Study on mechanical properties of cemented filling materials using by low-chlorine fly ash

Tengyu Shi¹, Siqi Zhang¹*, Ni Wen¹, Keqing Li¹, Ke Wang¹ and Haojing Ba¹
¹School of Civil and Resource Engineering, University of Science and Technology Beijing, Beijing 100083, China
*Corresponding author’s e-mail: zsq2017@ustb.edu.cn

Abstract. In this study, the blast furnace slag and desulfurized gypsum were used to make cementing materials, mixed with the tailings and fluidized bed municipal solid waste incineration (MSWI) fly ash to make high performance cementing filling material. The results show that: (1) The best ratio of test is low chlorine fly ash: slag: desulfurization gypsum = 20%: 68%: 12%, the MPC of cementing material is 82%, and the cement-sand ratio is 1:4, after curing for 28 days in a standard curing box with a curing temperature of 40°C and a relative humidity of 90%, the compressive strength reaches 22.81MPa, the flow rate reaches 240 mm. (2) The maximum amount of fly ash can reach 60%, after 28 days of curing, the sample strength is 8.70 MPa, the flow rate is 220 mm, both of which meet the requirements. (3) Comparing the slag system and cement system with 60% fly ash, it was found that the strength reached 10.36 MPa after 28 days of curing, the flow rate of the cement system was 215 mm, which did not reach the self-flow standard. It is possible to provide a low cost cementing filling material containing waste incineration fly ash in future.

1. Introduction
Recent years have witnessed the rapid development of the waste incineration industry in China. In the incineration process, fly ash containing a large amount of hazardous wastes such as heavy metals, soluble salts and dioxins is produced, which must be treated before discharge [1]. Maintenance and stabilization are the main methods for the treatment, while cement is the main material for solidifying the fly ash [2,3]. However, the hazard of high chlorine content in fly ash shall not be ignored because it not only aggravates the internal corrosion of cement kiln equipment, leading to abnormal operation [4], but also directly hinders the hydration process, thus increasing the solubility of heavy metals in the solidified body [5]. Therefore, the chlorine content in the fly ash from waste incineration is an important factor affecting its utilization in the cement industry.

The highly-efficient and low-pollution clean incineration technology-circulating fluidized-bed boiler technology developed in China in the past decade has such advantages as good smoke emission performance and dioxin formation control. It can also ensure that the emission of NOx, sulfide and acid gas can comply with environmental requirements. In addition, it has high incineration efficiency with coal as the auxiliary fuel, which can significantly reduce operating costs [6]. However, it also has such disadvantage as high self-consumption power consumption, large amount of fly ash discharge and abrasion of furnace refractory [7]. At present, China's incineration plants using fluidized bed technology reach 38% by volume and 40% by scale [8], second only to those using boiler grate technology.

Wang et al. [9] found that the chlorine and sulfur content of fly ash from fluidized bed are lower...
than that of fly ash from boiler grate. The average chlorine content of the two is 1.71% and 15.41%, respectively, and the average content of SO$_3$ is 2.875% and 10.67%. Due to coal blending, the heavy metal content is several times lower than that of the fly ash from boiler grate. When the chlorine content in the fly ash is low, the content of fly ash in the co-disposal of the cement kiln can be increased, thus realizing the scale application. The replacement of cement for construction as the basic material is low in disposal cost, low in resource consumption, and low in greenhouse gas emissions [10]. At present, China's research on waste incineration of low-chlorine fly ash is still in the basic stage. For example, Liu [11] found through fly ash effect and microscopic analysis that when the ratio of fly ash from fluidized bed to cement mass is 30%: 70% and 25%: 75%, the strength reaches 38.1MPa and 31.8MPa after 28d, indicating that the fly ash from fluidized bed has better pozzolanic activity. There are also some foreign studies on fly ash from fluidized bed. Wu et al. [12] have shown that fly ash from fluidized bed combustion can promote slag hydration. When the ratio of fly ash to slag is 3:7, after maintenance for 56 days, the strength can reach 72.4% (31.43 MPa) of the strength of ordinary Portland cement mortar test block. Jouni Rissanen [13] found that when the fly ash content is low (10% and 20%), it can reach almost the same strength (50MPa) as ordinary Portland cement system after 90 days. When the fly ash content is 40%, the compressive strength can still reach 88% (44MPa) of cement strength. Although many studies have shown that fly ash from fluidized bed has the potential to replace cement, further research is needed for verification.

