Stabilization/Solidification of cadmium in municipal solid waste incineration fly ash by using cemented backfill agent

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Abstract. Municipal solid waste incineration fly ash is generated from domestic waste after incineration. Its high concentration of heavy metal salts can cause serious harm to the human body after water leaching, and it was classified as hazardous solid waste. This paper focused on the ratio of cementitious materials through orthogonal test and the effect of different content of fly ash on the mechanical properties in filling materials. It was found that upper limit of fly ash accounts was 60wt. % in cementitious materials, the compressive strength of the filling material after curing for 28 days was reached 3.34 MPa, completing the strength requirement of filling material, and the leaching concentration of cadmium was less than the limits specified in standards of drinking water quality. The XRD results showed that the hydration reaction of cementitious system mainly produces mineral phases such as ettringite and C-S-H gel. The porosity and adsorption of C-S-H gel lead to the inclusion of Cd²⁺. Part of Cd²⁺ was entered the ettringite lattice to replace the Ca²⁺, forming a large number of ettringite with Cd²⁺ in it.

1. Introduction
In 2018, 200 million tons of domestic waste was produced by large and medium-size cities in China. Faced with such a large amount of domestic waste, secondary pollution and space limitation have emerged by the traditional method of concentrated landfill. Therefore, it is an inevitable trend to dispose of domestic waste by incineration, which has the notable advantages of reducing capacity, quantity and energy recovery[1], and is becoming a main way of the harmless disposal of domestic waste. However, heavy metal ions cannot be decomposed and converted during the incineration process, existing in fly ash after incineration. Therefore, the MSWI fly ash needs harmless treatment before landfill or resource utilization[2].

Cadmium is the most harmful substance of the 12 substances proposed by the United Nations Environment Programme in 1984, second only to mercury in terms of human toxicity[3]. At present, the most commonly disposal method for MSWI fly ash is solidification/stabilization(S/S) technology. The effect of S/S on most harmful heavy metals has been proved effectively[4]. There are many kinds of cement which can be used as curing agent, but the most commonly used is Portland cement[5]. However, due to the high production cost, poor curing performance and large emission of greenhouse gases, the use of Portland cement will cause environment problem. Therefore, we need to change the cement-based material system and to find a low-cost S/S system with better performance. The blast furnace slag have certain potential activity, after mixing with fly ash and other cementitious materials, hydration reaction can take place under certain conditions, forming a massive calcium silicate hydrates with low heavy metal toxicity leaching and better long-term stability[6]. The purpose of this paper is to reuse solid waste materials as cementitious materials and use tailings as aggregates to make filling materials. This study can realize the resource utilization of fly ash, and avoid the pollution and harm
caused by its storage and burial, also can avoid the effect of heavy metals on environment and human health, and reduce the adverse effect of Portland cement on the environment, greatly reducing the cost of cemented filling mining and improving the economic benefit of mine enterprises.

The mechanism and microstructure of cemented backfill materials were characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential scanning calorimetry (DSC), and Scanning Electron Microscopy and Energy Dispersive Spectrometer (SEM-EDS).

2. Materials

2.1 Iron tailings

The iron tailings provided by Jintaicheng Environmental Resources CO., Ltd (Hebei China) are used as aggregate. Its main compositions are SiO₂, CaO, MgO, Al₂O₃, Fe₂O₃, FeO and other metal oxides. The specific chemical composition is shown in table 1, and the granularity characteristic composition is shown in table 2. The main mineral phase of tailings is CaCO₃, foshagite, xonotlite and okenite, as shown in XRD analysis results in figure 1.

