The bottom ash from municipal solid waste and sewage sludge co-pyrolysis technology: characteristics and performance in the cement mortar and concrete

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Abstract. To efficiently and environmentally treat the municipal solid waste (MSW), co-pyrolysis technology was further developed by adding high heat value substance of sewage sludge (SS). As the co-pyrolysis technology for MSW and SS has been popularly developed, the production of the bottom ash is constantly increased. The treatment and utilization of this part of bottom has become an urgent issue. This work investigated the basic characteristics of the co-pyrolysis bottom ash and evaluated the application possibility of the co-pyrolysis bottom ash as building materials. The co-pyrolysis bottom ash possessed high chemical contents of CaO + MgO/SiO₂ + Al₂O₃ over 88 %. Excellent performance of comprehensive and flexural strength for cement mortar and concrete were realized with the co-pyrolysis bottom ash incorporated.

1. Introduction

In recent years, pyrolysis and gasification technology has been world widely applied to treat the MSW [1]. As a medium and small-scale MSW treatment technology, it possessed advantages of small floor area, low investment and operation costs, simple operation and effective control of secondary pollution [2]. However, in the engineering application, there are still problems that demand solutions. For example, in the rural areas of China where do not implement classified collection and transportation of the MSW, the high moisture content and low calorific value of the MSW greatly prohibited the working stability of this technical [3]. As a consequence, most pyrolysis and gasification processes cannot operate independently without adding external energy as electricity or biomass fuel [4]. One the other hand, the improvement of municipal facilities promoted the construction of small and medium-sized sewage treatment plants in a large number [5]. Thus, the small amount, scattered and long distance from the disposal centres also cause the municipal sewage disposal problems in small and medium-sized towns. Therefore, the co-pyrolysis technology of municipal solid waste and municipal sewage has been developed to be the promising solutions [6]. And the advantages of this technology have been wide reported with the wide applications [7]. However, a large number of the bottom ash was produced after the co-pyrolysis process. With the further development of the co-pyrolysis technology of MSW and SS, the production of bottom is constantly increased [8]. And analysing the characteristics of these ash and properly making secondary utilization has become an urgent problem to be solved. The municipal solid waste (MSW) pyrolysis bottom ash has been reported to be reused as admixture in cement mortar and...
concrete [9, 10]. However, due to the low content of silicon, magnesium and other elements required for the utilization of building materials, the resource utilization of the bottom ash exhibited limited comprehensive performance [11]. Compared with MSW, the dried SS possessed a higher calorific value [12]. And the content of silicon and magnesium as building materials in the bottom ash of SS after the high temperature treatment is higher than that in MSW [13]. Therefore, the bottom ash from the co-pyrolysis of MSW and SS might be a potential material as building materials.

In this paper, the basic characteristics of the bottom ash after co-pyrolysis of MSW and SS as cement admixture was investigated. And the co-pyrolysis bottom ash was applied in producing cement mortar and concrete product. The comprehensive strength of cement mortar and concrete product was analysed according to different dosage. This will be of great significance to the further development of co-pyrolysis process of MSW and SS.

2. Materials and methods

2.1. Methods
The bottom ash was obtained from co-pyrolysis of MSW and SS at high temperature reaction above 950 ℃ in the double solution furnace designed in the previous study [3]. The furnace burns over fifty thousand tons of MSW per year since 2017. The dried SS with moisture content lower than 50 % was co-pyrolysis with MSW at different concentration. MSW and SS was co-pyrolyzed with proportion 1:9, 2:8, 3:7 and 4:6, hereinafter referred to as H1, H2, H3 and H4 respectively. To investigate the performance of the bottom ash as substitute for cement in cement mortar and concrete, the obtained bottom ash was grinded with uneven particle size for 5 min, so that the ash can pass through the 100 mesh screens. The cement used in this test is ordinary Portland cement, the strength grade is 52.5 MPa, and the standard sand is international standard sand (ISO). Fine aggregate is river sand and coarse aggregate is granite gravel.

