



# Article Comparison of the Properties of Coal Gasification Fly Ash and Pulverized Coal Fly Ash as Supplementary Cementitious Materials

Feng Luo <sup>1</sup>,\*<sup>1</sup> and Yujie Jin <sup>2</sup>

- Key Laboratory of Automobile Materials of Ministry of Education, Department of Materials Science and Engineering, Jilin University, Changchun 130025, China
- <sup>2</sup> Department of Materials Science and Engineering, Jilin Jianzhu University, Changchun 130118, China; jinyujie@jlju.edu.cn
- \* Correspondence: luofeng@jlu.edu.cn

Abstract: Using industrial waste as part of the raw material to produce cement-based materials is considered to be a sustainable cement and concrete materials production method. Coal gasification fly ash (hereafter CGFA) is a solid waste produced during the coal gasification process. Similar to pulverized coal fly ash (hereafter PCFA), it is also a kind of fly ash discharged from combustion coal furnaces. With the development of coal gasification technology, more and more CGFA needs to be treated. Based on the successful experience of PCFA as a supplementary cementitious material in cement-based materials, CGFA is used as a supplementary cementitious material in this paper. A comparison of the performance of two coal-based fly ashes as a supplementary cementitious material (hereafter SCM) was conducted. The effects of two fly ashes on the fluidity and strength of cement mortar were discussed, and the mechanism was analyzed from the mineral composition and morphology of hydration products. At the same time, the properties of CGFA and ultrafine CGFA (UFCGFA) as an SCM were compared. The results show that CGFA has more negative effects on the fluidity of cement mortar than PCFA. But it has a greater contribution to the strength of cement mortar than PCFA. X-ray diffraction (XRD) and scanning electron microscopy (SEM) results show that the active components of CGFA participate in the hydration reaction faster, showing a stronger pozzolanic reactivity than PCFA. Ultrafine treatment of CGFA not only improves the pozzolanic activity but also reduces the negative effect on the fluidity of cement mortar. The contribution of UFCGFA to the fluidity and strength of cement mortar can be greatly improved.

**Keywords:** coal gasification fly ash; fluidity; compressive strength; hydration product; microstructure; pozzolanic activity

## 1. Introduction

The production of cement involves a large number of high-temperature calcination and grinding processes, so the cement industry has been a high-energy-consumption and high-carbon-dioxide-emission industry [1,2]. Cement is one of the world's most used building materials. Carbon dioxide emission from cement production accounts for 5% of the total carbon emissions in human life and production [3]. Various methods can be used to reduce the amount of cement used in buildings, such as developing new types of bonding materials and designing more steel structures buildings. Among many methods to reduce the amount of cement, it is very important to use a large number of SCMs to partly substitute Portland cement in cement-based material. This is because most of the SCMs are industrial solid wastes with pozzolanic activity, which can be used directly without undergoing high-temperature calcination. Most industrial solid wastes can be used only by simple grinding, such as granulated blast furnace slag [4–6], steel slag [7], copper slag [8], phosphorus slag [9,10], sewage sludge ash [11], etc. Compared with cement, the energy



**Citation:** Luo, F.; Jin, Y. Comparison of the Properties of Coal Gasification Fly Ash and Pulverized Coal Fly Ash as Supplementary Cementitious Materials. *Sustainability* **2023**, *15*, 14960. https://doi.org/10.3390/ su152014960

Academic Editor: Chunjiang An

Received: 8 September 2023 Revised: 4 October 2023 Accepted: 10 October 2023 Published: 17 October 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). consumption in the production process is greatly reduced. Some SCMs can directly replace part of cement without grinding, such as silica fume [12] and fly ash [3].

In the past decades, fly ash has been the most successful SCM because of the benefits of heat reduction and pozzolanic reactivity [12]. The morphology effect, active effect, and microaggregate effect of fly ash can improve the workability, later-age strength, and durability of cement-based materials [13,14]. At present, fly ash has become an essential component in concrete preparation, and the amount of fly ash in some concrete preparation has accounted for one-third of the amount of cementing materials. Fly ash can even completely replace cement to produce geopolymer cementing materials and subsequently green and low-carbon concrete [15]. However, due to the poor environmental protection of coal combustion power generation, more and more countries are limiting the scale of thermal power plants, and many European countries have shut down a number of thermal power plants [16]. The abatement of coal combustion power plants will be a trend in the following decades. Finding new sources of SCMs is a great need in order to meet more demand and the simultaneous reduction in supply [17]. It is necessary to develop new SCMs as well as study their impact on cement matrix properties.