### Table 1. Chemical composition of raw materials (mg·kg⁻¹).

| Components    | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO  | CaO   | MnO  | TiO₂ | Loss |
|---------------|------|-------|-------|------|-------|------|------|------|
| Tailings      | 35.56| 6.24  | 6.09  | 14.03| 26.17 | 0.12 | 0.17 | 7.81 |
| Slag          | 25.88| 13.75 | 1.28  | 5.79 | 49.53 | 37.54| 25.88| 1.28 |
| Desulfurization Gypsum | 1.50 | 0.65  | 0.35  | 0.64 | 39.09 | 0.16 | 0.03 | 18.29|
| MSWI fly ash  | 4.69 | 1.73  | 2.05  | 4.38 | 40.32 | 0.07 | 0.024| 0.03 |

### Table 2. The grain size characteristics of the value of raw materials.

| Materials name | D₁₀/μm | D₅₀/μm | D₉₀/μm |
|----------------|--------|--------|--------|
| Tailings       | 2.35   | 15.89  | 27.46  |
| Slag           | 0.37   | 2.00   | 4.68   |
| Desulfurization Gypsum | 0.35  | 0.56   | 4.38   |
| MSWI fly ash   | 2.75   | 16.40  | 76.00  |

*Note: D₁₀, D₅₀ and D₉₀ respectively achieve a sample of the cumulative size distribution percentage of 10%, 50% and 90% of the corresponding particle size.*

![XRD analysis of tailings](image)

Fig 1. XRD analysis of tailings.
2.2 Blast furnace Slag
The blast furnace slag is provided by Jintaicheng Enviromental Resources CO.,Ltd(Hebei China). Its main components including SiO$_2$, CaO and Al$_2$O$_3$ account for 90% of the total amount, which also contain a small amount of FeO, MgO, Na$_2$O, K$_2$O and Fe$_2$O$_3$, as shown in Table 1. The granularity characteristic composition is shown in table 2. The alkaline coefficient of slag is $M_o=(\text{CaO+MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)=1.398>1$, which belongs to alkaline slag; the quality coefficient is $K=(\text{CaO+MgO+Al}_2\text{O}_3)/(\text{SiO}_2+\text{MnO}_2+\text{TiO}_2)=2.507>1.2$, in accordance with the high active slag specified in GB/T203.78 granulated blast furnace slag in cement [7].

The XRD analysis of slag is shown in figure 2. Apart from partial carbonization during transportation to produce CaCO$_3$, there is no obvious crystal peak, indicating that the composition of mineral phase in slag is mainly glass phase, without obvious crystalline phase.

![XRD analysis of slag](image)

Fig 2. XRD analysis of slag.

2.3 Desulfurization gypsum
The desulfurization gypsum is provided by Jintaicheng Enviromental Resources CO.,Ltd(Hebei China). The content of CaO and SO$_3$ in gypsum is relatively high, followed by SiO$_2$, MgO and Al$_2$O$_3$. The main chemical components of desulfurized gypsum are shown in table 1 and particle size characteristics are shown in table 2. As shown in figure 3, it can be seen that the main composition of desulfurized gypsum is CaSO$_4$•2H$_2$O.
2.4 MSWI fly ash
The MSWI fly ash in this study is from Beijing Gaoantun waste incineration plant. The chemical composition are shown in table 1, the particle size characteristics are shown in table 2, and the leaching results of heavy metals are shown in table 3. As shown in table 3, the leaching concentration of Cd is nearly 520 times higher than that in the drinking water standard.

Table 3. Gaoantun fly ash as heavy metal leaching test results/(mg·L⁻¹).

| Components                         | Cu  | Zn  | Pb  | Cd  | As  | Hg  | Cr  |
|------------------------------------|-----|-----|-----|-----|-----|-----|-----|
| Gaoantun MSWI fly ash              | 6.8 | 31.7| 3.03| 2.6 | 0.0048 | 0.0038 | <0.01 |
| drinking water standard            | 1   | 1   | 0.01| 0.005| 0.01 | 0.01 | 0.01 |

3. Test method

3.1 Molding method
The test selects the mold of 40mm*40 mm*160 mm. Experiments need to mix tailings, cementitious materials and water, stir the mixture for 5 minutes, measure its fluidity, and then fill the slurry into the mold. When injecting slurry into the mold, it shall be carried out on the vibrating table to ensure that the slurry is filled with the mold.