The filling mining technology that uses tailings as aggregates to form cemented fillers in combination with cementing agents has been widely used worldwide due to its advantages of energy saving, safety and high efficiency. In recent years, it has been found that slag under the excitation of FGD gypsum can replace ordinary Portland cement as a cementing agent. Therefore, this paper takes the combination of low-chlorine fly ash, slag and FGD gypsum to replace ordinary Portland cement as the binding agent, and adds tailings to prepare full-solid waste high-performance mine filling material. This paper focuses on its mechanical properties and the addition amount of low-chlorine fly ash, with a purpose to realize large-scale utilization and harmless treatment of fly ash from waste incineration, and at the same time, to solve the problem in the low-cost replacement of cement-based binding materials in cement-filled mining.

2. Test material
Slag is from a steel plant in Hebei Province. Its specific surface area is 500m$^2$/kg after grinding [14]. FGD gypsum is from in a power plant in Hebei Province. Its specific surface area is 320m$^2$/kg after drying. Tailings is from an iron ore mine in Hebei Province, and its main mineral component is quartz. Cement used here is ordinary Portland cement P.O42.5 with specific surface area of 355m$^2$/kg. Fly ash from waste incineration (fly ash) is from the circulating fluidized bed in an incineration plant in Tangshan City. The chemical composition of each raw material is shown in Table 1. The XRD analysis result of the fly ash is shown in Figure 1. It can be seen that the main minerals of fly ash are quartz, calcite, anhydrite, calcium oxide, aluminum oxide and sodium sulfate.
Table 1. Chemical composition of the raw materials. (wt. %)

| Sample  | CaO   | Cl | SiO₂ | Al₂O₃ | MgO  | SO₃  | Fe₂O₃ | TiO₂ | Na₂O | K₂O | MnO |
|---------|-------|----|------|-------|------|------|-------|------|------|-----|-----|
| Slag    | 42.25 | —  | 26.35| 15.23 | 10.82| 1.82 | 1.21  | 0.98 | 0.56 | 0.39| 0.21|
| FGD     | 48.37 | 0.42 | 2.71 | 0.89  | 1.35 | 43.59| 0.53  | —    | —    | 0.27| —   |
| Gypsum  | —     | —  | 55.63| 9.64  | 5.33 | 2.01 | 9.40  | 0.66 | 2.23 | 2.00| 0.23|
| Tailings| 63.52 | —  | 20.26| 5.05  | 2.85 | 2.56 | 3.56  | —    | —    | 1.00| 0.28|
| Cement  | 27.24 | 3.38| 28.31| 15.04 | 9.40 | 0.66 | 6.38  | —    | —    | —   | —   |
| Fly ash | 63.52 | 1.27| 0.53 | 0.20  | 0.12 | 0.12 | 0.06  | 0.05 | 0.04 | 0.03| 0.02|

Figure 1. XRD analysis spectrum of MSWI fly ash.

3. Test method

3.1. Sample preparation
The mortar test block is prepared based on the experimental scheme. First, weigh the tailings, slag, FGD gypsum and water. Then, pour the tail sand into the stirring pot, add the binding material, and stir it for 5 minutes. After measuring the fluidity, place the slurry in a 40mm × 40mm × 160mm mold on the vibrating table and ensure that the slurry is filled with the mold. Next, seal it with plastic wrap and place it in a standard maintenance box with a temperature of 40 °C [15] and a relative humidity of 90% or more. After 3 days, remove the mold and test the 3D compressive strength of the test piece. After the mold is removed, place it in a standard maintenance box for 7 days and 28 days and measure the compressive strength.

3.2. Performance test
The compressive strength of the filled test piece is measured using a YES-300 digital display hydraulic pressure tester.

