 1 h. Then the solution is diluted to 100 mL for Ca, Na and K measurement, and the results show the acid insoluble AAEMs. In each step, the Ca, Na and

Table 2
Physicochemical properties of the sludge (dry basis).

Item	Unit	Value
Proximate analysis (dry basis)		
Ash	wt.%	35.173
Volatile matter	wt.%	55.487
Fixed carbon	wt.%	9.34
Ultimate analysis (dry basis)		
C	wt.%	22.07
H	wt.%	5.538
O	wt.%	31.26
N	wt.%	3.6
S	wt.%	1.379
Cl	wt.%	0.98
Mineral composition (dry basis)		
Ca	mg/g	31.52
Na	mg/g	3.61
K	mg/g	5.01

K species that dissolved in solutions, are measured by an ICAP 6000 Series. A weight basis is used for presentation of the contents of AAEMs. The relative standard deviation (RSD) is controlled within 5% by performing three replicates of the samples.

2.2.2. Characterization methods

A scanning electron microscope (JSM-7800 F, JEOL, Japan) with a scanning electron microscopy-energy dispersive spectrometer (SEM-EDS) with the typical accelerating voltage of 20 kV, is used to observe the morphology and composition of slagging samples. The contents are analyzed by XRF using an energy dispersive instrument (E3, Netherlands) with 0.05% error. The crystalline phase analysis is determined by powder XRD using a Rigaku D/MAC/max 2500 v/pc instrument (DX2700, China) with Cu K α radiation (40 Kv, 200 mA, $\lambda = 1.5418 \text{ \AA}$) with 0.05% error. Diffractometer data is acquired with a step size of 0.02° for 2θ values from 5 to 80° . The crystalline phases are analyzed based on the Jade 6.0 database.

3. Results and discussion

3.1. Morphology and composition of slagging samples

AAEMs are released from the fuel into the flue gas during incineration and are inclined to combine with fly ash, which results in reducing the melting point and promoting the conversion of ash into slag [26–28]. When gas enters the waste heat boiler, as the temperature decreased, AAEMs precipitate from the effluent gas and condenses on the high-temperature surface of the heat exchangers or other facilities, causing slagging and corrosion. The detailed images of slagging morphology obtained from SEM are shown in Fig. 2. The surface of slagging samples is inhomogeneous and contains numerous irregular particles. EDS analysis can determine the compositions and contents of the four slagging samples. Yu et al. [42] thought that the surface micrographs of samples rich in Ca and Cl contained numerous irregular materials, and homogeneous and smoother crystallites were characteristic of high amounts of Cl, S, Na and K. The sample collected from the furnace is characterized as high amounts of Ca, Al, Si, Mg, etc.

Table 1
Ash analysis of slagging sample compositions (wt.%).

Sample	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	SO ₃	P ₂ O ₅	Cl
FU	26.357	3.62	3.08	1.38	8.489	12.615	39.514	1.356	0.359	2.291	0.172
HTS	27.256	3.893	5.05	5.344	3.141	2.975	12.999	0.528	27.096	1.016	6.518
MTS	32.392	2.968	4.15	5.14	4.083	4.421	6.286	0.963	30.045	1.716	4.323
RT	29.331	3.418	20.942	0.8	1.82	2.792	6.125	0.408	7.503	0.909	1.517

Fig. 2. Results of SEM-EDS for four slagging samples during incineration.

elements. The two samples obtained from the high-temperature and medium-temperature superheaters are mainly composed of Ca, S, etc. elements, which has been also confirmed by some other researchers [37,43]. The slag from the reaction tower is characterized by high concentrations of Na, Ca, etc. elements. However, there are few reports on the slagging phenomenon in the reaction tower. As determined by EDS in the FU, the hardness of the slag is very high and contains many glassy crystallites and irregular materials due to relatively high contents of Ca and Si. Comparatively, Ca and S are enriched in HTS and MTS, and the morphology is inhomogeneous, indicating the presence of sulfates of Ca. The positions characterized as high amounts of Ca and Na in the RT, are relatively smooth. Therefore, it can be inferred that the irregular particles may be formed by the condensation, nucleation or coagulation of AAEMs [40].