2.2. Methods
The microstructure of the co-pyrolysis bottom ash was observed by scanning electron microscope (SEM), and the accelerating voltage was 10 kV. Chemical composition and content of the co-pyrolysis bottom ash was analysed through X Ray Fluorescence (XRF). Fineness, free calcium oxide content (f-CaO) and water requirement ratio are important indexes which were investigated according to the national standard of fly ash for cement and concrete (GB/T 1596-2017). The water requirement ratio was determined by the ratio of water addition when the fluidity reached 130-140 mm. The fluidity of the co-pyrolysis bottom ash in cement mortar were determined through test method for fluidity of cement mortar (GB/T 2419-2005).

| Material ratio for cement mortar strength test. |
|-----------------------------------------------|
| cement/kg | Water/mL | Standard sand/g | Co-pyrolysis bottom ash/g |
| HH        | 450      | 225             | 1350             | 45                          |
| H1-10 %   | 405      | 225             | 1350             | 90                          |
| H1-20 %   | 360      | 225             | 1350             | 135                         |
| H1-30 %   | 315      | 225             | 1350             | 45                          |
| H2-10 %   | 405      | 225             | 1350             | 90                          |
| H2-20 %   | 360      | 225             | 1350             | 135                         |
| H2-30 %   | 315      | 225             | 1350             | 45                          |
| H3-10 %   | 405      | 225             | 1350             | 90                          |
| H3-20 %   | 360      | 225             | 1350             | 135                         |
| H3-30 %   | 315      | 225             | 1350             | 45                          |
| H4-10 %   | 405      | 225             | 1350             | 90                          |
| H4-20 %   | 360      | 225             | 1350             | 135                         |
| H4-30 %   | 315      | 225             | 1350             | 45                          |
Table 2. Material ratio for concrete strength test.

|            | Cement/kg | Coarse aggregate/kg | Fine aggregate/kg | Water/L | Standard sand/kg | Co-pyrolysis bottom ash/kg |
|------------|-----------|---------------------|-------------------|---------|-----------------|----------------------------|
| HH         | 14.44     | 12.388              | 28.880            | 7.98    | 27.512          | 1.444                      |
| H1-10 %    | 12.996    | 12.388              | 28.880            | 7.98    | 27.512          | 1.444                      |
| H1-20 %    | 11.552    | 12.388              | 28.880            | 7.98    | 27.512          | 2.888                      |
| H1-30 %    | 10.108    | 12.388              | 28.880            | 7.98    | 27.512          | 4.332                      |
| H2-10 %    | 12.996    | 12.388              | 28.880            | 7.98    | 27.512          | 1.444                      |
| H2-20 %    | 11.552    | 12.388              | 28.880            | 7.98    | 27.512          | 2.888                      |
| H2-30 %    | 10.108    | 12.388              | 28.880            | 7.98    | 27.512          | 4.332                      |
| H3-10 %    | 12.996    | 12.388              | 28.880            | 7.98    | 27.512          | 1.444                      |
| H3-20 %    | 11.552    | 12.388              | 28.880            | 7.98    | 27.512          | 2.888                      |
| H3-30 %    | 10.108    | 12.388              | 28.880            | 7.98    | 27.512          | 4.332                      |
| H4-10 %    | 12.996    | 12.388              | 28.880            | 7.98    | 27.512          | 1.444                      |
| H4-20 %    | 11.552    | 12.388              | 28.880            | 7.98    | 27.512          | 2.888                      |
| H4-30 %    | 10.108    | 12.388              | 28.880            | 7.98    | 27.512          | 4.332                      |

The flexural strength and compressive strength test for cement mortars were carried out according to the test method for strength of cement mortar (ISO697:1989), and the material ratio is shown in Table 1. Three specimen parallel samples were made for each proportion and demoulding shall be carried out within 24 h. The strength of concrete mixed with different proportions of co-pyrolysis bottom ash was also analysed. For concrete mixing method, the proportion of the materials was mixed according to the strength grade of 30 MPa concrete (C30). The specific material ratio is shown in Table 2. The test process was conducted according to standard for test methods of mechanical properties of ordinary concrete (GB/T50081-2002) [14].

3. Results and discussion

3.1. Morphology and physical properties

The micro morphology and appearance of the four co-pyrolysis ashes are shown in Fig 1 and Fig 2.

![Figure 1. SEM images of four kinds of co-pyrolysis bottom ash.](image1)

![Figure 2. Fig.2-2 Appearance images of four kinds of co-pyrolysis bottom ash.](image2)

As exhibited in Figure 1, the co-pyrolysis bottom ash H1 shows loose and irregular particle structure. The structure of H2 is similar to that of H1, but the particle surface is relatively smooth. H3 has more compact massive structure, and H4 exhibit irregular shape and compact structure. With the increase of
SS content, the calorific value of unit mass co-pyrolysis raw materials increased resulting higher temperature during the co-pyrolysis process. Liquid phase can be formed in at high temperature and smooth particles surface can be formed under the action of surface tension [15]. From Figure 2, the colour of the bottom ash after co-pyrolysis gradually changes from dark grey to dark brown with the increase of SS.