Coal gasification technology is a new technology to utilize coal, which has been developed rapidly in the past ten years. Coal gasification technology has been regarded as one of the green ways to utilize coal resources [18]. In China, a large number of coal chemical enterprises have been approved for construction. It is expected that by 2025, the consumption of coal as raw material for the coal chemical industry in China will exceed 1.8 billion tons. As coal power generation can produce a lot of fly ash, coal gasification also produces a lot of coal gasification fine ash. With the rapid development of the coal chemical industry, the emissions of CGFA exceed 33 million tons every year [19]. At present, the treatment of CGFA is mainly based on stacking and landfilling. These two methods took up a large amount of land, and the government began to severely restrict the use of land. The green treatment of CGFA has become the key to the sustainable development of enterprises. Due to the technical limitations of the coal gasification process, the content of unburned carbon in coal gasification fly ash is relatively high, even up to 60% of the mass fraction [20]. The existence of a high carbon residue in CGFA limits its utilization, especially in cement concrete applications. Because the content of unburned carbon in coal gasification coarse slag is relatively small, its application in cement-based materials has been preliminarily studied. Li et al. [21] confirmed that active mineral phases from coal gasification slag contribute significantly to the pozzolanic reactions between slag and cement or lime. But residual carbon from slag hinders the cementitious reaction of slag and cement or lime. In recent years, techniques have been developed to separate unburned carbon from fine coal gasification slag, including a physical flotation method and chemical methods [22]. These technologies make possible the preparation of low unburned carbon content, which contributes to the large-scale application of coal gasification slag in building materials.

In recent years, there have been a few studies on the application of coal gasification fly ash in building materials, especially in cement-based materials. Luo [23] studied the feasibility of using decarbonized coal gasification waste residues as the admixture of cement-based materials, and the results showed that coal gasification fly ash had better pozzolanic reactivity than coal gasification coarse slag. The fineness of CGFA particles showed a harmful effect on the fluidity of fresh cement binders, but the fineness of CGFA particles had a positive effect on the pozzolanic activity and thus was beneficial to the strength of cement mortar [24]. However, the research on the application of coal gasification fly ash in cement-based materials is still in the preliminary stage, and a few studies have focused on CGFA as a usable SCM. The formation process of CGFA is very similar to coal fly ash (PCFA). It is necessary to study the application of coal gasification fine ash as an SCM. A comparison of the performance of CGFA and PCFA as SCMs is necessary and very important because it can provide theoretical guidance for making better use of two kinds of solid wastes to prepare cement mortar or concrete. However, research on this subject is limited. The objective of this study was to compare the properties of two kinds of fly ash and to study the difference between two kinds of fly ash on cement-based materials' properties when they are used as SCMs. The fluidity of fresh cement slurry and the mineral composition and micromorphology of hardened cement-based materials were investigated in this paper. At the same time, the ultrafine treatment of CGFA was carried out, and the influence of ultrafine treatment on the performance of CGFA as an SCM was discussed. The research in this paper can not only solve the problem of resource utilization of CGFA and realize the sustainable development of the coal chemical industry but also provide a new way to prepare green and low-carbon cement-based building materials.

#### 2. Materials and Methods

#### 2.1. Raw Materials

The CGFA was collected from Inner Mongolia YiYai Group, LTD., Ordos city, Inner Mongolia province, China. The coal gasifier is from China Aerospace Corporation. Ultrafine CGFA was created in the following way. CGFA was ground in a ball mill for 60 min, and a zirconia ball, named UFCGFA, was used as the grinding medium. The PCFA was from Shenghua Energy Company LTD., Beijing, China. Portland cement was purchased from YaTai Cement Company (Changchun, China) with a grade of PO 42.5. Standard sand with a fineness modulus of 3.0 in line with GB178-1997 [25] was used in this paper. The oxide composition and the XRD spectra of CGFA, PCFA, and cement are shown in Table 1 and Figure 1, respectively. According to the results, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and Fe<sub>2</sub>O<sub>3</sub> are the main components of both fly ashes. The content of CaO in CGFA is higher than that in PCFA. SEM photographs of raw materials are shown in Figure 2. Both fly ashes contain a large number of spherical particles. This morphology is closely associated with the rapid cooling process during production. However, it can be observed that more small particles adhere to the surface of the spherical particles in the CGFA. The particle size of PCFA, CGFA, and UFCGFA was measured using a laser particle size analyzer, and the results are shown in Table 2. The average particle sizes of CGFA, UFCGFA, and PCFA are 11.91 µm, 2.69 µm, and 13.13 µm, respectively. The specific surface areas of CGFA, UFCGFA, and PCFA are  $1.76 \text{ m}^2/\text{g}$ ,  $1.88 \text{ m}^2/\text{g}$ , and  $1.06 \text{ m}^2/\text{g}$ , respectively.