As shown in Fig. 3, the results obtained from slagging compositions and EDS analysis are consistent with the conclusions determined by XRF, which indicate that the contents of AAEMs are relatively high in the slagging samples. According to Song et al. [44] and Oleschko et al. [45], alkali metals were easily released in the form of chloride or sulfate. Therefore, the content of Na, K, Cl and S

in the FU is relatively low, and the main reason is that alkali metals can be released into the flue gas with the release of Cl and S during incineration. In addition, Qi, et al. [46] found that minerals such as Si and Al can inhibit the release of alkali metals by forming high melting point of aluminosilicate. The measured results also indicate that a small amount of alkali metals still exists in the furnace, which proving that a small amount of gas phase alkali metals may react with silicon aluminum oxide to form aluminosilicate. The alkaline earth metal Ca can also react with SiO_2 , etc. to form a low melting point compound at a high temperature, which can adheres to the furnace, which is confirmed by Poole et al. [35] and Okuno et al. [47]. Therefore, the content of Ca is relatively high and reached to 19% in the furnace. The slagging samples collected from superheaters are mainly consisted of Ca and S. Compared with HTS, as the gas temperature decreased in the MTS, the deposition process of AAEMs on the surface of the superheater is enhanced, which indicate that the temperature has an important role in the condensation of gaseous AAEMs [40]. For example, the content of Ca is increased from 20.47% to 24.45% with reducing the gas temperature. Moreover, some of the alkali metals Na and K also precipitate from the flue gas and adhere to the heat exchanger, which is also proved by Lebel et al. [27]. In the RT, slurry is employed to realize deacidification during incineration, so the content of Ca is relatively high in the slagging sample. In addition, the weight percentage of Na reaches to 20.8%, which indicating that alkali metal Na can be trapped from the gas during deacidification, resulting in slagging and deterioration of materials.

3.2. Occurrence modes of AAEMs in slagging samples

The total amount of Ca, Na and K determined in each step (the stack column) and the total contents of Ca, Na and K via microwave digestion in the slagging samples (denoted by asterisks), are described in Fig. 4. The results of the extraction experiments indicate that most of the Ca, Na and K are acid-insoluble, approximately accounting for 90.8%, 93%, and 92.3% of the total content, respectively in the FU. And the amount of Ca, Na and K in water-soluble, ammonium acetate-soluble and acid-soluble modes is relatively low in comparison to the existing forms of insoluble AAEMs. According to Phongphiphat et al. [48], the slagging samples consisting of AAEMs are mainly generated by reaction between Ca, Na, and K and silicon aluminum oxide in the FU. However, for the slagging samples from the high-temperature surface of the superheaters, Ca

Fig. 3. Contents of Ca, Na, K, Cl and S in four slagging samples.

Fig. 4. Summation of AAEMs contents using different extraction methods.

is mainly present in the ammonium acetate-soluble form, and Na and K are mainly present in the water-soluble mode. For example, in the HTS, the acetate-soluble form of Ca approximately accounts for 72%, and the water-soluble forms of Na and K approximately accounts for 94% and 90%, respectively. This is mainly because AAEMs are easily volatilized into the flue gas in the form of chlorides and sulfates during incineration and similar conclusion is also gained by Brossard et al. [28] and Otsuka [32]. And as the gas temperature decreased due to waste heat recovery in the waste heat boiler, the AAEMs will condense and deposit on the surface of the superheaters. For example, compared with HTS, the content of ammonium acetate-soluble Ca increases about 21% in the MTS, indicating that gaseous Ca can precipitate from the flue gas with decreasing temperature. In addition, acid-soluble and insoluble AAEMs did not observably increase, indicating that they are present when the slagging samples are initially formed and did not obviously precipitate from the flue gas. For the slagging sample collected from the RT, the results are similar to those of HTS and MTS. The conclusions indicate that Ca mainly exists in the form of ammonium acetate-soluble form, and Na is mainly water-soluble. The alkali metal K is not found in the slagging sample, indicating that K is not trapped in the RT. In addition, the content of acid-soluble Ca increases, indicating that other types of Ca compounds form during deacidification.

