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Basic Research on Co-treatment of Municipal Solid Waste Incineration Fly Ash and Municipal Sludge for Energy-Saving Melting

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ABSTRACT: MSWI fly ash and municipal sludge are solid wastes. Melting vitrification treatment was a resource utilization method. However, the flow temperature of grate furnace MSWI fly ash and municipal sludge was high (>1325 °C), which increased the energy consumption in the melting process. MSWI fly ash contained a large amount of CaO, and municipal sludge contained a large amount of SiO₂, Al₂O₃, and Fe₂O₃. The temperature of melting vitrification can be reduced using these two kinds of CITY garbage as raw materials to change the proportion of ingredients. The eutectic characteristics of MSWI fly ash and municipal sludge and the phase diagrams of CaO-SiO₂-Al₂O₃ (C-S-A) and CaO-SiO₂-Al₂O₃ Fe₂O₃ (C-S-A-F) were analyzed in this paper. It established a low melting point mixing system. The results showed that when the amount of municipal sludge was 50-70%, the flow temperature of the mixtures was <1215 °C, which was significantly lower than that of MSWI fly ash (1490 °C) and municipal sludge (1325 °C). The optimal range of low melting point components was 14.1–36.3% CaO, 21.6–40.4% SiO₂, 6.7-12.6% Al₂O₃, and 6.3-11.4% Fe₂O₃. At 400–1400 °C, the minerals in the mixtures mainly changed as follows:



 $CaCO_3 + SiO_2 + Al_2O_3 \rightarrow Ca_2SiO_4 + Ca_3SiO_5 + Ca_2Al_2SiO_7 + Ca_3Al_2O_6 + Ca_{12}Al_{14}O_{33} \rightarrow CaAl_2Si_2O_8$. In the melting experiment, with the increase in temperature, most of the phases in the mixtures might become amorphous. Therefore, the low melting point phase anorthite (CaAl_2Si_2O_8) only accounted for a small part of the final molten product.

1. INTRODUCTION

MSWI fly ash and municipal sludge belong to solid waste. According to the data from China's National Bureau of Statistics, the total amount of municipal waste disposal in China in 2020 was 235 million tons.¹ In China, about 50% of municipal solid waste was incinerated, reducing the mass by 70-80%, with a volume reduction rate of 85-95% and a high energy recovery rate.^{2,3} MSWI would produce by-product MSWI fly ash. The incineration volume of MSWI fly ash has increased from 122 million tons in 2019 to 146 million tons in 2020. Due to the rapid growth of MSWI, the output of fly ash would grow at a frequency of 5–10% per year.^{1,2,4} MSWI fly ash mainly came from the air pollutant purification equipment at the rear of the waste incinerator,⁵ and it was a hazardous waste because it contained high alkali metal chloride, heavy metal, polychlorinated dioxin, and furan.^{6,7} If it was not disposed of properly, it would cause serious harm to the environment and human health.8,9 MSWI fly ash was the bottleneck of the development of the MSWI industry.¹⁰ Municipal sludge was a by-product of the sewage treatment process of urban sewage treatment plants. In addition to a large amount of water, municipal sludge also contained many toxic components that were difficult to degrade, such as organic

matter, heavy metals, salts, pathogenic microorganisms, and parasitic eggs.¹¹ Therefore, it was also challenging to treat it as a resource.

The main disposal methods of municipal sludge in China were landfill and incineration, accounting for 47 and 23%, respectively.^{12–14} Most of the disposal methods of MSWI fly ash in China were safe landfill and cement kiln solidification.^{15,16} However, with economic development, landfills rose sharply, land resources were increasingly scarce, and landfill treatment methods were restricted. Landfills consumed a lot of chelating agents and faced the risk of re-leaching heavy metals.¹⁷ Meanwhile, the landfill treatment method did not conform to the environmentally friendly concept and did not achieve the purpose of solid waste utilization. In addition, in recent years, traditional cement production enterprises had

