

# Partially Replacing Fly Ash with Limestone Powder in the Paste - Influence and Characterization

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**Abstract:** Paste filling is an important research direction of coalmine "green mining" which can dispose coalmines solid waste and achieve environmental protection. The mechanical properties such as compressive strength, workability, ultimate tension value, shear strength and splitting strength of paste, in which the fly ash was partially replaced by limestone powder, was studied. Adiabatic temperature rise, setting time, shear strength, permeability, frost resistance and dry shrinkage of different substitution rate were investigated and the results were compared with traditional paste. The test results showed that the influence of limestone powder on workability, permeability and frost resistance performance of paste was slight, the setting time of paste were shortened, adiabatic temperature rise and mechanics performance of paste were decreased, dry shrinkage value was increased with limestone powder content increasing.

**Keywords:** Coalmine, fly ash, limestone powder, mechanical properties, paste, workability.

## 1. INTRODUCTION

Paste filling is a mining method for coalmines solid waste processing including rock, fly ash, limestone powder, slag, poor soil, city solid waste and other solid waste into high concentration slurry which has the characteristic of critical velocity and does not need to be dehydrated, and using large filling industrial pump (with gravity) transport the slurry into goaf and replacing coal resources [1]. It is a major reform in coal mining technology and important research direction of "green mining" [2]. The traditional paste filling materials include rock, fly ash, Portland cement and additive combination, but the transport cost of fly ash is high in some coalmines due to the far distance to power plant. Using limestone powder replace fly ash can not only reduce project cost, but also protect environment, reduce paste temperature rise, increase paste workability, and has good economic benefit and social benefit, and has great significance on improving crack resistance of paste.

There are two kinds of views on the influence of limestone powder on paste. One view is that the limestone powder is an inert admixture and does not participate in cement hydration process, but play a role in micro filling influence [3]. The other view is that the limestone powder participates in the cement hydration process and has an influence on working performance, mechanical properties and durability of paste [4-8]. This paper studied the mechanical properties such as lay binding specificity, dry shrinkage, adiabatic temperature rise, setting time and durability of paste under the condition of different dosage of limestone powder. It can

provide the theoretical foundation for improving stability and security of filling body, reducing filling cost and improving filling efficiency.

## 2. EXPERIMENTAL

### 2.1. Materials

The experimental cement was 42.5 ordinary Portland cement produced by Shaanxi Qinling Mountains cement Group Co., Ltd.

The coarse aggregate was common coalmine rock aggregate with continuous gradation of 5~60 mm. The particle grade is divided into 3 level-small, medium and large (the maximum particle size were 20mm, 40mm, 80mm respectively). The mass ratio of small rock, medium rock and large rock was 20:30:50, and the amount of limestone powder in rock aggregate was negligible.

The fly ash used in the tests was produced by Baqiao thermoelectric power plant. The fineness was 14.8%, and the water demand ratio is 98%.

Tap water was used in the experiments.

BD-V type concrete super plasticizer with density of 1.2 g/cm<sup>3</sup>, pH value of 7.05, and adding amount is 0.6% of cementations materials.

The physical properties and test results of chemical analysis of limestone powder are shown in Table 1.

The particle size analysis test results of cement, fly ash and limestone powder are shown in Table 2.

### 2.2. Mixture Ratio

Based on the mixture ratio of one project, the comparative tests of paste durability and mechanical properties were done, the paste mix ratio are shown in Table 3.

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**Table 1.** The physical properties and test results of chemical analysis of limestone powder.

Density, g/cm <sup>3</sup>	Specific area, m <sup>2</sup> /kg	Activity index, %	CaCO <sub>3</sub> , %	SiO <sub>2</sub> , %	Al <sub>2</sub> O <sub>3</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	MgO, %	K <sub>2</sub> O, %	Other, %
2.71	592	69	82.5	12.2	1.58	2.34	0.46	0.35	0.57

**Table 2.** The particle size analysis test results of cement, fly ash and limestone powder.

Materials	Content of different particle size range (%)					
	<3	3~16	16~32	32~65	65~80	>80
Limestone powder	35.42	19.23	1.34	18.20	7.69	18.12
Fly ash	15.21	39.21	18.36	20.25	5.21	1.76
cement	20.02	20.29	19.45	30.29	5.94	4.01

**Table 3.** The paste mix ratio.

Test number	Water binder ratio	Fly ash, %	Limestone powder, %	Material consumption of 1m <sup>3</sup> paste, kg				
				Cement	Rock	Fly ash	Limestone powder	Water
C1	0.79	60	0	96	1123	144	0	190
C2	0.79	50	0	120	1123	120	0	190
C3	0.79	30	30	120	1123	140	140	190
C4	0.79	25	25	120	1123	60	60	190
C5	0.79	15	35	120	1123	51.4	68.6	190
C6	0.79	35	15	120	1123	68.6	51.4	190
C7	0.79	0	50	120	1123	0	120	190

Water reducing agent dosage is 0.5%, air entraining agent content is 0.055%, and water binder ratio is 45%.