The fluidity of the filling slurry is measured using a NLD-3 type fluidity meter.
4. Test result and discussion

4.1. Strength test of fly ash content

According to the previous experiments [15], the tentative cement-to-sand ratio is 1:4, the slurry concentration is 82%, and the FGD gypsum proportion in cementing material is 10%. The five gradients of fly ash proportion are designed as 0%, 20%, 40%, 60%, and 80%. The test scheme is shown in Table 2, and the strength results are shown in Figure 2.

| Number | Cement-sand ratio | Concentration | Tailings (g) | FGD Gypsum (%) | Fly ash (%) | Slag (%) | Water (ml) | Fluidity (mm) |
|--------|-------------------|---------------|--------------|----------------|-------------|----------|------------|--------------|
| A1     | 1:4               | 82%           | 960          | 10             | 0           | 90       | 225        |              |
| A2     |                   |               |              |                | 20          | 70       | 238        |              |
| A3     |                   |               |              |                | 40          | 50       | 263.5      | 230          |
| A4     |                   |               |              |                | 60          | 30       |            | 220          |
| A5     |                   |               |              |                | 80          | 10       | 208        |              |

It is found from Table 2 that the fluidity of the slurry increases first and then decreases with the increase of the mixing amount of fly ash. When the amount exceeds 60%, the fluidity does not reach the standard of 220 mm at which point the filling slurry can flow by itself. When the amount reaches 20%, the fluidity reaches 238 mm. This is because the fly ash hydration reaction rate is slow and the fly ash will gradually harden in the later stage. The early fly ash is equivalent to the water reducing agent [16], which will increase the slurry fluidity. In addition, the fly ash can serve as the ball in the slurry. Its adsorption effect on the surface leads to the morphological effect of the electric double layer structure, thus significantly improving the fluidity. But the capacity of the particles approaches saturation in this process [16,17].

It is found from Figure 2 that the strength decreases with the increase of the mixing amount of fly ash. The filling test piece made based on Formula A5 has the strength of only 2.74 MPa after 28 days of maintenance, failing to meet the requirement of mine filling, that is, 5 MPa. The blocks made based
on other formulas all meet the strength requirement. The fly ash is similar to the cementing material such as slag in terms of component, but it has a different mineral composition and structure and is inactive, so the use of fly ash will reduce the active components in the system thus reducing the hydration product, resulting in a decrease in the strength of the test piece. The fly ash is strong in water absorption, thus reducing the amount of water required for hydration, resulting in incomplete hydration and a decrease in the strength of the test piece. Therefore, when the fly ash content is 20%, the compressive strength reaches the maximum of 22.81 MPa; when the fly ash content is 60%, the strength is 8.70 MPa after 28d maintenance, which basically meets the requirements.

4.2. Strength test of FGD gypsum content
When the fly ash content is 20% and the other test conditions are the same, this paper designs five gradient FGD gypsum content, namely, 6%, 8%, 10%, 12%, and 14%. See Table 3 for the test scheme, and see Figure 3 for the strength test results.

| Number | Cement-sand ratio | Concentration (%) | Tailings (g) | FGD Gypsum (%) | Fly ash (%) | Slag (%) | Water (ml) | Fluidity (mm) |
|--------|-------------------|-------------------|--------------|----------------|-------------|----------|------------|---------------|
| B1     | 1:4               | 82                | 960          | 6              | 74          |          |            | 198           |
| B2     |                   |                   |              | 8              | 72          |          |            | 215           |
| B3     | 1:4               | 82%               | 960          | 10             | 20          | 70       | 263.5      | 245           |
| B4     |                   |                   |              | 12             | 68          |          |            | 240           |
| B5     |                   |                   |              | 14             | 66          |          |            | 232           |

Figure 3. Determination strength results of the amount of gypsum.