3.3. Crystalline phase analysis of AAEMs in slagging samples

As shown in Fig. 5, XRD analyses are conducted to determine the main crystalline phase to study the detailed compositions and compounds in the four slagging samples. The absorbance band areas of each crystalline phase are related to their percentages [49]. Acid-insoluble diopside ($\text{Ca}_2\text{MgFeSi}_4\text{O}_{12}$), gehlenite ($\text{Ca}_2\text{MgAl}_2\text{Si}_2\text{O}_{10}$) and sodium and potassium aluminum silicates ($\text{NaAlSi}_2\text{O}_6$, KAlSi_2O_6) make up the main AAEM phases in the FU; however, other occurrence forms of AAEMs are relatively small. In addition, some AAEMs will be released in the form of chloride as CaCl_2 , NaCl or KCl during incineration [18,50]. In the HTS and MTS, the Na and K crystalline phases are alkali chlorides, such as NaCl or KCl, whereas the Ca crystalline phases are mainly sulfates, indicating that CaCl_2 is sulfated in the presence of SO_2 or SO_3 during incineration. This conclusion is consistent with that of XRF analysis in Fig. 3. Considering that the melting point of CaCl_2 is 1055 K, that of NaCl is 1074 K and that of KCl is 1043 K, when the gas temperature exceeds

Fig. 5. XRD patterns of four slags during MSWI. The main crystalline phases can be shown as (1) Anhydrite CaSO_4 , (2) Halite (NaCl), (3) Sylvite (KCl), (4) Diopside ($\text{Ca}_2\text{MgFeSi}_4\text{O}_{11}$), (5) Pirssonite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), (6) Sodium carbonate hydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), (7) Gehlenite ($\text{Ca}_2\text{MgAl}_2\text{Si}_2\text{O}_{10}$), (8) Sodium aluminum silicate ($\text{NaAlSi}_2\text{O}_6$), and (9) Potassium aluminum silicate (KAlSi_2O_6).

the melting point of the reactants, the gaseous reaction plays an important role in the sulfation of CaCl_2 , NaCl, and KCl. The main reaction is as follows: $2\text{CaCl}_2 (\text{g}) + 2\text{SO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{g}) + \text{O}_2 (\text{g}) = 2\text{CaSO}_4 (\text{s}) + 4\text{HCl} (\text{g})$, where the CaCl_2 can be replaced by NaCl and KCl. However, alkali metal (Na or K) sulfates are not obviously found, indicating that CaCl_2 might be able to undergo displacement reactions with alkali metal sulfates to inhibit their formation, which is also confirmed by Pyykönen et al. [23]. In the RT, The main crystalline phases are pirssonite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and sodium carbonate hydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). Before the flue gas enters the reaction tower, most of the CaSO_4 has deposited in the flue gas, and NaCl and residual NH_3 react with the lime slurry ($\text{Ca}(\text{OH})_2$) during the deacidification process in the RT. When the gas temperature is relatively low, R1-R3 can become dominant due to Hou's process (for soda manufacture). This result also indicates the reason that peak positions of NaCl disappear in the RT slag. The major reactions can be expressed as follows:

Fig. 5 also presents the various band positions for the main crystalline phases in the four slagging samples. For example, the diopside bands in the FU are mainly characterized by peaks at 29.8° , 35.0° , and 35.5° ; the anhydrite bands in the HTS and MTS are found in peaks at 25.4° , 31.3° , 38.6° , and 40.8° ; and the pirssonite bands in the RT show peaks at 28.2° , 33.6° and 35.8° . The different bands of each crystalline phase indicate that the crystal structure planes are diverse, representing $(-2\ 2\ 1)$, $(-1\ 3\ 1)$, and $(2\ 2\ 1)$ for diopside; $(2\ 0\ 0)$, $(1\ 0\ 2)$, $(2\ 0\ 2)$, and $(1\ 2\ 2)$ for anhydrite; and $(3\ 1\ 1)$, $(2\ 0\ 2)$, and $(3\ 5\ 1)$ for pirssonite. The main absorbance band is characterized by a peak at 29.8° for diopside, 25.4° for anhydrite, and 33.6° and 35.8° for pirssonite. This is the main key positions that cause the content of Ca, Na, and K to increase in the slagging samples.