### 2.3. Experimental Method

- (1) Mixture properties were tested based on the "Standard test method for the performance of ordinary concrete mixture" (GB/T 50080—2002).
- (2) Compressive strength was tested based on the "Standard test method for the mechanical property of concrete" (GB/T 50081—2002). Cube specimens (150 mm×150 mm×150 mm and 100 mm×100 mm×100 mm) were used, and the tester was multifunctional dynamic hydraulic servo universal testing machine (3000 kN).
- (3) Modulus of elasticity was tested based on GB/T 50081—2002. Prism specimens (150 mm×150 mm×300 mm) was used, and the tester was multifunctional dynamic hydraulic servo universal testing machine (3000 kN). Strain gauges was attached on the opposite side of specimen in order to measure the deformation
- (4) Dry shrinkage performance was tested based on "Long-term performance and durability test procedures of concrete" (GBJ 82—85). Prism specimens (100 mm×100

mm×515 mm) were used. Specimen placed on the shelf measuring dry shrinkage vertically, dial gauge was fixed on specimen and let glass sheet and dial gauge fully contact. The value on dial gauge set as basic value, and the dry shrinkage age begin from this value date. The deformation valued (1,3,7,14,28,60d) were marked down.

- (5) Permeability test was tested based on GBJ 82—85, cone type specimen (150 mm×175 mm×185 mm) was used.
- (6) Frost resistance was tested based on GBJ 82—85, specimens (100 mm×100 mm×400 mm) was used.

## 3. RESULTS AND DISCUSSION

### 3.1. Mechanical Properties

The test results of compressive strength, split tensile strength, ultimate tensile strain and compressive modulus of elasticity of paste under different limestone powder mixing amount are shown in Table 4.

From the above test results:

- (1) The limestone powder mixing amount had a less impact on the VC value and gas content of paste under the condition of same water binder ratio.

**Table 4. Results of mechanical deformation properties for paste.**

Test number	VC value	Gas, %	Compressive strength, MPa			Split tensile strength, MPa			Ultimate tensile strain		Compressive modulus of elasticity, GPa	
			7d	28d	90d	7d	28d	90d	28d	90d	28d	90d
C1	3.0	3.8	8.7	16.2	29.2	0.47	1.16	2.39	63	86	28.6	36
C2	2.0	3.6	12.1	25.1	34.6	0.82	1.68	2.86	69	95	29.0	36.5
C3	3.0	3.1	11.1	15.2	24.1	0.52	1.13	2.11	60	80	28.2	35.0
C4	4.0	3.1	14.0	23.1	26.2	0.96	1.52	2.22	65	91	28.3	35.1
C5	4.0	3.5	12.7	20.6	22.1	0.81	1.31	1.96	63	80	28.2	35.0
C6	4.0	3.6	12.6	25.0	31.5	0.80	1.63	2.75	68	93	28.6	36.1
C7	3.0	3.5	11.1	16.2	17.3	0.71	0.96	1.39	55	71	27.0	34.9

- (2) Setting the compressive strength (28d) to 100%, through using limestone powder replace partially fly ash, the growth rate of compressive strength (7d) unchanged, but the compressive strength (90d) low around 20% than the paste with single fly ash.
- (3) Through using limestone powder replace partially fly ash, the compressive strength, splitting tensile strength, ultimate tensile values decreased with increasing the amount of limestone powder, but compressive elastic modulus has less change. The interface between aggregate and cement were the weak link in the paste, its strength was only about 1/3 of body strength, therefore the strength of interfacial zone is the main reasons for affecting the strength of paste. The cementing materials of paste is reduced relatively by using limestone powder replace fly ash, it will make the bond strength between coarse and fine aggregate and cement reduced and affect the mechanical properties such as lay binding, splitting tensile strength and tensile strength.