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used high-temperature calcination of cement clinker to harmlessly dispose of MSWI fly ash.¹⁸ The treatment method of adding MSWI fly ash to cement could avoid the risk of releaching heavy metals.^{19,20} However, water washing pretreatment was required to remove chloride from MSWI fly ash before entering the cement kiln.^{21,22} At the same time, the addition of MSWI fly ash was limited because the high proportion of MSWI fly ash would lead to a decline in cement quality.^{23,24}

In contrast, the melting vitrification treatment method had the following advantages: (1) No water washing pretreatment and (2) it could significantly reduce the volume and decompose toxic organic substances such as PCDD/Fs.^{25–27} At the same time, the molten glass slag could be used as asphalt, paving aggregate, landfill cover, concrete aggregate, or glass ceramics. The glass material had a Si–O threedimensional network structure. The melting vitrification treatment method could fully wrap the non-volatile heavy metals and solidify them into a stable glass material, the volatile heavy metals were enriched, recovered, and reused in the secondary ash.^{28–30} However, the equipment operation of melting vitrification technology was high energy consumption, so reducing treatment temperature and energy consumption was the primary task.²⁵

Therefore, some scholars had studied the flux that could reduce the temperature of melting vitrification. It was reported^{31,32} that fine river sand, colorless glass, and bentonite could reduce the flow temperature of MSWI fly ash, where fine river sand reduced the flow temperature by 152 °C. These substances were rich in Si, and the stable Si-O-Si grid structure could more effectively control the leaching of heavy metals. However, the characteristic temperature of the CaO-SiO₂ system was still very high, and some studies had showed that Al_2O_3 was the critical component in further reducing the melting point.^{33,34} Municipal sludge rich in SiO₂ and Al₂O₃ was a better choice.³⁵ Using SiO₂ and Al₂O₃ from sludge could reduce the temperature of melting vitrification of MSWI fly ash by 182 °C, but the content of Na₂O, K₂O, and MgO in MSWI fly ash is high.³⁶ For most MSWI fly ash, CaO could be used to form a CaO-SiO₂-Al₂O₃ ternary system with SiO₂ and Al₂O₃ in sludge. The composition ratio of CaO-SiO₂-Al₂O₃ was adjusted to form a low melting point phase and reduce the temperature of melting vitrification of MSWI fly ash.³⁴ Therefore, the energy-saving co-melting of municipal sludge and MSWI fly ash was a promising treatment method.

In this paper, MSWI fly ash (mainly containing Ca) and municipal sludge (mainly containing Si, Al, and Fe) were selected as raw materials. The proportion of ingredients was changed to reduce the flow temperature of melting vitrification. The following aspects were discussed: (1) the energy-saving effect of the co-melting process of MSWI fly ash and municipal sludge, (2) the main factors affecting the energy-saving effect and determining the best ratio; (3) the phase transformation in the melting process and the surface morphology and composition of the obtained glass slag. It provides basic research for the development of MSWI fly ash and municipal sludge vitrification technology.

2. MATERIALS AND METHODS

2.1. Materials. The MSWI fly ash used in this study came from an MSWI plant equipped with a grate furnace in Hengyang, China. The furnace temperature of the MSWI plant was 900-1250 °C. The flue gas purification system of the plant

included a semi-dry flue gas scrubber and bag filter. The municipal sludge was dewatered sludge from a sewage treatment plant in Wuhan after centrifugal treatment, with a moisture content of 75.9%. The TC (total carbon) and TOC (total organic carbon) of municipal sludge were 63.98 and 55.25 g/kg. MSWI fly ash and municipal sludge were referred to as FA and MS.

The XRF equipment of the S4 Pioneer series in Brooke, Germany, was used to analyze the chemical composition by Xray fluorescence. The results are shown in Figure 1.



chemical composition

Figure 1. Main chemical composition of MSWI fly ash and municipal sludge.

It could be seen from Figure 1 that the contents of CaO and Cl in MSWI fly ash were high, accounting for 58.44 and 15.31%, respectively, while the main components in municipal sludge were SiO₂, Al_2O_3 , and Fe₂O₃, accounting for 49.76, 15.47, and 13.93%, respectively.