Table 1. Compositions of original materials (by weight, %).

Smples	SiO <sub>2</sub>	$Al_2O_3$	TiO <sub>2</sub>	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
CGFA	46.31	19.04	0.77	23.04	1.32	5.21	1.02	2.07	1.06
PCFA	50.86	21.26	0.80	10.86	2.03	6.73	1.09	0.82	1.65
Cement	20.31	5.15	-	63.5	1.46	4.52	-	-	2.03

Note: LOI = loss of ignition.



Figure 1. XRD spectra of CGFA, PCFA, and cement.



Figure 2. SEM photographs of raw materials.

<b>Table 2.</b> Physical properties of CGFA, PCFA, and UFCGF
--

Samulas		Particle	Specific Surface Area		
Samples	D <sub>10</sub>	D <sub>50</sub>	D <sub>90</sub>	D <sub>av</sub>	(m²/g)
Cement	1.53	6.77	20.93	9.64	0.56
CGFA	1.68	7.10	25.86	11.91	1.76
UFCGFA	0.87	2.14	5.37	2.69	1.88
PCFA	0.96	4.72	53.88	13.13	1.06

#### 2.2. Mix Proportions, Preparation, and Curing

In this experiment, in order to investigate the effect of two fly ashes on the strength of cement, a series of cement mortars was prepared. Cement mortar was prepared by using PCFA or CGFA instead of cement 10%, 30%, and 50% by weight. A pure cement mortar sample was used as a standard reference sample. The ratio of cementitious material to sand was 1:3, and that of water to cementitious material was 1:2. The mix ratio of cement mortar is shown in Table 3. The preparation and curing methods of mortar samples were carried out in full accordance with GB/T 17671-2021 [26] (test method of cement mortar strength). The sample mold size was 40 mm  $\times$  40 mm  $\times$  160 mm, and the specimens were cured at 20 °C  $\pm$  2 °C.

Table 3. Mixture ratios of cement mortars.

Samples	Cement (g)	PCFA (g)	CGFA (g)	UFCGFA (g)	Sand (g)	Water (g)
C-100	450	-	-		1350	225
PCFA-10	405	45	-		1350	225
PCFA-30	315	135	-		1350	225
PCFA-50	225	225	-		1350	225
CGFA-10	405	-	45		1350	225
CGFA-30	315	-	135		1350	225
CGFA-50	225	-	225		1350	225
UFCGFA-10	405			45	1350	225
UFCGFA-30	315			135	1350	225
UFCGFA-50	225			225	1350	225

#### 2.3. Test Methods

The chemical composition of two fly ashes was examined by using an inductively coupled plasma emission spectrometer, and the loss on ignition (LOI) was obtained through calcination at 950 °C for 2 h. The mineralogical composition of raw materials and hardened cement paste was examined by using the X-ray diffraction method (DX-2700 X-ray diffractometer with Cu Ka radiation at 35 kV and 25 mA). The micrograph of raw materials and hard-ened cement paste was observed by using a scanning electron microscope (JEOL, IT300). The fluidity of fresh cement paste was measured according to the Chinese standard GB/T 2419-2005 [27]. The fluidity experiment was carried out five times, and the experimental results were averaged. If there was a value that was more or less than 10% from the average, this value was removed, and the remaining 4 numbers were averaged. The compressive strength of cement-based mortar was measured under GB/T 17671-1999 [28]. The compressive strength was tested 6 times, and the experimental results were averaged. If there was a value that was more or less than 10% from the average, this value was removed, and the remaining 5 numbers were averaged. The specific surface areas of PCFA, CGFA, and UFCGFA were determined through the Brunauer–Emmett–Teller method (using an SSA-3600, Builder Co., Beijing, China). The TG curves of the samples were measured in an air atmosphere by using an A020 thermal analyzer manufactured by Beijing HengJiu Experimental Equipment Co., Ltd. (Beijing, China).