Although limestone powder is an inert material and can't react with cement, many fine particles (less than  $16\mu\text{m}$ ) exist in limestone powder and filled in the interface between cement and aggregate or cement particles, so it can improve the particle gradation of base material and paste workability. The influence of limestone powder on paste compressive strength improvement decreased with increasing paste age. Therefore, limestone powder was helpful to improve the early strength of paste. The reason is that the limestone powder can promote  $\text{C}_3\text{S}$  early hydration,  $\text{Ca}^{2+}$  can be released when  $\text{C}_3\text{S}$  which exist in cement begin hydrating, and the migration ability of  $\text{Ca}^{2+}$  is higher than  $\text{SiO}_4^{2-}$  ion clusters [9-11]. According to the theory of adsorption, when the  $\text{Ca}^{2+}$  spread to nearby  $\text{CaCO}_3$  particles surface,  $\text{CaCO}_3$  particles surface produce physicochemical adsorption action on  $\text{Ca}^{2+}$  that cause the concentration of  $\text{Ca}^{2+}$  near  $\text{C}_3\text{S}$  particles decreased, the hydration speed of  $\text{C}_3\text{S}$  become acceleration, and the early strength of paste improved because  $\text{C}_3\text{S}$  is the main contribution of the cement strength. From the paste compressive strength (7d), no matter what the volume of limestone powder is, the paste strength is higher than paste without limestone powder [12-17].

### 3.2. Lay Binding Specificity

The shear strength tests of two groups of paste were done by using five level loading normal stress (0.5, 1, 1.5, 2, 2.5 MPa). The test results are shown in Table 5.

From the above test results, the ultimate shear strength, cohesion and friction coefficient of paste decreased by using limestone powder replace partially fly ash under the same condition of lay treatment measures and lay interval time.

### 3.3. Setting Time

The setting time comparison test between single fly ash and mix of fly ash and limestone powder was done, the test results are given in Table 6. Among them, water reducing agent dosage is 0.5%, temperature is 20 degrees, and relative humidity is 50%.

From the above test results, the initial setting time is shortened by 11 h 56 min and the final setting time is shortened by 8 h 8 min by using limestone powder replace 50% of fly ash.

### 3.4. Dry Shrinkage

The paste dry shrinkage test results are shown in Table 7.

From the test result, the early age dry shrinkage influence is small by using limestone powder replace fly ash, but after 7 days, the shrinkage rate of the mixed limestone powder paste increased significantly than that of the single fly ash paste. When the water binder ratio and admixture amount is constant, the shrinkage ratio of paste increased with increasing of the amount limestone powder in the admixture.

To the dry shrinkage performance influence of limestone powder, in addition to the above reasons, the accelerating influence of cement hydration cause by limestone powder is an important reason for paste early dry shrinkage enlargement. Research shows that water needed by cement hydration accounts for only 25% of the cement quality (water cement ratio is 0.25), the amount of cement reduce unceasingly with limestone powder added, but water doesn't change and far above the water needed by cement hydration, so more and more water exist in paste body, and the dry

Table 5. Results of shear strength for paste.

Test number	$\sigma=2.5\text{Mpa}$ Shear strength, Mpa		Peak value, MPa				Remant value, MPa				Friction value, MPa			
			f		c		$f_r$		$c_r$		$f_t$		$C_t$	
	28d	90d	28d	90d	28d	90d	28d	90d	28d	90d	28d	90d	28d	90d
C1	6.71	8.32	1.52	1.60	3.21	4.42	0.98	1.08	1.02	0.78	0.92	0.78	0.82	1.26
C3	5.33	6.51	1.38	1.22	1.82	3.93	0.73	1.02	0.82	0.73	0.41	0.72	0.53	0.81

Table 6. Results of setting time for paste.

Test number	Initial setting time	Final setting time	Initial setting penetration resistance(Mpa)
C1	29h17m	31h18m	12.5
C3	17h21m	23h10m	10.5

Table 7. Results of dry shrinkage ratio for paste.

Test number	Dry shrinkage ratio, $10^{-6}$						
	1d	3d	7d	14d	21d	28d	60d
C2	25	42	69	117	142	186	241
C4	27	45	76	138	156	206	262
C5	29	47	80	152	173	217	278
C6	27	45	73	126	146	195	251
C7	30	48	85	167	189	229	298

shrinkage of paste increases gradually with increasing of the amount of limestone powder and the extend of the age [18, 19]. Although limestone powder has certain inhibitory influence on dry shrinkage of paste, but it is very limited, so limestone powder is unfavorable for restraining dry shrinkage of paste.