The phase composition of MSWI fly ash and municipal sludge is shown in Figure 2. The phase composition of MSWI fly ash was relatively complex, whose phase was mainly calcium salts such as $CaCO_3$ and $CaSO_4$, some chlorides such as NaCl and KCl, and a small amount of SiO_2 . The phase composition of municipal sludge was relatively simple, mainly containing quartz and a small amount of $KAl_2(AlSi_3O_{10})(OH)_2$.

It could be seen from Figure 3a,b that MSWI fly ash had a granular appearance, loose sample, small average particle size, and pronounced agglomeration; at high magnification, the micromorphology of MSWI fly ash could be observed as flaky and spherical. As shown in Figure 3c,d, municipal sludge exhibited particle agglomeration, dense particles, and varying particle sizes; at high magnification, municipal sludge's micromorphology could be observed in layered accumulation and aggregation.

2.2. Experimental Conditions. *2.2.1. Sample Preparation.* MSWI fly ash and municipal sludge were dried in a 105 °C oven for 24 h to make the moisture content <0.2%, ensuring the accuracy of subsequent raw material weighing, and a pulverizer dispersed the dried agglomerated MSWI fly ash and municipal sludge. The particle size analysis of MSWI fly ash and municipal sludge in this paper ensured the consistency of raw material particle size in the experimental process. The influence of the particle size on the activation energy of solid phase reaction and the experimental results was eliminated. The laser particle size analyzer (Dandong Better



Figure 2. XRD diffraction pattern of raw materials: (a) MSWI fly ash and (b) municipal sludge.



Figure 3. SEM of raw materials: (a) ×300 FA, (b) ×5000 FA, (c) ×300 MS, and (d) ×5000 MS.

BT-9300H(T)) was used to measure the particle size of MSWI fly ash and municipal sludge, as shown in Figure 4.

It could be seen from Figure 4 that the particle size of MSWI fly ash was mainly concentrated in 1–34 μ m, accounting for

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Figure 4. Particle size distribution of MSWI fly ash and municipal sludge raw materials.



Figure 5. TG-DSC of raw materials and mixtures (a) MSWI fly ash and municipal sludge and (b) different content of municipal sludge.



Figure 6. High-temperature in situ thermal analysis of different content of municipal sludge: (a) 0%, (b) 30%, (c) 40%, (d) 50%, and (e) 100%.

93.93% of the total particle size, and the particle size was small and relatively uniform; the particle size of municipal sludge was mainly 1 \sim 100 μ m, accounting for 85.22% of the total particle size, municipal sludge was relatively coarse, and the particle size uniformity was poor compared with MSWI fly ash.

2.2.2. Research Methods of Melting Characteristics. 2.2.2.1. Analysis of Thermal Reaction Characteristics. The heating behavior of MSWI fly ash and municipal sludge in the air atmosphere was analyzed by differential scanning calorimetry (TG-DSC), and the equipment used was NETZSCH 449 F3. The experimental conditions were as follows: 10 mg sample, platinum crucible, air atmosphere, heating rate of 10 $^{\circ}$ C/min, heated to 1200 $^{\circ}$ C.

2.2.2.2. Melting Characteristic Temperature Analysis. According to the Determination of fusibility of coal ash (GB/T219-2008), the characteristic temperature of MSWI fly ash, municipal sludge, and their mixtures was tested by the triangular cone method.³⁷ The gray cone's hemispherical temperature (HT) and flow temperature (FT) were mainly investigated.

HT: the temperature at which the gray cone deforms to a nearly hemispherical shape during the heating process, that is, the height is about half of the bottom length; FT: the temperature at which the ash cone melts into a liquid, develops into a thin layer with a height of less than 1.5 mm, or gradually shrinks and finally disappears.

2.2.2.3. High-Temperature In situ Analysis Method. S/ DHTT-TA-III high-temperature in situ thermal analyzer could express the characteristic temperature of MSWI fly ash and municipal sludge more intuitively. The change characteristics in the melting process were used to further analyze the melting characteristics of MSWI fly ash and municipal sludge samples.