#### 3. Results and Discussion

#### 3.1. Comparison of the Properties of CGFA and PCFA

## 3.1.1. Fluidity

The fluidity test results of cement mortar containing PCFA or CGFA are shown in Figure 3. The fluidity of the reference sample was 205 mm. The effect of two kinds of fly ash on the fluidity of mortar after replacing cement showed different trends. When the replacement level of PCFA was 10%, 30%, and 50%, the fluidity of cement mortar was 211 mm, 213 mm, and 212 mm, respectively. Compared with the reference samples of pure cement mortar, the fluidity of all mortars was increased. The increase in the fluidity of cement mortar is due to the ball-bearing effect of PCFA, and this is one of the main reasons why PCFA can be widely used in cement-based materials as an SCM [13]. For the mortar sample containing CGFA, the fluidity was 209 mm when the replacement amount of CGFA was 10%, which is a small increase compared with the reference sample. But when the replacement level of CGFA was 30%, the liquidity dropped to 180 mm. The liquidity even dropped to 150 mm when the replacement level of CGFA was 50%. This shows that CGFA is beneficial to fluidity at a low content, but it has a great negative effect when the content exceeds 10%. The effect of SCM on the fluidity of mortar is mainly related to the particle shape, particle size, and specific surface area. There are a lot of small particles on the surface of CGFA spherical particles. The attached small particles are not conducive to the "ball effect" of fly ash particles and improve the fluidity. These attachments increase the friction coefficient between particles, resulting in the ball effect being greatly reduced. On the other hand, compared with fly ash, CGFA contains more irregular particles, which also leads to an increase in friction between particles, resulting in a decrease in fluidity. In addition, from Table 2, it can be seen that the specific surface area of CGFA is larger than that of PCFA. A large specific surface area means that the surface will adsorb more free water, which will also reduce the fluidity of mortar [29,30].



Figure 3. The fluidity results of cement mortar containing PCFA or CGFA.

The effects of two fly ashes on the compressive strength of mortar with fly ash contents of 10%, 30%, and 50% after 3 d, 28 d, and 90 d of hydration time were examined in the experiment. The results are shown in Figure 4. In comparison to the reference sample, the 3-day compressive strength of all CGFA-cement or PCFA-cement mortar decreased, which is due to the low early pozzolanic activity of the two fly ashes. Compared with the PCFA-cement mortar, the compressive strength of CGFA-cement mortar was higher when they had the same replacement amount. When the replacement content was 10%, 30%, and 50%, the 3-day compressive strength of CGFA-cement mortar sample was 1.02%, 7.09%, and 8.05% higher than that of PCFA-cement mortar sample, respectively. This result indicates that the early pozzolanic activity of CGFA is higher than that of PCFA.



Figure 4. The compressive strength of different cement mortar.

According to the results of the 28 d compressive strength test, both fly ashes showed good pozzolanic activity. Compared with the reference sample, the compressive strength of the PCFA-cement mortar sample was 97.71%, 93.44%, and 64.82%, respectively, when the replacement cement content was 10%, 30%, and 50%. The compressive strength of the CGFA-cement mortar sample was 98.51%, 104.47%, and 78.20%, respectively. The 28-day compressive strength of the CGFA-cement mortar sample was 0.8%, 11.03%, and 13.38% higher than that of the PCFA-cement mortar sample, respectively. According to the national standard "fly ash used for cement and concrete" (GB/T 1596-2017) [31], the strength activity index is the percentage of the 28 d compressive strength of fly ash mortar and pure cement mortar when fly ash replaces cement by 30%. Then, the strength activity index of PCFA and CGFA were 93.44% and 104.47%, respectively. When the hydration age reached 90 days, the compressive strength of the two kinds of fly ash on the mortar had almost no change when the dosage was 10% and 30%. However, the compressive strength of CGFA-cement mortar was 5.8% higher than that of PCFA-cement mortar when the replacement amount was 50%. The above experimental results show that the pozzolanic activity of CGFA is higher than that of PCFA.

#### 3.1.3. XRD Analysis

The XRD patterns of 3 d, 28 d, and 90 d hydration products of PCFA or CGFA-cement are shown in Figure 5. The hydration products of pure cement were also used as reference samples. As can be seen from Figure 5, alite, belite, and CH are the main crystalline phases in the products. Alite and belite are due to the presence of unhydrated cement

particles, and CH is the main hydration product of cement. Quartz is from the cement clinker. From the diffraction angles 20 of 18.089, 34.088, and 47.123, it can be seen that the main difference between samples is the diffraction peak intensity of CH. With the increase in the amount of PCFA or CGFA replacing cement, the diffraction peak of CH gradually decreased. Under the same substitution quantity, the CH diffraction peak of the sample containing CGFA was lower, which indicates that more calcium hydroxide was consumed. Only weak CH diffraction peaks appeared in CGFA-50 samples after 3 days of hydration. It was also observed that mullite diffraction peaks appeared in the hydration products when the replacement amount of PCFA was 30% and 50%. Mullite is from the PCFA. In the 28-day hydration products, the diffraction peaks of unhydrated  $C_3S$  and  $C_2S$  could not be seen in the pure cement samples, but the diffraction peaks of CH continued to increase. There were CH diffraction peaks in the three samples containing PCFA, but there were almost no CH diffraction peaks in CGFA-30 and CGFA-50 samples. When the age reached 90 days, the presence of CH could be observed in CGFA samples containing 10% content, while CH could hardly be seen in CGFA samples containing 30% and 50% content. For PCFA samples, a CH diffraction peak existed in all samples. This also shows that CGFA has a faster pozzolanic reaction than PCFA.