It can be seen from Table 3 that the fluidity does not reach the standard at which point the filling slurry can achieve complete self-flow when the gypsum content is 6% or 8%, which is because insufficient gypsum and coagulation time will lead to the phenomenon of instantaneous condensation, meaning that the mortar condenses and hardens too early with low fluidity. When the mixing amount is 10%, the fluidity reaches the optimal value. It can be seen from Figure 3 that the strength increases
first and then decreases with the increase of gypsum content, and the strength of each test block can reach more than 5 MPa after 28 days of maintenance. Some studies have found that FGD gypsum has a significant excitation effect on fly ash, which can increase the setting time and the strength of the paste. However, excessive FGD gypsum will lead to the existence of a large amount of hemihydrate gypsum in the system. With more active Al₂O₃ dissolved in the fly ash vitreous, ettringite continues to emerge. Both of them are expansive, and the abundant existence of them will lead to a decrease of strength [18], which is consistent with the results. When the mixing amount exceeds 12%, the rate of strength increase begins to decrease. Therefore, with the influence of the setting time on the fluidity and strength taken into consideration, when the gypsum content is 12%, the fluidity reaches 240 mm, and the strength reaches 19.28 MPa.

4.3. Test on the best MPC of cementing material

When the fly ash content is 20%, the gypsum content is 12%, and the other test conditions are the same, this paper designs four concentration gradients, namely, 78%, 80%, 82%, and 84%. The test plan is shown in Table 4, and the strength test results are shown in Figure 4.

| Number | Cement-sand ratio | Concentration | Tailings (g) | FGD Gypsum (%) | Fly ash (%) | Slag (%) | Water (ml) | Fluidity (mm) |
|--------|-------------------|---------------|--------------|----------------|-------------|----------|------------|--------------|
| C1     | 1:4               | 78%           |             |                |             |          |            | 336.5        | 268          |
| C2     |                   | 80%           | 960         | 12             | 20          | 68       |            | 300          | 252          |
| C3     |                   | 82%           |             |                |             |          |            | 263.5        | 235          |
| C4     |                   | 84%           |             |                |             |          |            | 227          | 205          |

It is found from Table 4 that the fluidity decreases with increasing concentration. When the concentration is 84%, the fluidity is only 205 mm. But the excessive amount of water dilutes the slurry, leading to segregation, which has a certain influence on the fluidity performance. As the water content continuously reduces, the amount of water required for the hydration reaction becomes
insufficient, leading to lower fluidity.

It is found from Figure 4 that the strength increases with increasing concentration, and that the strength values all meet the requirements after 28 days of maintenance. With lower concentration, when there is more water required for the hydration reaction, the free water will be filled in the voids of the solidified body, resulting in a decrease in strength. When the concentration reaches 84%, the rate of increase in strength slows down, which is because holes caused by thick slurry [19] result in a decrease in strength. Therefore, the optimum concentration is taken as 82%, at which points the slurry is the strongest with good fluidity performance.

4.4. Test on best cement-sand ratio

When the fly ash content is 20%, the concentration is 82%, and the other test conditions are the same, this paper designs eight cement-sand ratio gradients, namely, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7 and 1:8. The test plan is shown in Table 5, and the strength test results are shown in Figure 5.

| Number | Cement-sand ratio | Concentration | Tailings (g) | FGD (%) | Fly ash (%) | Slag (%) | Water (ml) | Fluidity (mm) | Strength (MPa) |
|--------|-------------------|---------------|--------------|---------|-------------|----------|------------|--------------|----------------|
| D1     | 1:1               | 82            | 25           | 86      | 12          | 20       | 68         | 263.5        | 150            |
| D2     | 1:2               | 160           |              |         |             |          |            |              |                |
| D3     | 1:3               | 212           |              |         |             |          |            |              |                |
| D4     | 1:4               |               | 960          | 12      | 20          | 68       | 263.5      | 240          |                |
| D5     | 1:5               |               |              | 82      | 12          | 20       | 68         | 255          |                |
| D6     | 1:6               |               |              |         | 12          | 20       | 68         | 250          |                |
| D7     | 1:7               |               |              |         | 12          | 20       | 68         | 242          |                |
| D8     | 1:8               |               |              |         |             |          |            | 235          |                |