2.2.3. Melting Test and Product Performance Analysis Method. By mixing MSWI fly ash and municipal sludge in a

certain proportion, the change of characteristic temperature and crystal phase during the co-disposal of MSWI fly ash and municipal sludge was discussed. MSWI fly ash and municipal sludge were uniformly mixed. The sample (15 g) was put into the crucible and later into the muffle furnace. The furnace door was closed to be raised to the preset temperature and to keep warm. The crucible was taken out to cool naturally to room temperature. After the sample was cooled, the sample was crushed to be saved for subsequent detection and analysis. In this experiment, the set temperatures were 800, 1000, 1200, and 1400 °C with a heating rate of 10 °C/min and a holding time of 30 min.

The microcosmic appearance of raw materials and the micro area composition of products were analyzed using a scanning electron microscope (SEM-EDS) with the equipment model JSM-6490LV. The phase composition of the raw material and the molten sample was measured by X-ray diffraction (XRD). The XRD equipment with the Cu K α radiation source was D8Advance, Brooke, Germany. The scanning range was 15– 70°, and the scanning speed was 5°/min. The tube current was 20 mA, and the tube voltage was 40 kV.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric Analysis of MSWI Fly Ash and Municipal Sludge. TG-DSC of raw materials is shown in Figure 5a. The thermal weight loss of MSWI fly ash in the atmosphere was mainly divided into three stages: the first stage was 30-530 °C, removal of adsorbed water and crystal water, as well as decarboxylation of residual organics, the weight loss rate was 3.31%. The second stage was 530-738 °C, with an apparent endothermic peak at 695 °C due to carbonate decomposition, and the weight loss rate was 19.79%. The third stage was 738-1200 °C, volatilization of metal chloride with a low boiling point, and the weight loss rate was 9.24%. The thermal weight loss of municipal sludge in the atmosphere was divided into two stages: first, the water in the municipal sludge was removed, and the weight loss rate was 6.19% (30–195 °C). Secondly, according to the DSC curve, there was an exothermic peak at 327 °C, mainly due to the combustion exothermic of organic matter and fixed carbon in municipal sludge.

TG-DSC of mixtures (the content of municipal sludge was 30, 40, and 50%) was divided into four stages and shown in Figure 5b, as follows:

- (1) At 30–200 °C, the adsorbed water and crystal water of the mixtures were removed.
- (2) At 200–600 °C, according to the DSC curve, there were two exothermic peaks at 327 and 480 °C, mainly due to the combustion exothermic of organic matter and fixed carbon in municipal sludge (200–600 °C).
- (3) At 600–750 °C, there was an endothermic peak at 680 °C due to carbonate decomposition (600–750 °C).
- (4) At 750–1200 °C, there was an endothermic peak at 850 °C due to the volatilization of metal chloride with a low boiling point.

3.2. Co-melting Characteristics of MSWI Fly Ash and Municipal Sludge. The melting characteristics of MSWI fly ash, municipal sludge, and mixture samples were further analyzed by a high-temperature in situ thermal analyzer, as shown in Figure 6.

As could be seen from Figure 6, when the sample temperature was 600 °C, its morphology remained unchanged. With the increase in temperature, it could be observed in Figure 6(a2), (b2), (c2), and (d2), that visible white smoke was gradually produced. According to TG-DSC, this white smoke might be the volatilization of metal chloride with a low boiling point, and the volatilization process was intense at about 1000 °C.^{38–40} The volatilization process gradually ended when the temperature was >1300 °C. In Figure 6e, no volatiles were observed, showing that all visible volatiles came from MSWI fly ash rather than municipal sludge.

As the temperature increased, the liquid phase gradually formed and the mixtures began to melt. At 1400-1600 °C, the mixtures completely melted. According to Figure 6(a5), (b5), (c5), (d5), and (e5), the complete melting temperature of the mixtures first decreased and then increased with the increase of municipal sludge addition. When the amount of municipal sludge was 50% (Figure 6(D5)), the temperature was the lowest.