Figure 5. XRD patterns of 3 d, 28 d, and 90 d hydration products of PCFA or CGFA-cement.

#### 3.1.4. SEM Observation

The microstructure of the cement hydration sample containing PCFA and CGFA is shown in Figure 6. In the hydration products of pure cement, it can be seen that with the increase in age, the cement structure becomes more and more dense, but well-crystallized CH is always visible. The spherical particles of PCFA and CGFA were selected to observe the hydration process. It can be seen from Figure 6 that, after 3 days of hydration, the PCFA particles still have a smooth surface, the CGFA particles have a small amount of aggregate on the surface, and both particles show integrity. When the hydration age reaches 28 days, the surface of PCFA particles is no longer smooth, and a certain amount of hydration products are attached to the surface. On the surface of CGFA, a large number of needle-like hydration products can be seen, and the hydration products interweave with each other to form a dense network structure. When the hydration age reaches 90 days, the surface of PCFA particles is no longer smooth, and a large number of pits appear. Compared with PCFA, the particle structure of CGFA is more incomplete because the particle edge is fuzzier and there are a lot of flaky hydration products connected with the particle edge. This shows that with the increase in reaction age, PCFA particles and CGFA particles interact with the surrounding cement hydration environment. Compared with PCFA particles, the disintegration of the CGFA particle structure is more obvious, indicating that the reaction is more rapid. This is consistent with the XRD results above.



Figure 6. The microstructure of cement hydration sample containing PCFA and CGFA.

## 3.2. Comparison of the Properties of CGFA and UFCGFA

## 3.2.1. Fluidity

The fluidity of pure cement mortar and two kinds of CGFA-cement mortar with different particle sizes was tested, and the replacement cement amount of coal gasification slags was also 10%, 30%, and 50%. The results are shown in Figure 7. The CGFA of two particle sizes had the same effect on the fluidity of cement mortar. When the amount of cement replaced by CGFA was 10%, the fluidity of mortar could be improved. When the amount of cement replaced by CGFA was more than 10%, the fluidity of the mortar was lower than that of the reference sample. But the fluidity of mortar containing UFCGFA was greater than that of mortar containing CGFA when the content of UFCGFA was the same as that of CGFA. Moreover, as the amount of substitution increased, the liquidity gap became wider and wider. When the replacement amount was 10%, 30%, and 50%, the fluidity of UFCGFA-cement mortar was 2 mm, 10 mm, and 15 mm larger than that of CGFA-cement mortar, respectively. A possible reason is that the particle size of CGFA is reduced after grinding, and the dilution and dispersion effect of cement particles is more significant, which is conducive to fluidity. On the other hand, the small particles gathered on the spherical surface are separated during the grinding process, which reduces the friction between particles and also facilitates the improvement of fluidity.



Figure 7. Fluidity of CGFA or UFCGFA-cement mortar.

### 3.2.2. Compressive Strength

The effects of two fine CGFA on the 3-day and 28-day compressive strength of cement mortar are shown in Figure 8. It can be seen that the negative influence of CGFA on the early compressive strength was reduced after ultrafine treatment. The 3-day compressive strength of CGFA was 89.6%, 74.8%, and 55.7% when the dosage was 10%, 30%, and 50%. However, the 3-day compressive strength increased to 99.1%, 87%, and 68.7% of the standard sample when the UFCGFA dosage was 10%, 30%, and 50%, which increased by 9.6%, 12.2%, and 13%, respectively. With the increase in the replacement amount of UFCGFA, the improvement effect was more obvious. For 28-day compressive strength, the compressive strength was 112.3%, 116.1%, and 79.3% when the replacement amount of UFCGFA was 10%, 30%, and 50%. Compared with CGFA-cement mortar samples, the compressive strength results of UFCGFA-cement mortar were increased by 13.8%, 11.6%, and 11.1%, respectively. With the increase in the replacement amount of UFCGFA, the improvement effect had a downward trend. This is the opposite of the effect of the 3-day intensity.



