Experimental study on the performance of goaf filling materials with high content of fly ash

Xiaodong Wang

R & D Center of Mine Disaster Control and Environment Management Technology, Xi’an Research Institute of China Coal Technology & Engineering Group Corp, Xi’an 710054, China

Email: 381898629@qq.com

Abstract. In this paper, fly ash is studied as the main cementing material for coal mine goaf filling. The performance of the filling materials with 90% fly ash such as compressive strength, impermeability, viscosity, additive effect and diffusion rule are studied experimentally and theoretically. The results show that compressive strength and impermeability are positively correlated with cement content when water-solid ratio is 0.7:1.0 with 90% fly ash. The compressive strength increases slowly in the early stage while it increases with a faster speed in the later stage. The compressive strength of the material after 60 days of curing is 1.90 times that of 28 days. Additive could promote the activity of fly ash and improve hydration reaction. The interparticle porosity is reduced, but strength at early stage and impermeability are increased. The viscosity of the filling material has an obvious shear thinning phenomenon as shear rate increases. An inflection point appears when shear rate is 30s⁻¹. The filling material with high content of fly ash presents the rule of horizontal diffusion and longitudinal accumulation in goaf filling treatment. The diffusion distance and accumulation height are positively correlated with grouting pressure.

1. Introduction

Coal resources play a key role in Chinese energy supply [1, 2]. In the long history of mining, about 2 million hectares of coal subsidence areas have been formed in China, and it is increasing at a rate of 70 000 hectares per year. Problems such as surface collapse, ground crack, construction (structure) building damage and environmental deterioration are easily occur in those widely distributed subsidence areas, which brought negative effects on the urbanization and environmental protection. Grouting is an important method for goaf treatment and grouting materials is the key [3]. However, due to the high cost of grouting materials, such method is not widely used in subsidence areas.

Coal for power generation accounts for more than 50% of China’s total coal consumption. Coal-fired waste such as fly ash, slag, and flue gas desulfurization gypsum are being produced in large quantity [4]. In 2017, the output of fly ash is around 6 000 million tons, 70% was used in construction industry and agriculture, with the left 30% dumped into the ash pond or stacked on farmland, ravines or slopes[4]. Actually, fly ash is a volcanic ash substance consisting of potential active materials, toner, and some inert substances, the main components are SiO2, Al2O3, Fe2O3, and CaO, etc., with high potential activity, so it is the best blend of cement[5].When the mass ratio of alkali slag, fly ash, sodium silicate, gypsum to water is 1.0:1.0:1.04:0.26:1.65, the performance of the cement slurry was optimal[3].A type of fly ash microsphere (FAM) collected directly from a high-temperature furnace...
using ceramic dust tubes to high-strength concrete. FAM has a relatively high level of early activity and could significantly improve pore structure at late ages [6]. Some researcher investigated the mechanical enhancement effect of multiple salt activators (CaCl₂, Na₂SO₄ and CaSO₄·2H₂O) on the FABC paste, and compared with the most widely used alkaline activator (NaOH and Ca(OH)₂) [7]. And FA and 0.7% SP enhance the flowability and spreading ability of fresh grouts, and bentonite can enhance the stability. The performance of cement-based grouts with 20-30% class F FA, 0-5% bentonite, 0.7% SP and volume ratios of 2:1-3:1 can satisfy the requirements of high performance, environmental friendliness and low costs in geotechnical and underground engineering [8]. Rubberized concrete interlocking bricks have been developed by utilising crumb rubber (10%) and fly ash (56%) as partial replacements of sand and OPC, respectively [9-11]. At the same time, some people investigated the shear and flexural behavior of HPSCC beams with no coarse aggregate and compressive strength of above 100MPa [12]. Wang et al. (2012) used microcalorimetry tested the effects of different amounts of fly ash and slag on cement hydration heat and heat release rate. The mixing of fly ash and slag improved the stability of calcium in cement hydration products [13]. Feng et al. (2011) studied how to stimulate the potential activity of fly ash, and obtained that alkaline activator, chloride salt activator and sulfate activator could promote the pozzolanic activity of fly ash [14]. Qi et al. (2015) studied the compressive strength, porosity, electrical resistivity, and hydration process of coal mine subsidence areas filling materials mixed with coal refuses, fly ash, cement and water [15].