The theoretical calculation results of the C-S-A phase diagram and the effect of the Fe_2O_3 content on the C-S-A ternary system were verified by measuring the ash fusion temperatures (AFTs). The ash cone's characteristic temperature was the hemispherical temperature (HT) and the flow temperature (FT).

MSWI fly ash, municipal sludge, and their mixtures in different proportions were melted in the ash melting instrument. The results were shown in Figure 7. HT and FT showed the same trend. When the ratio of municipal sludge was \geq 40%, the HT and FT decreased significantly. The FT was the same when the municipal sludge content was 50–70%. The lowest FT was 1204 °C, 19.2 and 11.1% lower than 1490 °C of single melting MSWI fly ash (0%) and 1325 °C of single melting municipal sludge (100%).

It should be noted that when municipal sludge addition was 50 to 70%, the change range of AFTs became narrow, and the



Figure 7. Melting characteristics of the mixture.

temperature difference was very tiny. At this time, the melting process of the mixtures changed rapidly, and it could vary from the solid phase to the flowing liquid phase in a small temperature range. This phenomenon might be caused by the rapid fusion of the solid phase, and the liquid phase formed had low viscosity and can easily spread out.⁴¹

3.3. Analysis of the Eutectic Phase Diagram of MSWI Fly Ash and Municipal Sludge. The phase diagram of the C-S-A ternary system and the C-S-A-F pseudoquaternary scheme are drawn using the phase diagram module in the thermodynamic software FactSage 7.2.⁴²

Since CaO₂ SiO₂, and Al₂O₃ were the main elements in MSWI fly ash and the municipal sludge mixture. The ternary phase diagram was obtained by thermodynamic calculations. The minimum melting temperature of the phase diagram was 1184.3 °C with a content of 61.47% SiO₂, 25.12% CaO, and 13.41% Al₂O₃. The main crystalline phases of the slag system were anorthite (CaAl₂Si₂O₈) and wollastonite (CaSiO₃). The MSWI fly ash and municipal sludge were compounded, and the mixtures are marked in Figure 8. MSWI Fly ash and municipal sludge were located in the crystallization zone of CaO and Mullite, respectively, and their liquidus temperature was high, resulting in a high melting point. With the increase of municipal sludge doping, the crystallization zone of the mixtures underwent CaO \rightarrow Ca₂SiO₄ \rightarrow CaSiO₃ \rightarrow $CaAl_2Si_2O_8 \rightarrow Mullite$ transformations, and the melting temperature first decreased and then increased. The lowtemperature melting zone of the compound mixtures was the crystallization zone of anorthite (CaAl₂Si₂O₈) and the crystallization zone of wollastonite (CaSiO₃). At this time, the liquidus temperature of the mixtures decreased, and the low-temperature zone was concentrated in the range of 50-80% of municipal sludge addition.

It can be seen from Figure 8 that the actual measured melting temperature was the same as the trend calculated theoretically, proving that the relative contents of CaO, SiO_2 , and Al_2O_3 significantly influenced the melting temperature.

With the increase of municipal sludge doping, the content of Fe_2O_3 in the mixtures increased. Therefore, the influence of different ranges of Fe_2O_3 on the melting process of the C-S-A ternary system was explored, as shown in Figure 9.

When the proportion of Fe_2O_3 was 0.1 and 0.15, respectively, and the doping amount of municipal sludge was



Figure 8. Phase diagram of the C-S-A ternary system.

50% and 80%, respectively, the mixtures were located near the 1300 °C isotherm and belonged to the low-temperature melting zone (Figure 9a,b). With the increase of Fe₂O₃/C-S-A-F from 0.1 to 0.15, the low-temperature melting zone of the phase diagram of the C-S-A-F pseudoternary system gradually expanded (the enlarged area in Figure 9). With the increase of the Fe₂O₃ content, the minimum melting temperature of the pseudoquaternary system phase diagram increased slightly. When Fe₂O₃/C-S-A-F = 0.1, the minimum temperature of the system was 1150.3 °C; when Fe₂O₃/C-S-A-F = 0.15, the minimum temperature increased slightly, which was still lower than the minimum melting temperature of the C-S-A ternary system (1183.4 °C).