Figure 8. The compressive strength of cement mortar with CGFA or UFCGFA.

From the 3-day and 28-day compressive strength, it can be seen that the mechanical properties of cement mortar after ultrafine treatment of CGFA are improved, especially the early strength of 3 days. This is mainly due to the reduction in particle size and mechanical activation. On the one hand, the reduction in particle size can fill the tiny pores of the mortar so that the "micro-aggregate" effect of the UFCGFA is more significant. On the other hand, the mechanical grinding process increases the specific surface area of the particles, plays an active role in the particle surface, and accelerates the rate of pozzolanic reaction in cement hydration. Thus, the mechanical properties of mortar are improved.

#### 3.2.3. XRD Analysis

The XRD diffraction spectra of seven pastes with curing times of 3 and 28 days are shown in Figure 9. According to the experimental results, there were unhydrated C<sub>2</sub>S and CH in the hydration products of all samples after 3 days of hydration. With the increase in cement substitution, the diffraction peak of CH became lower and lower. This is mainly due to the reduction in the cement clinker. But a closer look at the images reveals that the diffraction peak of CH in the hydration products of UFCGFA cement is weaker at the same substitution amount. This means that more CH is consumed in the UFCGFA-cement sample, which indicates that the UFCGFA has faster pozzolanic reactivity than the CGFA. Especially when the replacement amount reaches 50%, the obvious diffraction peak of CH can be seen in the hydration products of CGFA-cement, while CH can hardly be seen in the hydration products of UFCGFA cement. This indicates that within 3 days, the CH produced in the early hydration process reacted with the active silica and aluminum oxide in the UFCGFA. This is also one of the reasons for the high early strength of UFCGFA cement mortar. The XRD pattern of hydration products at 28 days is basically consistent with that at 3 days and also shows that the diffraction peak of CH in the hydration products of UFCGFA cement is weaker at the same substitution amount. Combined with the strength test results, it can be confirmed that the pozzolanic activity of the CGFA was further improved after the ultrafine treatment. This is a good sign for an SCM.



Figure 9. XRD diffraction spectra of cement mortar with CGFA or UFCGFA.

#### 3.2.4. TG Analysis

Thermogravimetric analysis (TG) of the hydration products at 3 and 28 days of curing was performed, and the results are shown in Figures 10 and 11, respectively. The first stage of weight loss between room temperature and 200 °C is due to the loss of weakly bound water on the gel solid. The second weight loss at about 450 °C corresponds to the de-hydration of calcium hydroxide. The third weight loss at about 700 °C corresponds

to the decomposition of calcium carbonater resulting from the carbonation of calcium hydroxide. The chemical equation involved is shown in Equations (1) and (2).

$$Ca(OH)_2 = CaO + H_2O \tag{1}$$

$$CaCO_3 = CaO + CO_2$$
(2)



**Figure 10.** Thermogravimetric analysis of cement hydration sample containing CGFA and UGCGFA after 3 days of hydration.



**Figure 11.** Thermogravimetric analysis of cement hydration sample containing CGFA and UGCGFA after 28 days of hydration.

As can be seen from Figure 10, there are obvious differences in the thermogravimetry of the three samples belonging to CH, whether due to the decomposition of CH or calcium

carbonate. For C-100 samples, the thermogravimetry at 450 °C and 700 °C is 1.63% and 1.71%, respectively, while for CGFA, it is 0.97% and 1%. The lowest values were 0.49% and 0.96% for UFCGFA samples, respectively. This is consistent with the results of XRD experiments. This indicates that UFCGFA samples have a faster reaction rate of pozzolanic activity and thus consume more CH. As shown in Figure 11, the C-100 sample has a mass loss of 1.40% at 450 °C, while the other two samples have no obvious stepped thermogravimetry after a 28-day hydration age. According to the experimental results of the TG curve, the reaction rate of volcanic ash was indeed improved after the ultrafine treatment of CGFA.

## 4. Conclusions

The properties of PCFA and CGFA as SCMs were compared in this paper. The main conclusions are as follows:

- 1. PCFA has a positive effect on the fluidity of cement mortar, while CGFA has a negative effect on cement mortar. In the scope of this study, PCFA can improve the fluidity of cement mortar after replacing cement. It has a positive effect on the cement mortar when the replacement cement content of CGFA is less than 10%. However, when the amount of cement replaced by CGFA exceeds 10%, the fluidity of cement mortar is negatively affected.
- 2. The compressive strength of CGFA-cement mortar is higher than that of PCFA-cement mortar when they have the same replacement amount. The XRD pattern of the hydration product shows that the consumption of CH in the CGFA-cement mortar is faster. Compressive strength and XRD results show that CGFA has higher pozzolanic activity than PCFA.
- 3. Ultrafine treatment of CGFA can not only greatly improve the pozzolanic activity but also eliminate the negative impact on the fluidity of cement mortar.
- 4. This study is beneficial to the application of CGFA as an SCM in cementitious materials, especially for the application of coal gasification slag instead of fly ash.
- This research provides practical guidance for the application of CGFA in cement-based materials, which has positive significance for the sustainable development of the coal chemical industry and cement industry.