Based on XRD results, Fig. 6 illustrates the total Ca, Na and K contents as determined by XRF and chemical extraction

Fig. 6. Comparison of AAEM contents determined by XRF and chemical extraction.

experiments, respectively. The results gained from XRF are consistent with those of chemical extraction in the FU, HTS and MTS, except for RT. The contents of Ca and Na determined by XRF are 30.9% and 20.8%, respectively, while that determined by chemical extraction are 18.5% and 12.7%, respectively. The main reason is that the slagging sample in the reaction tower contains a large amount of carbonate (CaCO_3 , Na_2CO_3). When XRF analysis is carried out, only Ca and Na are considered, and the remaining content of CO_3 (release as CO_2 , named as loss on ignition (LOI)) is not considered, resulting in a larger weight fraction of Ca and Na. The all CO_2 in the RT are assumed to come from CaCO_3 and Na_2CO_3 and the weight fraction of CO_2 can be determined by that of CaO and Na_2O . The real contents of Ca and Na in the slagging sample can be obtained after conversion by the following formulas:

$$W_{\text{Ca}}(\%) = \frac{W_{\text{CaO}}}{100 + M_{\text{CO}_2} \left(\frac{W_{\text{CaO}}}{M_{\text{CaO}}} + \frac{W_{\text{Na}_2\text{O}}}{M_{\text{Na}_2\text{O}}} \right)} \frac{M_{\text{Ca}}}{M_{\text{CaO}}}$$

$$W_{\text{Na}}(\%) = \frac{W_{\text{Na}_2\text{O}}}{100 + M_{\text{CO}_2} \left(\frac{W_{\text{CaO}}}{M_{\text{CaO}}} + \frac{W_{\text{Na}_2\text{O}}}{M_{\text{Na}_2\text{O}}} \right)} \frac{2M_{\text{Na}}}{M_{\text{Na}_2\text{O}}}$$

where W presents the weight fraction; M presents the relative atomic mass: $M_{\text{C}} = 12$; $M_{\text{O}} = 16$; $M_{\text{Na}} = 23$; $M_{\text{Ca}} = 40$. The results are shown as black solid squares and circles in Fig. 6. The contents of Ca and Na determined after considering released CO_2 are 20% and 13.4%, respectively and the results are basically consistent with the results obtained by the extraction experiment. This also shows that the AAEM carbonates are the main components in the slagging sample from the RT.

3.4. Analysis of the migration paths of AAEMs during incineration

Fig. 7 illustrates the release and migration paths of AAEMs, which can be predicted based on some conclusions provided by other researchers and our experimental results. At the beginning of incineration, a large proportion of Ca, Na, and K are released as gaseous metallic calcium, sodium, and potassium from raw materials, such as CaCl_2 , NaCl , and KCl . Meanwhile, a small amount of AAEMs can react with silicon and aluminum oxides, etc. to form Ca-diopsides and gehlenite and Na- (or K-) aluminosilicates, which can adhere to the furnace. The gaseous AAEM chlorides can react with

Fig. 7. Mechanisms of Na, K and Ca transformation, condensation and corrosion.

SO_2 to form AAEM sulfates in the oxidizing atmosphere when the temperature reaches the melting point of the reactants. When AAEM chlorides and sulfates leave the furnace and enter the waste heat boiler, the AAEM vapors or aerosols can condense onto the surface of the superheaters as gas temperature decreased, which will cause slagging and corrosion phenomenon. In addition, when some uncondensed NaCl enters the reaction tower, in which NH_3 and CO_2 are present, the process for soda manufacture is carried out and generates NaHCO_3 . The lime slurry (Ca(OH)_2) added in the deacidification process will react with baking soda (NaHCO_3) to form pirssonite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), which can contribute to the slagging phenomenon in reaction tower.