It is found from Table 5 that the fluidity increases first and then decreases with the increase of the sand content. When the cement-sand ratio is 1:4, the fluidity meets the requirements. The iron ore tailings contain a large amount of tiny particles, which can improve the fluidity of the mortar with a small amount, and lead to a decrease in the plasticity with an excessive amount. It can be seen from
Figure 5 that the strength increases with the increase of the cement-sand ratio. However, when the ratio is 1:8, the strength is reduced to 4.26 MPa after 28 days. The iron ore tailings contain the calcium silicate component similar to cement, which is of a certain activity. The use of an appropriate amount of tailings under the premise of not reducing the fluidity leads to a slight reduction in strength but an increase in the toughness and performance of the mortar [20]. However, the tailings do not have cementing properties, and excessive tailings will lead to the reduction in hydration products. Therefore, considering the results of fluidity and strength, following the principle of using fly ash as much as possible, the cement-sand ratio should be set as 1:4 at which point the flow performance is good, and the strength reaches 16.64 MPa after 28 days.

4.5. Test of ordinary Portland cement system

Based on the above test results, when the concentration, the cement-sand ratio, and the maintenance conditions are the same, this paper replaces the cement with binding materials such as slag and FGD gypsum, and prepares mortar test blocks in the ordinary Portland cement system in which the fly ash content is 0%, 20%, 40%, and 60%. The test plan is shown in Table 6, and the strength test results are shown in Figure 6.

| Number | Cement-sand ratio | Concentration (%) | Tailings (g) | Cement (%) | Fly ash (%) | Water (ml) | Fluidity (mm) |
|--------|-------------------|-------------------|-------------|------------|-------------|------------|---------------|
| E1     | 1:4               | 82                | 960         | 100        | 0           | 263.5      | 220           |
| E2     |                   |                   |             | 80         | 20          | 245        |               |
| E3     |                   |                   |             | 60         | 40          | 225        |               |
| E4     |                   |                   |             | 40         | 60          | 215        |               |

Figure 6. Determination strength results of Portland cement system with the amount of fly ash.

It is found from Table 6 that the amount of fly ash has a certain influence on the fluidity of the cement system. When the fly ash content is 20%, the fluidity performance is the best, reaching 240mm. When the fly ash content reaches 60%, the fluidity only reaches 215mm. Some studies have found that the right amount of fly ash can reduce the plastic viscosity and yield stress of cement mortar, and at the same time, increase its fluidity [20]. It can be seen from Figure 6 that the
incorporation of fly ash reduces the strength of the test piece, especially the strength at the early stage. Greater amount of the mixing content leads to more significant decrease in strength. When the fly ash content is 20%, the strength after 7d and 28d of maintenance is close to or exceeds that of the test block without fly ash addition. Therefore, the optimum content of fly ash in the cement system is 20%, at which point the fluidity performance is the strongest, the strength reaches 31.89 MPa; the maximum content is 40%, at which point the fluidity is 225 mm, and the strength is 25.06 MPa.

5. Conclusion
The content of chlorine and sulfur in the fly ash in the circulating fluidized bed is small. The combination of low-chlorine fly ash and the slag in the high-mixing-content fluidized bed can replace the ordinary Portland cement to prepare the full tailings cement filling material under the excitation of FGD gypsum.

When ratio of fly ash: slag: FGD gypsum of the cementing material is 20%: 68%: 12% (the specific surface area of slag is 500 m²/kg; that of the FGD gypsum is 320 m²/kg), the concentration is 82%, and the cement-sand ratio is 1:4, the test block's strength will reach 16.33 MPa after 28 days in a standard maintenance tank with a temperature of 40 °C and a relative humidity of over 90%.

 Compared with the ordinary Portland cement system, the slag system has a higher strength than the slag system after 28 days. But when the fly ash content reaches 60%, the fluidity of the cement system does not reach the standard of complete self-flow. The low-chlorine fly ash-slag-FGD gypsum system with the fly ash content of 60% and the fluidity of 220mm can have the strength of 7.45MPa after 28d, which can meet the filling strength requirements and the self-flow standard.

Acknowledgement
This work was supported by the key research and development program of Hebei province [Grant Number 18273807D].