**Author Contributions:** Conceptualization, F.L.; methodology, F.L. and Y.J.; investigation, F.L. and Y.J.; resources, Y.J.; writing, F.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work is financially supported by the science and technology development plan project of Jilin Province (no. 20230508042RC).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Zhou, Y.; Li, W.; Peng, Y.; Tang, S.; Wang, L.; Shi, Y.; Li, Y.; Wang, Y.; Geng, Z.; Wu, K. Hydration and fractal analysis on Low-heat Portland cement pastes by thermodynamic-based methods. *Fractal Fract.* **2023**, *7*, 606–633. [CrossRef]
- Li, Y.; Zhang, H.; Huang, M.; Yin, H.; Jiang, K.; Xiao, K.; Tang, S. Influence of different alkali sulfates on the shrinkage, hydration, pore structure, fractal dimension and microstructure of low-heat Portland cement, medium-heat Portland cement and ordinary Portland cement. *Fractal Fract.* 2021, *5*, 79–106. [CrossRef]
- 3. Huang, J.; Li, W.; Huang, D.; Wang, L.; Wu, C.; Wang, B.; Deng, H.; Tang, S.; Shi, Y.; Li, Y.; et al. Fractal analysis on pore structure and hydration of magnesium oxysulfate cements by first principle, thermodynamic and microstructure-based methods. *Fractal Fract.* **2021**, *5*, 164–181. [CrossRef]