The above results show that Cl and S in the raw materials have an important influence on the release of AAEMs. The content of ash rich in Cl and S increases with the addition of sludge and the release of AAEMs is promoted, thereby enhancing the problem of slagging and corrosion caused by AAEMs. Therefore, the pretreatment of sludge is an effective way to solve this problem. In this paper, the treatment method of sewage sludge is sludge granulation [51,52], which can be achieved by a granulator. As shown in Fig. 8, the furnace running time of different feeding methods is counted in the actual plant and the difference between average running time and maximum time or minimum time is used as the uncertainty. It can be found that there is a significant difference in the running time due to the slagging problem by comparing three incinerators using different raw materials, for example, pure waste incineration is approximately 7–13 months, waste and sludge is 2–4 months, and waste and granulated sludge is 4–8 months. These results show that sludge granulation can significantly increase the furnace running time. The main reason can be considered that sludge granulation reduces the mutual contact area between sludge and waste during incineration, and thus reduces the chances of Cl and AAEMs forming chlorides. Therefore, the release of AAEMs is

Fig. 8. Furnace running time caused by slagging for three different feeding methods.

inhibited during incineration, and the slagging and corrosion problems caused by AAEMs are also weakened. In addition, the weight of sludge is increased after granulation, which can reduce the quantity of ash entrained by flue gas. Finally, the additives in the sludge granulation process may also inhibit the release of AAEMs. As a result, the running time can be extended.

4. Conclusions

In this paper, the slagging mechanisms caused by AAEMs during MSW and sewage sludge co-incineration are systematically studied through extraction experiments and characterization methods. The slagging samples obtained from four typical positions, named as furnace, high-temperature superheater, medium-temperature superheater and reaction tower, are selected to indirectly reveal the transformation and deposition mechanisms of AAEMs. Furthermore, the effect mechanisms of sludge granulation on the release of AAEMs and furnace running time are analyzed through comparing three different feeding methods. The main conclusions can be shown as:

- (1) The AAEMs mainly present insoluble forms, such as diopside ($\text{Ca}_2\text{MgFeSi}_4\text{O}_{12}$), gehlenite ($\text{Ca}_2\text{MgAl}_2\text{Si}_2\text{O}_{10}$) and sodium and potassium aluminosilicates ($\text{NaAlSi}_2\text{O}_6$, KAlSi_2O_6), in the furnace, as determined by crystalline analysis results by XRD. The alkaline earth metal (Ca) primarily presents in ammonium acetate-soluble form as CaSO_4 , and the alkali metals (Na and K) are primarily in water-soluble form as NaCl and KCl in the superheaters. In reaction tower, pirssonite ($\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ are the main existence forms.
- (2) The AAEMs in waste mainly release in the form of gaseous CaCl_2 , NaCl and KCl. Meanwhile, a small amount of AAEMs can react with silicon and aluminum oxides, etc. to form aluminosilicates, which can adhere to the furnace. The gaseous AAEM chlorides can also react with SO_2 to form AAEM sulfates, which can cause slagging phenomenon on the high-temperature surface of superheaters. Compared with HTS, the content of ammonium acetate-soluble Ca increases approximately 21% in the MTS. In addition, when some uncondensed NaCl enters the reaction tower, the slagging phenomenon will occur under the combined action of soda manufacture and deacidification process.
- (3) During MSW and sewage sludge co-incineration, sludge granulation inhibits the release of AAEMs via reducing mutual contact area between sludge and waste, increasing the weight of sludge and adding additives. The slagging and corrosion problems caused by AAEMs are also weakened. The results show that sludge granulation can significantly increase the running time. Pure waste incineration is approximately 7–13 months, the co-incineration of waste and sludge is 2–4 months, as well as the co-incineration of waste and granulated sludge is 4–8 months.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Jing Zhao: Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft. **Xiaolin Wei:**

Conceptualization, Supervision, Methodology. **Yufeng Zhang:** Data curation, Visualization, Software. **Teng Li:** Conceptualization, Methodology, Supervision.