At present, there are researches on the replacement of cement in concrete, mortar, and paste materials with fly ash. Fly ash could replace part of cement to reduce cost. However, there are few studies on rheological properties, impermeability and microstructure of goaf filling materials with high content of fly ash. By analyzing the strength, viscosity, impermeability and microstructure of the goaf filling materials with high content of fly ash, the influence of fly ash content on the performance will be demonstrated, offering valuable references for further application of goaf filling material with fly ash.

2. Test materials and methods

2.1. Raw materials
The main raw materials for the filling materials with high content of fly ash are as follows:

P·O 42.5, with a specific surface area of 369 m²/kg, initial setting time of 256 min, and the final setting time of 311 min. Table 1 shows the performance indicators of P·O 42.5.

Fly ash, Grade II power plant ash, with water requirement of 76%, and its loss on ignition is 5.29%. Table 2 shows the main chemical composition.

And drinking water.

Table 1. Performance indicators of P·O 42.5.

| MgO (%) | SO₃ (%) | Loss on ignition (%) | Specific surface area (m²/kg) | Stability | Initial setting time (min) | Final setting time (min) | Flexural strength (MPa) 3 days | Flexural strength (MPa) 28 days | Compressive strength (MPa) 3 days | Compressive strength (MPa) 28 days |
|---------|---------|---------------------|-----------------------------|-----------|---------------------------|--------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1.55    | 1.97    | 2.06                | 369                         | Qualified | 256                       | 311                      | 5.6                           | 8.2                           | 24.8                          | 49.9                          |

Table 2. The main chemical composition of fly ash.

| Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | TiO |
|-------------|------|-------|-------|-----|-----|-----|
| Content (%) | 51.23| 34.16 | 3.15  | 2.96| 1.12| 1.18|
2.2. Test methods

The weight ratio of high content fly ash filling material is shown in Table 3. With water-solid ratio of 0.7:1.0 and cement to fly ash ratio of 1:9, 2:8 and 3:7, mixing with appropriate amount of additive, high content of fly ash goaf filling material was prepared.

Table 3. Filling material composition ratio(w/%)..

| Number | Cement | Fly ash | water | additive |
|--------|--------|---------|-------|----------|
| 1      | 1      | 9       | 7     |          |
| 2      | 1      | 9       | 7     | 1%       |
| 3      | 1      | 9       | 7     | 2%       |
| 4      | 1      | 9       | 7     | 3%       |
| 5      | 1      | 9       | 7     | 4%       |
| 6      | 1      | 9       | 7     | 5%       |
| 7      | 2      | 8       | 7     |          |
| 8      | 3      | 7       | 7     |          |

And then, samples with 70.7×70.7×70.7 mm size were prepared for compressive strength test. Samples with an upper diameter of 70 mm, a lower diameter of 80 mm, and a height of 30 mm were prepared for impermeability test. Demould time of both kinds of samples were 3 days.

As shown in Figure 1, place the samples in the Water Maintenance Tank of SBY-32B for curing.

Figure 1. Constant temperature and humidity curing box.

Unconfined compressive strength and impermeability pressure test were carried out in accordance with JGJ/T70-2009, Standard Test Method for Building Mortar Basic Performance.

As shown in Figure 2, the samples should be tested in time after they are removed from the maintenance site. Wipe the surface of the samples before the test and measure the size. Check their appearance. Calculate the pressure area of the sample. Place the sample on the lower pressure plate of the testing machine, the pressure surface of the sample is perpendicular to the top surface during forming, and the center of the sample is aligned with the center of the lower pressure plate of the testing machine. Start the testing machine, when the upper pressure plate is close to the sample, adjust the ball seat to balance the pressure on the contact surface. The pressure test is applied continuously and uniformly at a rate of 0.25 kN per second. When the sample is close to failure and begins to deform rapidly, stop adjusting the accelerator of the testing machine until the sample is broken, and then record the failure load.