3.2 Compressive strength Determination
The pressurized plate should be removed before the compressive test. The center difference between the half prism and the pressure plate of the press machine should be within 0.5mm, and the part of the prism exposed to the pressure plate is about 10mm. The loading speed of the press should be controlled in the 0.02kN/s~0.2kN/s, and should be strictly mastered when approaching the damage. The compressive strength is calculated according to equation 1.

\[
R_c = \frac{F_c}{A}
\] (1)

In the formula: 
- \(R_c\)—compressive strength (MPa);
- \(F_c\)—Breaking load(kN)
- \(A\)—Area under pressure 40mm * 40mm = 1600mm²

The result of compressive strength is the average value of the compressive strength of three test blocks, which was accurate to 0.01 MPa. If one of the 3 strength values exceeds the average of 10%, it...
should be rejected with the average of the remaining 2 values as the final result. If there are more than 2 strength values exceeds the average of 10%, then this set of test block is invalid.

3.3 Heavy metal leaching test
The national environmental protection standard “toxic leaching method of solid waste -- horizontal oscillation method"(HJ557 -- 2009)[9] was adopted to determine the leaching toxicity. The test needs to break samples into all particles through the sieve 3mm diameter and weigh dried sample 10g, then place it in the volume of the extraction bottle of 250ml. The next step is to calculate the volume of the required extract liquid according to the liquid-solid ratio of 10:1 (L/kg). After adding the leaching agent, the leaching bottle is vertically fixed on the horizontal oscillating device. After vibrating for 8 h at room temperature, the extraction bottle was removed and set for 16 h. A 0.45 microporous membrane was installed on the pressure filter to collect the leaching liquid for analysis. The leaching agent uses deionized water.

4. Results and Discussion

4.1 Experiment
The purpose of this experiment is to study the effect of different fly ash content on the working performance of filling materials. The amount of fly ash is 0%, 20%, 40%, 60%, 80% and 100% of the total quality of cementitious materials respectively. According to the previous research results[10], it is assumed that slurry concentration is 80%, the ratio of mortar to tailing is 1:4, and the quality ratio of cementitious material is slag:desulfurization gypsum =80%:20%. The test prepares the filling test block according to(GB17671-1999)“Cement mortar strength test method” , and maintenances under the conditions of 35℃, 90% humidity ,test results are shown in figure 4.

![Fig 4. Results of compressive strength test for fly ash content.](image)

As shown in figure 4, the compressive strength of the filling block decreases with the increase of fly ash content. This is because the original fly ash donot have cementation, with the increase of fly ash content, the amount of cementitious materials such as slag reduce, resulting in the decrease of the formation of hydration reaction, so the compressive strength of the filling block decreased. After 3d and 7d of curing, the compressive strength of filling block with 0% fly ash is higher than the filling block with 20% fly ash. After curing for 28d, the compressive strength of filling block with 20% fly
ash is higher than the filling block with 0% fly ash. This is due to the fly ash with strong alkaline, in the long-term effect of a small amount of fly ash will have a certain alkali excitation of slag, so that the potential activity of the slag can be completely released, thus promoting hydration reaction, and causing the compressive strength to become higher. The leaching results are shown in table 4.

Table 4. Leaching results of fly ash content test.

| Sample | Curing time | As  | Cd  | Cr  | Pb  | Sb  | Sn  | Zn  |
|--------|-------------|-----|-----|-----|-----|-----|-----|-----|
|        | 3d          | ND  | ND  | 0.0060 | ND | ND | ND | 0.0020 |
| B1     | 7d          | ND  | ND  | 0.0030 | ND | 0.0140 | ND | 0.0010 |
|        | 28d         | ND  | ND  | 0.0100 | ND | ND | ND | 0.0010 |
| B2     | 3d          | ND  | ND  | 0.0120 | ND | ND | ND | ND |
|        | 7d          | ND  | ND  | 0.0030 | ND | ND | ND | 0.0010 |
|        | 28d         | ND  | ND  | 0.0100 | ND | ND | ND | 0.0010 |
| B3     | 3d          | ND  | ND  | 0.0140 | ND | ND | ND | ND |
|        | 7d          | ND  | ND  | 0.0030 | ND | ND | ND | 0.0020 |
|        | 28d         | ND  | ND  | 0.0100 | ND | ND | ND | 0.0010 |
| B4     | 3d          | ND  | ND  | 0.0150 | ND | ND | ND | ND |
|        | 7d          | ND  | ND  | 0.0040 | ND | ND | ND | 0.0010 |
|        | 28d         | ND  | ND  | 0.0110 | ND | ND | ND | ND |
| B5     | 3d          | ND  | ND  | 0.0340 | ND | ND | ND | 0.0010 |
|        | 7d          | ND  | ND  | 0.0100 | ND | ND | ND | ND |
|        | 28d         | ND  | ND  | 0.0220 | ND | ND | ND | 0.0010 |
| B6     | 3d          | ND  | ND  | 0.0400 | ND | ND | ND | 0.0010 |
|        | 7d          | ND  | ND  | 0.0390 | ND | ND | ND | 0.0010 |
|        | 28d         | ND  | ND  | 0.0260 | ND | ND | ND | ND |