Therefore, an appropriate amount of Fe_2O_3 could reduce the melting temperature of the C-S-A ternary system.⁴³ With the increase of the Fe_2O_3 content and the expansion of the low-temperature melting zone, adding Fe_2O_3 could broaden the mixture's adaptation range of the raw material composition and enhanced the inclusiveness of molten raw material composition.

According to the above results, the better range of low melting point components was 14.1-36.3% CaO, 21.6-40.4% SiO₂, 6.7-12.6% Al₂O₃, and 6.3-11.4% Fe₂O₃.

3.4. Phase Transformation Behavior of MSWI Fly Ash and Municipal Sludge during Co-melting. From the XRD (Figure 10), it could be observed that the phase transition behavior of MSWI fly ash changed with municipal sludge addition and temperatures.

When the roasting temperature was 400 °C (Figure 10a), the main phase in MSWI fly ash was $CaCO_3$, and small amounts of $CaSO_4$, CaClOH, KCl, and NaCl. With the increase in the amount of sludge, the SiO_2 content in the mixtures increased, and the diffraction peak intensity gradually increased, while the diffraction peak intensity of other phases decreased. At this time, no new phase was generated, which indicated that MSWI fly ash, municipal sludge, and mixtures had not undergone phase transformation.

When the temperature increased to 600 °C, the main phase in MSWI fly ash was still $CaCO_3$. But the diffraction peak intensity was slightly lower than that at 400 °C, $CaCO_3$ decomposed gradually, while other phases had no obvious changes. With the increase in the amount of sludge, new phases ($Ca_{12}Al_{14}O_{33}$ and $Ca_3Si_2O_7$) were formed in the mixture.

Most CaCO₃ decomposed (Figure 10c) and the main crystalline phase in MSWI fly ash changed to CaO; at this time, a small amount of CaCO₃, KCl, and NaCl remained in the sample.⁴⁴ A large number of new phases (such as Ca₂SiO₄, Ca₃SiO₅, Na₂Ca₃Si₂O₈, Ca₄Fe₉O₁₇, Ca₂Al₂SiO₇, Ca₃Al₂O₆, and Ca₁₂Al₁₄O₃₃) were generated in the mixture.

When the roasting temperature was 1000 °C (Figure 10d), the CaCO₃ phase in the MSWI fly ash disappeared. While KCl and NaCl did not change significantly with the increase in temperature. $Ca_4Fe_9O_{17}$ in the mixtures reacted with SiO₂ to form $Ca_3Fe_2(SiO_4)_3$.

As shown in Figure 10e, the main phase in MSWI fly ash had no noticeable change and was still CaO. KCl, NaCl, and other chlorides in MSWI fly ash volatilized. The phases in the mixtures were $Ca_{12}Al_{14}O_{33}$, $CaAl_2Si_2O_8$, and $Ca_3Fe_2(SiO_4)_3$, while the phases of Ca_2SiO_4 , Ca_3SiO_5 , $Na_2Ca_3Si_2O_8$, $Ca_2Al_2SiO_7$, and $Ca_3Al_2O_6$ disappeared.

When the temperature increased to 1400 °C (Figure 10f), only $CaAl_2Si_2O_8$ was left in the MSWI fly ash and mixture. There was a small amount of SiO_2 in municipal sludge, and other phases changed from crystalline to amorphous. Compared with the change of $CaAl_2Si_2O_8$ diffraction peak intensity, the diffraction peak intensity of MSWI fly ash was the lowest due to the small content of Al_2O_3 and SiO_2 in MSWI fly ash. The diffraction peak intensity of mixtures decreased with the increase of municipal sludge addition. The cause seemed to be the decrease of the melting point of the mixtures and



Figure 9. Liquidus projection of the C-S-A-F pseudoquaternary system: (a) Fe_2O_3/C -S-A-F = 0.1 and (b) Fe_2O_3/C -S-A-F = 0.15.

increase of the liquid phase and part of $CaAl_2Si_2O_8$ melted and became amorphous.