Figure 3 is a picture of impermeability test. First, Samples are cured to the specified time in the curing chamber. Then, take the samples out and dry the surface. Third, samples are sealed with sealing materials and are put into the mortar permeameter for water permeability test. The pressure starts from 0.1 MPa and increases to 0.2 MPa at constant pressure for 1h, then increases by 0.1MPa every 1h thereafter. Note down the water pressure, water amount and time when there is water seepage at the end of the sample.
3. Results and discussion

3.1 Mechanical properties of the filling materials
According to Table 3, samples of 70.7×70.7×70.7 mm size were prepared and cured for 3 days, 7 days, 28 days and 60 days respectively, then compressive strength was measured. Samples with cement to fly ash ration of 1:9 is referred to as C1F9, cement to fly ash ration of 2:8 is referred to as C2F8, and 3:7 as C3F7. As shown in Figure 4, when water-solid ratio is 0.7:1.0, the compressive strength of C1F9, C2F8 and C3F7 increases with the curing time. The compressive strength of the samples cured for 60 days are 2.23 times(C1F9), 1.90 times(C2F8), and 1.42 times(C3F7) that of the samples curing for 28 days. The compressive strengths of the samples cured for 28 days are 2.92 times(C1F9), 2.50 times(C2F8), and 2.47 times(C3F7) of 7 days respectively. So we obtained that the compressive strength of the filling material is positively correlated with curing time.

With water-solid ratio remains 0.7:1.0, the compressive strength of the samples C2F8 cured for 3 days is 12 times of C1F9, and C3F7 is 15 times of C1F9. Samples curing for 7 days, the compressive strength of C2F8 is 17.75 times of C1F9, and C3F7 is 36.5 times of C1F9. Curing for 28 days, the compressive strength of C2F8 is 15.20 times of C1F9, and C3F7 is 30.91 times of C1F9. Curing for 60 days, the compressive strength of C2F8 is 12.97 times of C1F9, and C3F7 is 19.65 times of C1F9.

It shows that compressive strength of the filling material is positively correlated with the cement content, but negatively correlated with fly ash content. The ash hydration reaction is slow, which contributes a lot to the strength growth in the later stage.

The samples of filling material with cement to fly ash ratio of 1:9 mixing with 1% additive(C1F9+1%additive), mixing with 2% additive(C1F9+2%additive), mixing with 3% additive(C1F9+3%additive), mixing with 4% additive(C1F9+4%additive) and mixing with 5% additive(C1F9+5%additive) are prepared and tested. As shown in Figure 5, compressive strength of the filling material increases significantly, but it decreases with the addition of additive.

With water-solid ratio remains 0.7:1.0, the compressive strength of the samples mixed with 1% additive is 18.87 times, 11.37 times, 9.86 times, 6.28 times of the sample without additive curing for 3 days, 7 days, 28 days, and 60 days respectively. The compressive strength of C1F9+2%additive is 52.50 times, 27.46 times, 20.28 times, 11.86 times of the samples without additive after cured for 3 days, 7 days, 28 days, and 60 days respectively. The compressive strength of C1F9+3%additive are 130.75 times, 70.92 times, 31.14 times, 16.41 times of the samples without additive. The compressive strength of C1F9+4%additive are 100.62 times, 60.75 times, 29.00 times, 15.51 times the samples without additive after cured for 3 days, 7 days, 28 days, and 60 days respectively. And the compressive strength of C1F9+5% additive are 99.12 times, 50.45 times, 24.57 times, 13.78 times the samples without additive after cured for 3 days, 7 days, 28 days, and 60 days respectively.
It follows that when the water-solid ratio, cement to fly ash ratio and the activator are constant, the compressive strength of filling materials with high content of fly ash first increases and then slowly decreases as additive amount increases. Best results can be achieved when 3% additive is mixed, with compressive strength of 1.05 MPa, 1.70 MPa, 2.18 MPa and 2.56 MPa curing for 3 days, 7 days, 28 days and 60 days respectively.

3.2 Impermeability of the filling materials
The impermeability test of the high content fly ash goaf filling material was carried out in accordance with the requirements of JGJ/T70-2009 Standard Test Method for Basic Performance of Building Mortar. When the samples were cured to 28 days, 60 days and 90 days, the permeability coefficient values were measured.