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Nomenclature

MSW	municipal solid waste
AAEMs	alkali and alkaline earth metals
SEM-EDS	scanning electron microscopy-energy dispersive spectrometry
XRF	X-ray fluorescence
XRD	X-ray diffraction
FU	furnace
HTS	high-temperature superheater
MTS	medium-temperature superheater
RT	reaction tower
RSD	relative standard deviation
LOI	Loss on ignition

Symbols

W	weight fraction (%)
M	relative atomic mass

References

- [1] Zhao YY, Zhan JY, Liu GR, Ren ZY, Zheng MH, Jin R, et al. Field study and theoretical evidence for the profiles and underlying mechanisms of PCDD/F formation in cement kilns co-incinerating municipal solid waste and sewage sludge. *Waste Manage* 2017;61:337–44.
- [2] Chin S, Jurng J, Lee JH, Hur JH. Oxygen-enriched air for co-incineration of organic sludges with municipal solid waste: a pilot plant experiment. *Waste Manage* 2008;28(12):2684–9.
- [3] Zhai YB, Peng C, Xu BB, Wang TF, Li CT, Zeng GM, Zhu Y. Hydrothermal carbonization of sewage sludge for char production with different waste biomass: effects of reaction temperature and energy recycling. *Energy* 2017;127:167–74.
- [4] Liu ZQ, Liu ZH, Li XL. Status and prospect of the application of municipal solid waste incineration in China. *Appl Therm Eng* 2006;26(11–12):1193–7.
- [5] Lai ZY, Ma XQ, Tang YT, Lin H. A study on municipal solid waste (MSW) combustion in N_2/O_2 and CO_2/O_2 atmosphere from the perspective of TGA. *Energy* 2011;36(2):819–24.
- [6] Shen BX, Lei Q. Study on MSW catalytic combustion by TGA. *Energy Convers Manage* 2006;47(11–12):1429–37.
- [7] You SM, Wang W, Dai YJ, Tong YW, Wang CH. Comparison of the co-gasification of sewage sludge and food wastes and cost-benefit analysis of gasification- and incineration-based waste treatment schemes. *Bioresour Technol* 2016;218:595–605.
- [8] Zha JR, Huang YJ, Xia WQ, Xia ZP, Liu CQ, Dong L, Liu LQ. Effect of mineral reaction between calcium and aluminosilicate on heavy metal behavior during sludge incineration. *Fuel* 2018;229:241–7.
- [9] Hu HY, Zhang X, Liu H, Chen DK, Li AJ, Yao H, et al. Mechanism of chromium oxidation by alkali and alkaline earth metals during municipal solid waste incineration. *P Combust Inst* 2015;35(2):2397–403.
- [10] Zhang H, He PJ, Shao LM. Fate of heavy metals during municipal solid waste incineration in Shanghai. *J Hazard Mater* 2008;156(1–3):365–73.
- [11] Wunsch P, Greilinger C, Bieniek D, Kettrup A. Investigation of the binding of heavy metals in thermally treated residues from waste incineration. *Chemosphere* 1996;32(11):2211–8.
- [12] Bashir MS, Jensen PA, Frandsen F, Wedel S, Dam-Johansen K, Wadenbäck J, Pedersen ST. Ash transformation and deposit build-up during biomass suspension and grate firing: full-scale experimental studies. *Fuel Process Technol* 2012;97(97):93–106.
- [13] Yoffe O, Wohlfarth A, Nathan Y, Cohen S, Minster T. Oil shale fueled FBC power plant-ash deposits and fouling problems. *Fuel* 2007;86(17):2714–27.
- [14] Nielsen HP, Baxter LL, Sclippa G, Morey C, Frandsen FJ, Dam-Johansen K. Deposition of potassium salts on heat transfer surfaces in straw-fired boilers: a pilot-scale study. *Fuel* 2000;79(2):131–9.
- [15] Frandsen FJ. Utilizing biomass and waste for power production: a decade of contributing to the understanding, interpretation and analysis of deposits and