3.2. Chemical Composition
The main chemical compositions of the bottom ash from co-pyrolysis of MSW and SS were determined by XRF and the results were shown in Table S3. According to Table 3, the main components of H1, H2, H3 and H4 are SiO2, Al2O3, Fe2O3, CaO, MgO and Na2O. The percentages of CaO + MgO/SiO2 + Al2O3 in the four kinds of the bottom ash are 89.17%, 91.02%, 88.41% and 89.05%, respectively. All those components can serve as the sources of hydration products including calcium silicate hydrates (C-S-H) and ettringite [16]. The main chemical components of common fly ash are also SiO2, Al2O3, Fe2O3, CaO, MgO, etc [17]. It was noticed that the main components of four kinds of fly ash are similar to those of fly ash.

| Oxidate | H1  | H2  | H3  | H4  |
|---------|-----|-----|-----|-----|
| SiO2    | 40.2| 42.2| 45.6| 47.7|
| Al2O3   | 13.4| 13.2| 12.7| 14  |
| TiO2    | 0.79| 0.82| 0.8 | 0.84|
| Fe2O3   | 7.62| 7.54| 7.12| 7.72|
| CaO     | 17  | 19.1| 18.4| 24.4|
| MgO     | 4.95| 4.98| 4.59| 6.23|
| Na2O    | 6.6 | 5.9 | 6.9 | 5.3 |
| K2O     | 0.83| 0.8 | 0.83| 0.81|
| SO3     | 0.11| 0.14| 0.09| 0.08|
| Cr2O3   | 0.33| 0.33| 0.29| 0.6 |
| MnO     | 0.32| 0.3 | 0.28| 0.28|
| CuO     | 0.1 | 0.09| 0.07| 0.08|
| ZnO     | 0.1 | ND  | 0.1 | ND  |
| Cl      | 0.26| 0.21| 0.36| 0.21|
| ZrO2    | 0.03| 0.03| 0.03| 0.03|
| PbO     | 1.3 | 1.2 | 1.4 | 1   |
| BaO     | ND  | 0.26| 0.26| ND  |
| (CaO+MgO/SiO2+Al2O3) | 85.17 | 91.02 | 88.41 | 89.05 |

3.3. Fineness, Water Demand and Setting Time of Mortar
Table 4 shows the analysis results of fineness, water demand and setting time of mortar for MSW and SS co-pyrolysis bottom ash. As shown in Table S4, the fineness of the co-pyrolysis bottom ash is close to that of cement after grinding which ensures its application possibility. The water demand of the co-pyrolysis bottom ash increases with the raised SS adding ratio. It is obviously, the CaO content in co-pyrolysis bottom ash is increased along with the raised SS adding ratio (shown in Table S3) which exists in the form of anhydrite in the co-pyrolysis ash. And the hydration of anhydrite needs a lot of bound water. Therefore, the water requirement of the co-pyrolysis bottom ash is increased but less than 105 %. During the hydration process, the hydration products precipitates in the form of crystals under alkaline condition, and forms a film through coprecipitation to separate the part not hydrated, thus delaying the hydration rate and adjusting the setting time [18]. The initial setting time of co-pyrolysis bottom ash is more than 90 min, and the final setting time is less than 600 min.
Table 4. Fineness, water demand, setting time of mortar and content of f-CaO

|        | Fineness | Water demand (%) | Initial setting time (h) | Final setting time (h) | f-CaO (%) |
|--------|----------|------------------|--------------------------|------------------------|-----------|
| H1     | 16.3     | 92               | 1:52                     | 5:50                   | 4.1       |
| H2     | 15.8     | 95               | 1:44                     | 5:37                   | 3.3       |
| H3     | 17.4     | 101              | 1:31                     | 4:56                   | 3.4       |
| H4     | 15.6     | 104              | 1:57                     | 5:33                   | 3.7       |

3.4. SO₃ and f-CaO
The contents of SO₃ and f-CaO significantly affect the setting time and volume expansion of the cement mortar and concrete which decide the comprehensive strength. It has been proved that high levels of SO₃ and f-CaO will case extended setting time and excessive volume expansion [19]. And resulting in poorer performance for the cement mortar and concrete products [20]. In this work, the contents of SO₃ and f-CaO in four co-pyrolysis bottom ash were carefully identified and the results are shown in Table S4. The contents of SO₃ follows the order of H1 > H2 > H3 > H4, while the contents of f-CaO follows the order of H1 < H2 < H3 < H4. Both the contents of SO₃ and f-CaO in the co-pyrolysis bottom ash are lower than the commonly fly ash. All these characters indicate that the co-pyrolysis bottom ash was promising additives for construction materials.