With the change in the temperature and the amount of sludge, the following transformations mainly occurred in the mixture

$$CaCO_3 \to CaO + CO_2 \tag{1}$$

$$CaO + SiO_2 \rightarrow Ca_3Si_2O_7/Ca_2SiO_4/Ca_3SiO_5$$
(2)

$$CaO + Fe_2O_3 \rightarrow Ca_4Fe_9O_{17} \tag{3}$$

 $CaO + Al_2O_3 \rightarrow Ca_{12}Al_{14}O_{33}/Ca_3Al_2O_6$ $\tag{4}$

$$CaO + SiO_2 + Al_2O_3 \rightarrow Ca_2Al_2SiO_7$$
(5)

$$\begin{aligned} \mathrm{Ca}_{2}\mathrm{SiO}_{4} &+ \mathrm{Ca}_{3}\mathrm{SiO}_{5} &+ \mathrm{Ca}_{2}\mathrm{Al}_{2}\mathrm{SiO}_{7} &+ \mathrm{Ca}_{3}\mathrm{Al}_{2}\mathrm{O}_{6} \\ &+ \mathrm{Ca}_{12}\mathrm{Al}_{14}\mathrm{O}_{33} \\ &\rightarrow \mathrm{Ca}\mathrm{Al}_{2}\mathrm{Si}_{2}\mathrm{O}_{8} \end{aligned} \tag{6}$$

Since the low energy consumption melting mainly depended on the transformation of minerals (the formation of a low



Figure 10. XRD diagram of the mixtures held at different roasting temperatures for 30 min: (a) 400 $^{\circ}$ C, (b) 600 $^{\circ}$ C, (c) 800 $^{\circ}$ C, (d) 1000 $^{\circ}$ C, (e) 1200 $^{\circ}$ C, and (f) 1400 $^{\circ}$ C.

melting point phase), which could be seen from the XRD pattern that the final XRD diffraction pattern of the molten product was anorthite $(CaAl_2Si_2O_8)$ in the low-temperature melting zone in the C-S-A system.

XRD results showed that the iron-containing compounds in the slag system were mainly Fe_2O_3 , $Ca_4Fe_9O_{17}$, and $Ca_3Fe_2(SiO_4)_3$. To better determine the valence state of iron in the slag system, the content of different valence iron in the mixtures with 50% municipal sludge content after heat treatment at 800 and 1000 °C was tested. The results showed that Fe^{2+} and Fe^{3+} were 0.73 and 4.22% (at 800 °C), as well as 0.17 and 4.78% (at 1000 °C). Divalent and trivalent iron coexisted in the slag system. But the main form was trivalent



Figure 11. EDS analysis of selected areas of samples with 50% municipal sludge content (a1) & (a2) area1 and its spectrum, (b1) & (b2) area2 and its spectrum.

iron, and the content increased slightly with the increase in temperature.

XRD serial number:1-CaO,2-CaCO₃,3-KCl,4-NaCl,5-Ca-ClOH,6-K₂Ca $(CO_3)_2$,7-SiO₂,8-Ca₂SiO₄,9-Ca₃SiO₅,10-Na₂Ca₃Si₂O₈,11-Ca₄Fe₉O₁₇,12-Ca₂Al₂SiO₇,13-Ca₁₂Al₁₄O₃₃,14-Fe₂O₃,15-Ca₃Al₂O₆,16-Ca₃Fe₂(SiO₄)₃,17-CaAl₂Si₂O₈,18-CaSO₄,19-KAl₂(AlSi₃O₁₀)(OH)₂, 20-Ca₃Si₂O₇