- corrosion products. *Fuel* 2005;84(10):1277–94.
- [16] Han J, Xu MH, Yao H, Furuuchi M, Sakano T, Kim HJ. Influence of calcium chloride on the thermal behavior of heavy and alkali metals in sewage sludge incineration. *Waste Manage* 2008;28(5):833–9.
 - [17] Wang JR, Chen FM, Zhao B, Li XJ, Qin L. Volatilisation and transformation behavior of sodium species at high temperature and its influence on ash fusion temperatures. *Fuel Process Technol* 2017;155:209–15.
 - [18] Abbas Z, Moghaddam AP, Steenari BM. Release of salts from municipal solid waste combustion residues. *Waste Manage* 2003;23(4):291–305.
 - [19] Wu DY, Wang YH, Wang Y, Li S, Wei XL. Release of alkali metals during co-firing biomass and coal. *Renew Energ* 2016;96:91–7.
 - [20] Glarborg P, Marshall P. Mechanism and modeling of the formation of gaseous alkali sulfates. *Combust Flame* 2005;141(1–2):22–39.
 - [21] Jiang FH, Zhang SY, Huang XH, Wang CW, Li H, Zhang YF. Sodium vapor capture by coal ash during sodium-rich coal combustion. *Appl Therm Eng* 2019;161:114–27.
 - [22] Capablo J, Ballester J. Experimental study of the kinetics of sulfation of alkali chloride deposits. *Fuel Process Technol* 2015;140:215–21.
 - [23] Pyykönen J, Jokiniemi J. Modelling alkali chloride superheater deposition and its implications. *Fuel Process Technol* 2003;80(3):225–62.
 - [24] Rosner DE, Nagarajan R. Transport-induced shifts in condensate dew-point and composition in multicomponent systems with chemical reaction. *Chem Eng Sci* 1985;40(2):177–86.
 - [25] Yu J, Qiao Y, Sun LS, Jin LM, Wang WX, Ma C. Detoxification of ashes from a fluidized bed waste incinerator. *Chemosphere* 2015;134:346–54.
 - [26] Tortosa Masía AA, Buhre BJP, Gupta RP, Wall TF. Characterising ash of biomass and waste. *Fuel Process Technol* 2007;88(11–12):1071–81.
 - [27] Lebel F, Rapin C, Mareche JF, Podor R, Chaucherie X, Guernion PY, Brossard JM. Development of a laboratory-scale pilot for studying corrosion on MSWI heat exchangers. *Mater Sci Forum* 2008;595–598:271–80.
 - [28] Brossard JM, Diop I, Chaucherie X, Nicol F, Rapin C, Vilasi M. Superheater fireside corrosion mechanisms in MSWI plants: lab-scale study and on-site results. *Mater Corros* 2011;62(6):543–8.
 - [29] Naqvi SR, Tariq R, Hameed Z, Ali I, Taqvi SA, Naqvi M, Niazi MBK, Noor T, Farooq W. Pyrolysis of high-ash sewage sludge: thermo-kinetic study using TGA and artificial neural networks. *Fuel* 2018;233:529–38.
 - [30] Van Lith SC, Alonso-Ramírez V, Jensen PA, Frandsen FJ, Glarborg P. Release to the gas phase of inorganic elements during wood combustion. Part 1: development and evaluation of quantification methods. *Energy Fuel* 2006;20(3):964–78.
 - [31] Liu YQ, Cheng LM, Zhao YG, Ji JQ, Wang QH, Luo ZY. Transformation behavior of alkali metals in high-alkali coals. *Fuel Process Technol* 2018;169:288–94.
 - [32] Otsuka N. A thermodynamic approach on vapor-condensation of corrosive salts from flue gas on boiler tubes in waste incinerators. *Corros Sci* 2008;50(6):1627–36.
 - [33] Shinata Y. Accelerated oxidation rate of chromium induced by sodium chloride. *Oxid Met* 1987;27(5–6):315–32.
 - [34] Lin H, Ma XQ. Simulation of co-incineration of sewage sludge with municipal solid waste in a grate furnace incinerator. *Waste Manage* 2012;32:561–7.