3.5. Comprehensive and flexural strength analysis
To evaluate the performance of the co-pyrolysis bottom ash as additives for construction materials, the comprehensive and flexural strength of cement mortar and concrete are investigated. The cement mortar and concrete were produced with different amounts of co-pyrolysis bottom ash added.

Figure 3. Comprehensive strength of the cement mortars with different co-pyrolysis bottom ash added.

Figure 4. Flexural strength of the cement mortars with different co-pyrolysis bottom ash added.
Fig 3 and Fig 4 present the compressive strength and the flexural strength of the cement mortar with different co-pyrolysis bottom ash incorporated in respectively. It can be seen from Figure 3 and Fig 4, both the compressive strength and flexural strength at 28 days are significantly greater than that at 3 days. And it is obviously that the compressive strength and flexural strength of cement mortar are greatly affected by the added ratio. When the added ratio of four kinds of co-pyrolysis bottom ash is 10%, the flexural strength of the cement mortar at 3 days is more than 5 MPa, and more than 8 MPa at 28 days. And the comprehensive strength of the cement mortar is over 55 MPa at 28 days curing. It is worthy noticing that H3 exhibits higher flexural strength than that of other three kinds of co-pyrolysis bottom ash which might be attributed to the proper percentage of SO3 and f-CaO. However, when the added ratio of four kinds of co-pyrolysis bottom ash reach 30%, the flexural strength and comprehensive strength of the correspond cement mortar is obviously lower than the pure cement mortar. This result indicates that the strength activity index of the co-pyrolysis bottom ash is lower than that of the pure silicate cement. Thus, the added ratio of the co-pyrolysis bottom ash in producing cement mortar should be limited.

The performance of the co-pyrolysis bottom ash as construction materials was further identified by incorporating it into concrete construction. Both of the compressive strength and flexural strength test of the concrete with different kinds and ratio co-pyrolysis bottom ash added were conducted. As shown in Figure 5 and Figure 6, the comprehensive strength and flexural strength of the prepared concrete products are over 40 and 4 MPa at 90 days curing respectively. When the incorporated ratio is 10 %, the compressive strength of concrete products added with H2 co-pyrolysis bottom ash exhibit the highest value. With the increasing of the incorporated ratio, the comprehensive strength of H1 added concrete is retained, while the H2, H3, and H4 added concrete products decrease. However, When the incorporated ratio reaches 30 %, the flexural strength shows universal decrease. This result might cause by the difference of chemical components in SS [21].
3.6. Analysis of hardening process

The content of SiO2 in the co-pyrolysis bottom ash of MSW and SS is more than 50%. Commonly, SiO2 mainly exists in the form of dicalcium silicate and tricalcium silicate, which can carry out hydration reaction [22]. The co-pyrolysis of MSW and SS was carried out at temperature over 950 °C for more than 4 h. After completed the reaction, the bottom ash was cooled to room temperature. Therefore, the main components were metastable vitreous in a thermodynamic state. It has been proved that the Si-O bond and Al-O bond constitute the structural bonds in the metastable vitreous. Si-O bond was proved to be existed in the form of [SiO4] tetrahedron, and H3SiO4- can be formed with the fracture of the surface under the excitation of alkaline environment which was promoted by the grounding process. Al-O bond was reported to form HSiO43-, H2SiO42- and H3SiO4- with the boosting of alkaline environment [23]. As a result, zeolite like hydration products were produced from the through the reaction of the Ca2+ and Na+ in co-pyrolysis bottom ash with silicate ion. With the consumption of silicate ion, hydration products were constantly produced and the comprehensive strength was obviously increased with the extension of time [24].

4. Conclusion

The basic characteristics of the co-pyrolysis bottom ash derived for the MSW and SS co-pyrolysis technology were investigated in this work. The analysed characteristics include micro morphology, chemical composition, fineness, water demand, setting time of mortar, contents of SO3 and f-CaO. Furthermore, the four kinds of co-pyrolysis bottom ash were incorporated to produce cement mortar and concrete. It can be obtained that the co-pyrolysis bottom ash derived for the MSW and SS co-pyrolysis technology possess the similar main contains of CaO + MgO/SiO2 + Al2O3 as that of the fly ash. And the contents of SO3 and f-CaO in the co-pyrolysis bottom ash are less than that in the fly ash. More importantly, When the co-pyrolysis bottom ash was added to produce cement mortar and cement products, comprehensive strength over 55 MPa at 28 days curing for cement mortar and 40 MPa at 90 days curing for cement can be realized. This result indicated that the co-pyrolysis bottom ash derived for the MSW and SS co-pyrolysis technology is promising additives for construction materials with proper incorporated ratio. Thus, greatly encouraged the further development of co-pyrolysis process of MSW and SS.

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