### 3.5. Durability

The test results of permeability and frost resistance of pastes are given in Table 8 and Table 9, respectively.

From the above test results, the replacement of fly ash by limestone powder present no adverse influence on the permeability and frost resistance performance of paste, and paste has good permeability and frost resistance performance.

The specific area of limestone powder is larger than cement and fly ash, and most are fine particles less than  $16\mu\text{m}$  and fill a large number of pores, so the influence of permeability performance of paste is very small by using limestone powder replace fly ash, the influence of frost resistance performance is also small by ensuring the gas content is above 3%. The permeability coefficient SK of paste will decrease with increasing of the amount of limestone, the influence of limestone powder on permeability performance and frost resistance performance is mainly because it improves the

compactness of paste, and it is mainly reflected in the following points:

- (1) The influence of micro aggregate filling was that the incorporation of limestone powder changed the void structure of paste after hardening and improve the uniformity of paste, can not only make the pores can be refined, but also improve the pore structure and interfacial transition zone between materials.
- (2) The influence of active was that the  $\text{CaCO}_3$  in limestone powder improve the surface state of powder particle when it reacts with  $\text{C}_3\text{A}$  in cement and become to carbon aluminates, it conducive to the bonding between the powder particles and hydration products and improve the pore structure.
- (3) The influence of nucleation influence was that limestone powder can accelerate the hydration of  $\text{C}_3\text{S}$ , so that can increase the hydration products, avoid concentration of crystal growth and reduce porosity.
- (4) The influence of water absorption influence was that limestone powder can promote the silicate hydration and various aluminates reaction, but it is not a kind of cementing material. The actual water cement ratio of paste involve limestone powder is less than ordinary paste with same composition, so that the hydration products becomes less and the density of paste becomes worse.

Table 8. Results of permeability of paste.

Test number	Seepage height, mm	Impervious grade
C1	50	>W11
C2	55	>W11
C3	50	>W11
C5	60	>W11
C7	50	>W11

Table 9. Results of frost resistance of paste.

Test number	Mass loss rate, %		Relative dynamic elastic modulus, %		Antifreeze grade
	25	50	25	50	
C1	0	0.3	97	98	>F50
C2	0	0.2	97	98	>F50
C3	0.3	0.5	97	96	>F50
C5	0	0	97	97	>F50
C7	0	0.3	98	99	>F50

Table 10. Results of adiabatic temperature rise for paste.

Test number	Adiabatic temperature rise, °C		
	1d	28d	Final
C1	2.8	18.7	20.7
C3	6.5	17.2	18.2

Initial temperature is 23.7°C

### 3.6. Adiabatic Temperature Rise

The test results of adiabatic temperature rise for paste are shown in Table 10.

From the above test results, The adiabatic temperature rise value of paste increased significantly in 1 day and begin to less than the paste with single fly ash after 1 day by using limestone replace fly ash, the adiabatic temperature rise value (28d) is 1.5°C lower than the paste with single fly ash and the ultimately adiabatic temperature rise value low 2.5°C

### CONCLUSION

(1) The mixing amount of limestone powder has a less impact on the VC value and Gas content of paste under the condition of same water binder ratio. Using limestone powder replaces partially fly ash, the compressive strength, splitting tensile strength, ultimate tensile values are decreased with increasing of the amount of limestone powder, but compressive elastic modulus has less change.

- (2) The ultimate shear strength, cohesion and friction coefficient were decrease by using limestone powder replace partially fly ash under the same condition of lay treatment measures and lay interval time.
- (3) The initial setting time, the final setting time and adiabatic temperature rise value decreased with increasing the amount of limestone powder.
- (4) The early age dry shrinkage influence is small by using limestone powder replace fly ash, but after 7 days, the shrinkage rate of the mixed limestone powder paste increased significantly than that of the single fly ash paste. When the water binder ratio and admixture amount is constant, the shrinkage ratio of paste increased with increasing of the amount limestone powder in the admixture.
- (5) The replacement of fly ash by limestone powder present no adverse influence on the permeability and frost resistance performance of paste, and paste has good permeability and frost resistance performance.
- (6) The main effect of fly ash in paste is occur two hydration reaction with  $\text{Ca(OH)}_2$  in cement, reduce the later

strength and filling gaps, and improve the workability of paste. Therefore, using limestone powder replace fly ash can also attain the aim of improving workability of paste. Limestone powder can be used to replace partially or fully fly ash in coalmine filling mining.

### CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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