 - [35] Poole D, Argent BB, Sharifi VN, Swithenbank J. Prediction of the distribution of alkali and trace elements between the condensed and gaseous phases in a municipal solid waste incinerator. *Fuel* 2008;87:1318–33.
 - [36] Yang YM, Wu YX, Zhang H, Zhang M, Liu Q, Yang HR, Lu JF. Improved sequential extraction method for determination of alkali and alkaline earth metals in Zhundong coals. *Fuel* 2016;181:951–7.
 - [37] Reichelt J, Pfrang-Stotz G, Bergfeldt B, Seifert H, Knapp P. Formation of deposits on the surfaces of superheaters and economisers of MSW incinerator plants. *Waste Manage* 2013;33(1):43–51.
 - [38] Kostakis G. Mineralogical composition of boiler fouling and slagging deposits and their relation to fly ashes: The case of Kardias power plant. *J Hazard Mater* 2011;185(2–3):1012–8.
 - [39] Hu BH, Huang QX, Buekens A, Chi Y, Yan JH. Co-gasification of municipal solid waste with high alkali coal char in a three-stage gasifier. *Energy Convers Manage* 2017;153:473–81.
 - [40] Zhao J, Wei XL, Li T, Li HX, Bin F. Behavior of alkali metals in fly ash during waste heat recovery for municipal solid waste incineration. *Energy Fuel* 2018;32(4):4417–23.
 - [41] Benson SA, Holm PL. Comparison of inorganics in three low-rank coals. *Ind Eng Chem Res* 1985;24(1):145–9.
 - [42] Yu J, Qiao Y, Jin LM, Ma C, Paterson N, Sun LS. Removal of toxic and alkali/alkaline earth metals during co-thermal treatment of two types of MSWI fly ashes in China. *Waste Manage* 2015;46:287–97.
 - [43] Chen GY, Zhang N, Ma WC, Rotter VS, Wang Y. Investigation of chloride deposit formation in a 24 MWe waste to energy plant. *Fuel* 2015;140:317–27.
 - [44] Song GL, Song WJ, Qi XB, Lu QG. Transformation characteristics of sodium of zhundong coal combustion/gasification in circulating fluidized bed. *Energy Fuel* 2016;30(4):3473–8.
 - [45] Oleschko H, Schimrosczyk A, Lippert H, Müller M. Influence of coal composition on the release of Na-, K-, Cl-, and S-species during the combustion of brown coal. *Fuel* 2007;86(15):2275–82.
 - [46] Qi XB, Song GL, Song WJ, Lu QG. Influence of sodium-based materials on the slagging characteristics of Zhundong coal. *J Energy Inst* 2017;90(6):914–22.
 - [47] Okuno T, Sonoyama N, Hayashi JI, Li CZ, Sathe C, Chiba T. Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass. *Energy Fuel* 2005;19(5):2164–71.
 - [48] Phongphiphat A, Ryu C, Finney KN, Sharifi VN, Swithenbank J. Ash deposit characterisation in a large-scale municipal waste-to-energy incineration plant. *J Hazard Mater* 2011;186(1):218–26.
 - [49] Hillier S. Accurate quantitative analysis of clay and other minerals in sandstones by XRD: comparison of a Rietveld and a reference intensity ratio (RIR) method and the importance of sample preparation. *Clay Miner* 2000;35(1):291–302.
 - [50] Du SL, Wang XH, Shao JG, Yang HP, Xu GF, Chen HP. Releasing behavior of chlorine and fluorine during agricultural waste pyrolysis. *Energy* 2014;74:295–300.
 - [51] Hulshoff Pol LW, de Castro Lopes SI, Lettinga G, Lens PNL. Anaerobic sludge granulation. *Water Res* 2014;38(6):1376–89.
 - [52] Kijo-Kleczkowska A, Sroda K, Kosowska-Golachowska M, Musial T, Wolski K. Mechanisms and kinetics of granulated sewage sludge combustion. *Waste Manage* 2015;46:459–71.