As shown in Figure 6, due to slow hydration reaction of fly ash, the permeability coefficient of the filling materials with high content of fly ash decreases with the increase of curing time. With water-solid ratio of 0.7:1.0, permeability coefficient of C1F9 curing for 60 days and 90 days are 0.61 times and 0.48 times of the samples curing for 28 days respectively. Permeability coefficient of C2F8 curing 60 days and 90 days are 0.51 times and 0.17 times of the samples curing for 28 days respectively. As for C3F8, 0.37 times and 0.16 times. Therefore, the permeability coefficient of the filling material is negatively correlated with the curing time.

At the same time, the permeability coefficient of C2F8 and C3F7 curing for 28 days is 0.31 times and 0.13 times of C1F9. The permeability coefficient of C2F8 and C3F7 curing for 60 days is 0.25 times and 0.08 times of C1F9. As curing for 90 days, permeability coefficient of C2F8 and C3F7 is 0.11 and 0.04 times of C1F9. It is obvious that the permeability coefficient is positively correlated with fly ash content, but negatively correlated with cement content.

![Figure 6. Permeability coefficient of the high content fly ash filling material.](image)

Through tests, the permeability coefficient of C1F9+3%additive samples are $19.8 \times 10^{-6}$ cm/s, $6.68 \times 10^{-6}$ cm/s, $3.81 \times 10^{-6}$ cm/s after curing for 28 days, 60 days and 90 days respectively, which are 0.25 times, 0.13 times and 0.10 times of C1F9. So we can conclude that the additives could reduce the permeability coefficient of the filling materials, and the permeability coefficient of C1F9+3% additives is between C2F8 and C3F7.

3.3 Microstructure analysis on the filling material
The microscopic morphology of the goaf filling material with high content of fly ash was observed by field emission scanning electron microscope. The instrument, JSM-7500F, was produced by JEOL, with magnification from 25 to 300 000, accelerating voltage from 0.1 kV to 30 kV, resolution of 1.0 nm/15kV and 1.4 nm/1kV. Based on the water-solid ratio of 0.7:1.0, samples of C1F9 and C1F9+3%additive cured for 28 days were selected for micro-mechanism analysis.

Figure 7 shows that SEM (scanning electron microscope) images of C1F9 and C1F9+3%additive samples. Figure 7(a) shows the microstructure of the filling material without additive. It indicates that C1F9 sample mainly consists of unhydrated fly ash particles and hydration product such as hydrated
calcium silicate, hydrated calcium aluminate, calcium hydroxide. Figure 7(b) shows SEM images of the filling material with 3% additive. The microstructure indicates that C1F9+3%additive is mainly composed of unhydrated fly ash particles and hydration products of calcium silicate, calcium hydrated alumina, calcium chlorate hydrochlorite, calcium hydroxide etc. The morphological forms of hydration products are mainly fibrous or clustered calcium hydrochlorate, calcium hydrated alumina in the form of hexagonal flakes, and calcium chlorate chlorate and flaky calcium hydroxide.

(a) The filling material with high content fly ash;     (b) with additive of 3%

Figure 7. SEM microstructure of filling material.

By comparing Figure 7(a) and Figure 7(b), the filling material with additive presents following characteristics: the pores are small and dense, some fly ash particles are missing and the surface is covered by hydration products; the hexagonal plate-like hydrated calcium chloroaluminate and hexagonal flaky calcium silicate hydrate are filled between the pores. These all indicates the activity of fly ash was activated. The compactness as well as the hydration reaction of the filling material with additive are better than the samples without additive. And the phenomenon further confirms the conclusion from Figure 5: the compressive strength of the filling material with additive is higher than that of material without additive. The high content fly ash filling material without activator present large pores in SEM microstructure, and the pores are filled with fibrous or clustered hydrated calcium silicate.