Drinking water standard

| Detection limit | 0.0100 | 0.0050 | 0.0500 | 0.0100 | 0.0050 | ND | 1.0000 |

ND=NOT DETECT

According to table 4, after curing for different ages, the leaching concentration of heavy metal in filling blocks meets the standard of drinking standard. In mine filling engineering, the compressive strength of filling material after curing 28 days is required to reach more than 3MPa. Therefore, on the basis of treating fly ash as much as possible, 60% fly ash content is selected for further research.

4.2 Mechanism analysis
The test is respectively mixed with 0% (no CdCl₂), 1% and 2% pure CdCl₂ agents of the total mass of fly ash, and make into paste blocks for mechanism analysis, which are divided into A1, A2 and A3, respectively.

4.2.1 IR analysis. It is shown in figure 5 that the absorption bands are mainly concentrated in 3417~3428cm⁻¹, 1626~1628cm⁻¹, 1442~1444cm⁻¹, 1120~1122cm⁻¹, 982~987cm⁻¹ and 594~598cm⁻¹. The absorption peak near 594cm⁻¹ is the bending vibration of the Si-O-Al bond; the absorption peak near 671cm⁻¹ is the symmetric stretching vibration of Al-O when Al³⁺ substitutes Si⁴⁺ in [SiO₄]⁴⁻ group forming [AlO₄]⁴⁻ group; the absorption band near 876cm⁻¹ characterizes the bending vibration of C-O bonds. The presence of C-O bonds is caused by the reaction of Ca(OH)₂ in the cementitious materials with CO₂ in air to generate a small amount of CaCO₃. The absorption peak near 987cm⁻¹ is caused by the Si-O asymmetric vibration in [SiO₄]⁴⁻ structure, which is the characteristic peak of C-S-H. The
absorption peak here reflects the increase in the amount of ettringite and C-S-H gel. The absorption band near 1122 cm\(^{-1}\) characterizes the stretching vibration of S-O bond in ettringite. The characteristic band near 1442 cm\(^{-1}\) is the characteristic band of C-S-H gel and ettringite, which is formed by hydration reaction of gel system, the reason of spectral bandwidth is low crystallinity of C-S-H gel. The absorption band at 1628 cm\(^{-1}\) is attributed to the bending vibration of the O-H bond in water, which is a characteristic of internal vibration absorption of crystal water, indicating that the slag-hydration reaction produces a substance containing crystal water. As the age of the reaction increases, the permeability of the [OH\(^{-}\)] absorption band decreases and free water gradually turns into crystallized water or adsorbed water by participating in the reaction. The spectral band around 3425 cm\(^{-1}\) is the stretching vibration band of water in the hydration product C-S-H gel, indicating that C-S-H gel is generated with increasing curing days. It can be also seen from the results that after curing for 28 days, the IR curve measured by adding different CdCl\(_2\) agent did not change significantly, indicating that the hydration products generated by hydration reaction were not significantly changed, basically presenting the same characteristic absorption band, just the transmission of the characteristic band decreased slightly with the increase of the agent content.