3.5. EDS Analysis. When the temperature reached 1400 $^{\circ}$ C, the mixtures completely melted, with a dense surface and no visible pores. To further determine the phase transition in the melting process, the samples with 50% municipal sludge content were analyzed by EDS (heated preservation at 1400 $^{\circ}$ C for 30 min). Figure 11 shows the selected two areas (area1 and area2) and their corresponding spectrum. Table 1

Table 1. Wt % of Different Elements Obtained from EDS Analysis of Samples

	element (wt %)							
area	0	Mg	Al	Si	Ca	Ti	Fe	
1	35.67	2.81	9.96	21.62	23.28	0.68	5.98	
2	35.92	2.53	9.98	21.59	23.26	0.44	6.27	

summarized the wt % of different elements obtained by EDS analysis in area1 and area2. The wt % of Ca, Si, Al, and O near area1 were 23.28, 21.62, 9.96, and 35.67%, respectively, and the wt % of Ca, Si, Al, and O near area2 were 23.26, 21.59, 9.98, and 35.92%, respectively. The elemental composition of the two regions was the same, and the composition was close to that of anorthite (CaAl₂Si₂O₈). The difference between the EDS results and crystal phase chemical formula composition

might be due to the dissolution of other elements in the lattice (such as Mg, Ti, Fe, etc.), which led to the deviation of the proportion of elements in the crystal. EDS results showed that the anorthite crystal phase was finally formed after melting, consistent with XRD.

4. CONCLUSIONS

In this paper, MSWI fly ash and municipal sludge were cotreated to reduce the temperature of melting treatment, energy consumption, and treatment cost. The characteristics of MSWI fly ash, municipal sludge, and their mixtures were analyzed, and melting experiments were conducted to analyze their crystalline phase transition. The specific conclusions were as follows:

- (1) According to the phase diagram calculation, the regulation of municipal sludge on MSWI fly ash components made the crystallization zone of MSWI fly ash transition from CaO to CaAl₂Si₂O₈, greatly reducing its melting temperature and saving energy consumption in the melting process. At the same time, Fe₂O₃ in municipal sludge further reduced the minimum melting temperature of the C-S-A phase diagram and expanded the area of the low-temperature melting zone. By mixing MSWI fly ash and municipal sludge in proportions of 1:1, 2:3, 3:7, and 1:4, the chemical components with lower melting points were obtained, namely 14.1–36.3% CaO, 21.6–40.4% SiO₂, 6.7–12.6% Al₂O₃, and 6.3–11.4% Fe₂O₃.
- (2) Through the verification of high-temperature in situ thermal performance and AFT measurement, the results show that the melting process of MSWI fly ash was

accompanied by the volatilization of a large number of low boiling point compounds. The melting point of the mixtures first decreased and then increased with the increase in the content of municipal sludge in MSWI fly ash. When the proportion of municipal sludge was \geq 40%, the characteristic temperatures decreased significantly. When the municipal sludge content was 50–70%, the FT value was the same. The co-treatment process reduced the FT of MSWI fly ash and municipal sludge by 286 and 121 °C, respectively.

- (3) The results of XRD and EDS showed that the minerals in the mixtures mainly underwent the following transformation with the increase of temperature: $CaCO_3 + SiO_2 + Al_2O_3 \rightarrow Ca_2SiO_4 + Ca_3SiO_5 + Ca_2Al_2SiO_7 + Ca_3Al_2O_6 + Ca_{12}Al_{14}O_{33} \rightarrow CaAl_2Si_2O_8$. Finally, the low melting point phase anorthite $(CaAl_2Si_2O_8)$ was formed.
- (4) In this study, it was found that the co-treatment of MSWI fly ash and municipal sludge was beneficial for reducing energy consumption in the melting process. Energy consumption was the bottleneck restricting the development of MSWI fly ash and municipal sludge fused glass resource. From the perspective of investors, the added value of products after disposal was also one of their concerns. The glass material and the product of co-disposal of MSWI fly ash and sludge could become a potential raw material for preparing glass ceramics.

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Notes

The authors declare no competing financial interest.

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