References
[1] Pan Y. (2015) Risk assessment of toxicity of domestic waste incineration fly ash and its resource utilization process. http://kns.cnki.net/kns/detail/detail.aspx?FileName=1015991153.nh&DbName=CDFD2016.
[2] Shi, H.S. (2007) Municipal waste incineration fly ash treatment technology and its resource utilization in cement production. Cement, 10: 1-4.
[3] Wang, W., Wu N. (2013) Research status of resource utilization of municipal solid waste incineration fly ash. Northern Environmental, 25: 27-28.
[4] Wu, B.R., Wang, D.Y., Chai, X.L. (2015) Dechlorination mechanism of municipal solid wastes incineration fly ash by biological process. China Environmental Science, 35:2470-2476.
[5] Li, X.D., Liu, Y.D. (2007) Experimental study on elution of chlorine from fly ash water and its sintering stabilization. Acta Scientiarum Naturalium Universitatisc Pekinensis, 6: 752-758.
[6] Chen, Y.C., Gui, B.F. (2005) Discussion of CFB technology used in living waste incineration. Jiangxi Energy, 4: 47-48.
[7] Bie, R.S., Wang, G.Q. (2003) Application of CFB combustion technology to incineration of municipal solid waste. Techniques and Equipment for Environmental Pollution Control, 4: 79-82.
[8] Xu, W.L., Wang, L.H. (2007) Current status and development forecast of waste incineration technology in China. China Environmental Protection Industry, 11: 24-29.
[9] Wang, L., Jin, Y.Y., Li, R.D. (2010) Pollution characteristics of municipal solid waste incineration fly ash. Environmental Science & Technology, 33: 21-26.
[10] Shi, H.S., Cheng, P., Guo, X.L. (2013) Research Status of Resource Utilization of Washed Municipal Solid Waste Incineration Fly Ash in Cement Production. Fly Ash Comprehensive Utilization, 6: 51-56.
[11] Liu, W.S., Zhang, C.H., Zhang D.J. (2008) Effect and Microscopic Analysis of Fluidized Bed
Fly Ash Solidification Incineration Fly Ash. Chinese Journal of Environmental Engineering, 09: 1260-1264.

[12] Wu, Y., Huang, R., Tsai, C. (2015) Utilizing residues of CFB co-combustion of coal, sludge and TDF as an alkali activator in eco-binder. Construction and Building Materials, 80: 69-75.

[13] Jouni, R., Katja Ohenoja, P.D.D.S., Paivo Kinnunen, P.D. (2017) Partial Replacement of Portland-Composite Cement by Fluidized Bed Combustion Fly Ash. J. Mater. Civ. Eng. 29: 04017061.

[14] Wang, K., Ni, W., Zhang, S.Q. (2018) Study on waste incineration fly ash-slag based gelling system and solid cadmium. Nonferrous Metals Engineering, 8: 123-127.

[15] Yang, H., Ni, W., Zhang, S.Q. (2018) Mechanism of solid cadmium in fly ash with metallurgical slag and cement incineration. Chinese Journal of Engineering, 40: 1027-1035.

[16] Zhu, X.L. (2015) Current Status and Technology Selection of Waste Incineration Power Generation Fly Ash Treatment. Electric Safety Technology, 17:59-62.

[17] Yan, X.H. (2018) Effect of Admixture on Mortar Performance and Mechanism. http://kns.cnki.net/kns/detail/detail.aspx?FileName=1018862295.nh&DbName=CMFD2018.

[18] Liu, Y., Fang, R., Cui, B.Q. (2018) Effect of Desulfurized Gypsum on Performance of Coal Powder Ash Filling Paste. Journal of Xianyang Normal University, 33:1-4.

[19] Lu, Q.Y., Du, J.F. (2018) Experimental study on the effect of iron tailings sand on the performance of dry mortar. Beton Chinese Edition — Ready-mixed Concrete, 9:30-32.

[20] Yang, Q.R., Zhao, Z.Z., Zhang, Q.Z. (2019) Influence of Several Factors on the Rheological Properties of Cement Mortar. Journal of Building Materials, 22:506-515.