![Fig 5. IR analysis of paste cured for 28d.](image)

**Fig 5.** IR analysis of paste cured for 28d.

4.2.2 **TG-DSC analysis.** The TG-DSC curve of paste with different dosage of CdCl\(_2\) agent is shown in figure 6. The endothermic peak is mainly between 150~200\(^\circ\)C, and exothermic peak is mainly between 850~900\(^\circ\)C. Through analysis, the corresponding endothermic peaks nearing 150\(^\circ\)C is caused by dehydration of C-S-H and ettringe and the dehydration of the semi-aqueous gypsum during the heating process. It is the absorption peaks for a small amount of free water, adsorption water and combined water in ettringe, C-S-H and gypsum. With the growth of the age, the combined water is reduced, indicating that the hydration reaction leads to the consumption of raw materials and hydration product generation. And about 850\(^\circ\)C, the exothermic reaction is caused by the transformation of C-S-H gel crystalline.
Fig 6. TG-DSC analysis of paste cured for 28d.

### 4.2.3 SEM-EDS analysis

The SEM-EDS results show the morphology of hydration products, solidification mechanism of cementitious system, results of component analysis in micro-regions and determine the existence form of Cd in the cementitious system. The SEM test results are shown in figure 7a, 7b and 7c. The table 5 represents the composition content of different micro-regions.

![Images of SEM analysis](image)

**Table 5. Results of component analysis in micro-regions(%)**

| number | C    | O    | Al   | Si   | S    | Ca   | Fe   | Cd   |
|--------|------|------|------|------|------|------|------|------|
| 1      | 25.63| 53.78| 7.92 | 5.26 | 1.28 | 6.23 | 0.68 | 0.33 |
| 2      | 24.46| 53.07| 7.42 | 5.27 | 1.43 | 6.73 | 0.52 | 0.18 |
| 3      | 20.25| 56.67| 8.35 | 3.86 | 1.02 | 7.68 | 0.66 | 0.12 |
It can be seen from figure 7(a, b, c) that the cementitious system, after hydration for 28 days, produces a large amount of needle-bar shape ettringe and unformed C-S-H gel, which is the main reason for the filling material to have a certain strength. According to the shape of picture and composition analysis, it is indicated that points 1~3, and 6~9 are ettringite. As they contained certain Ca, Al, O and S, it can be observed that there are some Cd bearing vanadium minerals or Cd bearing compound salts. However, point 4 and point 5 are analyzed as syringoid ettringite interspersed in C-S-H gel, and the presence of certain Cd was detected, indicating that some Cd\(^{2+}\) are wrapped in gel and then solidified. As shown in table 5, with the increase of the dosage of CdCl\(_2\), the amount of Cd\(^{2+}\) solidified by ettringe and C-S-H gel also increase.

5. Conclusion
The upper limit quality of fly ash is 60wt. %, and the quality ratio of the mortar to tailing is 1:4. The slurry concentration is 80%. After Curing for 28d, under the condition of the temperature of 35\(^{\circ}\)C, and the humidity of 95\%, the compressive strength of the filling block reaches 3.34MPa, satisfying the minimum strength requirement of the backfilling material, and the leaching concentration of the Cd\(^{2+}\) is less than standards for drinking water in accordance with Chinese Standard GB 5749-2006). The harmless treatment of cadmium in fly ash is completed. Through the analysis of IR, DSC and SEM-EDS of the paste block, it was shown that a large amount of ettringe and C-S-H gels were produced during the hydration reaction process, so that the filling material had a certain strength. Ettringe reacts with Cd\(^{2+}\) after adding the CdCl\(_2\) agent to generate a large number of cadmium containing compound salts, which then solidifies the Cd\(^{2+}\), while C-S-H gel also has a certain wrapping effect on the Cd\(^{2+}\) due to its amorphous characteristics, and then successfully S/S the Cd\(^{2+}\).

Acknowledgments
Grateful acknowledge is made to my supervisor Prof. Ni Wen who gives me considerable help by means of suggestion, comment and criticism. His encouragement and support have sustained me through frustration and depression. Also, I feel grateful to Dr. Zhang Siqi who gives me so much help.

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