- Yavuz, E.; Gul, N.I.K.; Kockal, N.U. Characterization of class C and F fly ashes based geopolymers incorporating silica fume. *Ceram. Int.* 2022, 48, 32213–32225. [CrossRef]
- Nedunuri, S.S.S.A.; Sertse, S.G.; Muhammad, S. Microstructural study of Portland cement partially replaced with fly ash, ground granulated blast furnace slag and silica fume as determined by pozzolanic activity. *Constr. Build. Mater.* 2020, 238, 117561–117572. [CrossRef]
- 6. He, X.; Ma, M.; Su, Y.; Lan, M.; Zheng, Z.; Wang, T.; Strnadel, B.; Zeng, S. The effect of ultrahigh volume ultrafine blast furnace slag on the properties of cement pastes. *Constr. Build. Mater.* **2018**, *189*, 438–447.
- Lun, Y.; Zheng, F. Effect of steel slag powder, fly ash, and silica fume on the mechanical properties and durability of cement mortar. *Mater. Express* 2019, 9, 1049–1054. [CrossRef]
- 8. Song, J.; Wang, L.; Zhu, J.; Feng, S.; Ouyang, Y.; Leng, F.; Song, J.; Zhang, L. Effect of the fineness of copper slag on the early hydration properties of cement-copper slag binder. *J. Therm. Anal. Calorim.* **2019**, *138*, 243–253. [CrossRef]
- Wang, L.; Guo, F.; Lin, Y.; Yang, H.; Tang, S.W. Comparison between the effects of phosphorous slag and fly ash on the C-S-H structure, long-term hydration heat and volume deformation of cement-based materials. *Constr. Build. Mater.* 2020, 250, 118807–118827. [CrossRef]
- 10. He, X.; Ye, Q.; Yang, J.; Dai, F.; Su, Y.; Wang, Y.; Bohumír, S. Physico-chemical Characteristics of Wet-milled Ultrafine-granulated Phosphorus Slag as a Supplementary Cementitious Material. *J. Wuhan Univ. Technol.* **2018**, *33*, 625–633. [CrossRef]
- 11. Mejdi, M.; Saillio, M.; Chaussadent, T.; Divet, L.; Tagnit-Hamou, A. Hydration mechanisms of sewage sludge ashes used as cement replacement. *Cem. Concr. Res.* 2020, *135*, 106115–106126. [CrossRef]
- 12. Wongkeo, W.; Thongsanitgarn, P.; Poon, C.-S.; Chaipanich, A. Heat of hydration of cement pastes containing high-volume fly ash and silica fume. *J. Therm. Anal. Calorim.* **2019**, *138*, 2065–2075. [CrossRef]
- 13. Wang, A.; Zhang, C.; Sun, W. Fly ash effects: I. The morphological effect of fly ash. *Cem. Concr. Res.* 2003, 33, 2023–2029. [CrossRef]
- 14. Wang, A.; Zhang, C.; Sun, W. Fly ash effects. *Cem. Concr. Res.* 2004, 34, 2061–2066. [CrossRef]
- 15. Abdulrahman, H.; Muhamad, R.; Visintin, P.; Shukri, A. Mechanical properties and bond stress-slip behaviour of fly ash geopolymer concrete. *Constr. Build. Mater.* **2022**, 327, 126909–126930. [CrossRef]
- Fořt, J.; Šál, J.; Ševčík, R.; Doleželová, M.; Keppert, M.; Jerman, M.; Záleská, M.; Stehel, V.; Černý, R. Biomass fly ash as an alternative to coal fly ash in blended cements: Functional aspects. *Constr. Build. Mater.* 2021, 271, 121544–121555. [CrossRef]
- Juenger, M.C.G.; Snellings, R.; Bernal, S.A. Supplementary cementitious materials: New sources, characterization, and performance insights. *Cem. Concr. Res.* 2019, 122, 257–273. [CrossRef]
- Yuan, N.; Zhao, A.; Hu, Z.; Tan, K.; Zhang, J. Preparation and application of porous materials from coal gasification slag for wastewater treatment: A review. *Chemosphere* 2022, 287, 132227–132243. [CrossRef]
- 19. Yang, P.; Suo, Y.; Liu, L.; Qu, H.; Xie, G.; Zhang, C.; Deng, S. Study on the curing mechanism of cemented backfill materials prepared from sodium sulfate modified coal gasification slag. *J. Build. Eng.* **2022**, *62*, 105318. [CrossRef]
- Guo, Y.; Li, H.; Qiu, G.; Li, Y.; Niu, Y.; Xu, J.; Jia, W.; Zhang, Y.; Wu, J.; Guo, F. Processing of coal gasification fine slag by different physical separation methods: Fate of typical heavy metals and comparison analysis on products. *Sep. Purif. Technol.* 2023, 306, 122675–122686. [CrossRef]
- 21. Li, Z.; Zhang, Y.; Zhao, H.; Chen, H.; He, R. Structure characteristics and composition of hydration products of coal gasification slag mixed cement and lime. *Constr. Build. Mater.* **2019**, *213*, 265–274. [CrossRef]
- Li, J.; Chen, Z.; Yuan, L.; Qiao, Y.; Yuan, Z.; Zeng, L.; Li, Z. Effects of flotation and acid treatment on unburned carbon recovery from atmospheric circulating fluidized bed coal gasification fine ash and application evaluation of residual carbon. *Waste Manag.* 2021, 136, 283–294. [CrossRef]
- 23. Luo, F.; Jiang, Y.; Wei, C. Potential of decarbonized coal gasification residues as the mineral admixture of cement-based material. *Constr. Build. Mater.* **2021**, *269*, 121259–121268. [CrossRef]
- Luo, F.; Wei, C. Effects of Decarbonized Coal Gasification Coarse Slag and Fine Ash on Properties of Cement Paste as Supplementary Cementitious Materials. J. Mater. Civil. Eng. 2022, 34, 04022281–04022290. [CrossRef]
- 25. GB179-1999; Standard Sand for Cement Strength Test. Chinese Standard: Beijing, China, 1979.
- 26. GB/T 17671-2021; Test Method of Cement Mortar Strength. Chinese Standard: Beijing, China, 2021.
- 27. GB/T2419-2005; Test Method for Fluidity of Cement Mortar. Chinese Standard: Beijing, China, 2005.
- 28. GB/T17671-1999; Method of Testing Cements-Determination of Strength. Chinese Standard: Beijing, China, 1999.
- 29. Berra, M.; Mangialardi, T.; Paolini, A.E. Reuse of woody biomass fly ash in cement-based materials. *Constr. Build. Mater.* **2015**, *76*, 286–296. [CrossRef]
- 30. Li, X.; Chen, Q.; Ma, B.; Huang, J.; Jian, S.; Wu, B. Utilization of modified CFBC desulfurization ash as an admixture in blended cements: Physico-mechanical and hydration characteristics. *Fuel* **2012**, *102*, *674–680*. [CrossRef]
- 31. GB/T1596-2017; Fly Ash Used for Cement and Concrete. Chinese Standard: Beijing, China, 2017.

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.