3.4 Effect of additive on properties of fly ash based filling materials

The fly ash activity comes from the depolymerisation ability of the vitreous and the active components such as soluble alumina and silica in the porous glass body and the glass beads. The more the content of the active components, the greater the chemical activity of the fly ash. CaO can react with active Al₂O₃ and SiO₂ in the presence of water to form hydrated product hydrated calcium aluminate and hydrated calcium silicate [15,16].

CaO+H₂O→Ca (OH)₂                                                                                                                         (1)
mCa (OH)₂+SiO₂+H₂O→mCaO·SiO₂·nH₂O                                                                                      (2)
mCa(OH)₂+Al₂O₃+H₂O→mCaO·Al₂O₃·nH₂O                                                                                   (3)

With additive, fly ash is activated by forming new mineral composition and decreasing ξ potential of the hydration product[16]. The Ca²⁺ and Cl⁻ in additive is capable of diffusion, which passes through the surface of the fly ash particles and reacts with the active Al₂O₃, and finally presents hydrated calcium chloroaluminate [17].

Ca²⁺ + Al₂O₃ + Cl⁻ + OH⁻→3CaO·Al₂O₃·CaCl₂·10H₂O                                                                     (4)

4. Seepage and diffusion rule of the filling material in goaf treatment

The RST-CC slurry rheometer was used to test the variation of the viscosity of the filling material with the shear rate. Using steady-state shear test, the shear rate was designed to be linear from 0 s⁻¹ increased to 60 s⁻¹, and then linearly reduced to 0 s⁻¹. The total test time was 120 s, the relationship between slurry viscosity and shear rate was real-time monitored and output.

As shown in Figure 8, based on water-solid ratio of 0.7:1.0, the viscosity of the filling material samples C1F9, C2F8 and C1F9+3%additive decreases significantly with the increase of the shear rate
in the early stage. And it means the shear thinning phenomenon occurs. Then the viscosity decreases with the increase of the shear rate. After reaching a minimum point, it begins to increase slowly, where shear thickening occurs[17]. The inflection point is at a shear rate of 30 s⁻¹. The viscosity of C2F8 sample is the highest, and the viscosity of C1F9 is higher than C1F9+3% additive.

![Figure 8. Filling material viscosity change curve.](image1)

![Figure 9. Curve of filling material diffusion radius with pressure.](image2)

The movement of liquid filling materials in the caving zone of the gob mainly includes horizontal diffusion and longitudinal accumulation due to the effective pore pressure and gravity. The horizontal diffusion distance and velocity are both greater than the longitudinal stacking height and velocity.

As shown in Figure 9, in the grouting practice of gob treatment, the grouting pressure has a significant influence on the slurry seepage radius of the filling material. When grouting pressure is small and slurry seepage radius is relatively small, grouting pressure exerts great influence on seepage radius. With the increase of grouting pressure, the slurry seepage range is constantly expanding. While the slurry resistance along the way increases, the influence of the grouting pressure on the slurry seepage range is significantly weakened. The effective pore pressure and energy loss in the goaf are positively correlated with the seepage radius due to the flow resistance of the slurry in the goaf. Given the lateral constraint effect of the outer edge resistance of the slurry seepage in the goaf, the energy of the slurry flowing vertically in the goaf increases, and the slurry seepage flows into the caving zone in the goaf, strengthening the fractured rock mass in the caving zone as well as improving the grouting effect in the goaf.

5. Conclusion

The following conclusions can be drawn based on this study:

(1) The compressive strength and impermeability of the filling materials are positively correlated with cement content. The strength of the filling material with 90% of fly ash increases slowly in the early stage but increases with faster speed in the later stage. The compressive strength of the material cured for 60 days is 2.22 times of 28 days.

(2) Additive plays an active role in improving the performance of the filling material. The additive works best when mixing amount is 3%. By promoting the activity of fly ash, accelerating the hydration reaction as well as reducing the interparticle pores, the early stage strength of the filling material are well improved. Under the action of additives, the strength of 28d and 60d filling materials is increased by 20.28 times and 11.86 times respectively.

(3) The viscosity of the high content fly ash filling material has obvious shear thinning and shear thickening phenomenon with the changes of shear rate. With additive, the impermeability of the filling material is notably improved. Under the action of additives, the permeability coefficient of filling material with 28d and 60d was reduced to 0.25 times, 0.13 times and 0.10 times respectively.

(4) The studied material shows horizontal diffusion and longitudinal accumulation in the goaf. The diffusion distance and accumulation height are positively correlated with grouting pressure.
Acknowledgements
The Author would like to acknowledge the Special Project of Science and Technology Innovation and Entrepreneurship Fund of Tiandi Science and Technology Co., LTD(No.2019-TD-MS014) and Science and Technology Innovation Project of Xi’an Research Institute of CCTEG(No.2019XAYMS11).

References
[1] Hu Bingnan, Guo Wenyan 2018 Mining subsidence area status, syntheses governance model and governance recommendation Coal Ming Technology 23 1-4
[2] Liu Feng, Li Shuzhi 2017 Discussion on the new development and utilization of underground space resources of transitional coal mines Journal of China Coal Society 42 2205-2213
[3] Pang Yunze, Liu Chunyuan, Zuo Liming, et al 2017 Experimental study on preparation and properties of new grouting material for goaf filling Bulletin of the Chinese Ceramic Society 36 2268-2274
[4] Wang Jianxin, Li Jing, Zhao Shibao, et al 2018 Research progress and prospect of resource utilization of fly ash in China Bulletin of the Chinese Ceramic Society 37 3833-3841
[5] Li Maohui, Yang Zhiqiang, Wang Youjian, et al 2015 Experiment study of compressive strength and mechanical property of filling body for fly ash composite cementitious materials Journal of China University of Ming & Technology 44 650-655, 695
[6] Wang Qiang, Wang Dengquan, Chen Honghui 2017 The role of fly ash microsphere in the microstructure and macroscopic properties of high-strength concrete Cem. Concrr. Compos. 83 125-137
[7] Liu Baoju, Shi Jinyan, Liang Hui, et al 2020 Synergistic enhancement of mechanical property of the high replacement low-calcium ultrafine fly ash blended cement paste by multiple chemical activators J. Build. Eng. 32 101520
[8] Sha Fei, Li Shucai, Liu Renji, et al 2018 Experimental study on performance of cement-based grouts admixed with fly ash, bentonite, superplasticizer and water glass Construction and Building Materials 161 282-291
[9] Amin Al-Fakih, Bashar S Mohammed, M M A. Wahab, et al 2020 Characteristic compressive strength correlation of rubberized concrete interlocking masonry wall Structures 26 169-184.
[10] A Al-Fakih, M Mubarak, B S Mohammed, et al 2020 Experimental study on axial compressive behavior of rubberized interlocking masonry walls Journal of Building Engineering 29 101107
[11] Bashar S Mohammeda, Mohd Shahir Liewa, Wesaam S Alaloulia, et al 2018 Development of rubberized geopolymer interlocking bricks Case Studies in Construction Materials 8 401-408
[12] Ehsan Nikbakhta, Amin Al-Fakiha, Chieng Chew Huia, et al 2019 An experimental investigation on the shear and flexural behavior of steel reinforced HPSCC beams Structures 19 286-295
[13] Wang Chong, Yang Changhui, Qian Jueshi, et al 2012 Behavior and mechanism of pozzolanic reaction heat of fly ash and ground granulated blastfurnace slag at early age Journal of the Chinese Ceramic Society 40 1050-1058
[14] Feng Guorui, Ren Yafeng, Zhang Xuyan, et al 2011 The activating experimental research of fly ash for mining filling material in Tashan Mine Journal of China Coal Society 36 732-737
[15] Li Hui, Zhu Ge Lijun, Shi Shi, et al 2012 Hydration products of fly ash based cementing material activated by NaOH Journal of the Chinese Ceramic Society 40 234-239
[16] Ke Guojun, Yang Xiaofeng, Peng Hong et al 2005 Progress of research on chemical activating mechanisms of fly ash Journal of China Coal Society 30 366-370
[17] Xie Youjun, Chen Xiaobo, Ma Kunlin, et al 2015 Effects of fly ash on shearing thinning and thickening of cement paste Journal of the Chinese Ceramic Society 43 1040-1046