

IMPROVEMENT OF CONCRETE DURABILITY BY COMPLEX MINERAL SUPER-FINE POWDER

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Abstract

The green concrete capable for sustainable development is characterized by application of industrial wastes to reduce consumption of natural resources and energy and pollution of the environment. KG powder is a complex mineral superfine powder made by grinding the mix of calcined coal gangue and slag in certain proportion. Through reaction with the concrete admixture, KG powder improved pozzolanic reaction, micro-aggregate filling, and concrete durability. The concrete cement content was reduced by 40%-60%. The concrete resistance to sulfate attack and acid rain was enhanced greatly. Application of complex mineral superfine powder is an effective way to reduce environment pollution and improve durability of concrete under severe conditions.

1. Introduction

Coal gangue is a rock included in the coal bed and a waste discharged during coal mining and transportation as well as the most industrial waste discharged in China. It is estimated [1, 2], that the amount of gangue calculated as 15% of the coal output, there would be 100 million ton increment annually. Most of the coal gangue is a clay rock; its main mineral composition consists of clay mineral, followed by primary mineral quartz, feldspar, mica and pyrite, carbonate. After calcination under high temperature of 700-900°, the clay mineral is dewatered and disintegrated, the carbon

component is removed with the deteriorative impurity burned out [3]. The crystal is disintegrated and transformed into amorphous non-crystal; this makes the coal gangue active. The activity depends on the phase composition of coal gangue and temperature of calcination as well [1, 4]. The calcined coal gangue is ground to a specific surface of more than 4500 cm²/g and content of SiO₂ and Al₂O₃ more than 80%. The active SiO₂ and Al₂O₃ in it can react with Ca(OH)₂ and produce CSH gel, calcium aluminate and calcium sulfoaluminate hydrates [5, 6].

2. Raw materials and Test Methods

2.1 Raw materials

2.1.1 Cement

In the tests the PO425 cement manufactured by Chongqing Tenghui Diwei Cement Plant was applied with specific surface 3300 cm²/g.

2.1.2 Coal gangue

The coal gangue is from the Huaying Mountain mine and treated by calcinations and grinding; its chemical composition is given in Table 1.

Table 1: Chemical composition of coal gangue and slag

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	IL	Specific surface (cm ² /g)
Slag	36.90	9.73	3.85	35.93	2.33			4300
Coal gangue	58.10	24.54	5.31	5.73	1.05	2.97		4100
Fly ash	41.10	25.9	1.02	3.2	0.55	0.56	7.9	3900

2.1.3 Slag

The blast furnace slag is from the steel plant of Chongqing Steel and Iron Corporation and is dried and ground. Its specific surface is 4300 cm²/g and the chemical composition is given in Table 1.

2.1.4 Fly ash

The fly ash is a dry one from the Chongqing Jiulongpo Electric Power Plant; its properties conform to the Chinese Standard GB1596-91, “Fly ash for cement and concrete,” as standard class II.

2.1.5 Fine aggregate

Medium size sand from Sichuan Jianyang with a modulus of fineness $M_x = 2.32$; normal grading with the silt content 0.8%.

2.1.6 Coarse aggregate

Crushed limestone is from Xiaoquan, Chongqing City with a size of 5-20 mm and normal continuous grading. The content of flaky and elongated particles is <3% and the crushing index $\leq 6\%$.

2.1.7 Admixture

A complex retarding super-plasticizer FDN with slight air entraining, water reduction rate 23% and other properties conforming to the requirements for first class one in Chinese standard “Admixtures for concrete” (GB8076-2000), the dosage of the admixture is 1.2%.

2.1.8 KG powder

The KG powder is a mix by grinding the calcined coal gangue with slag, fly ash and silica fume. Its specific surface is 4900 cm^2/g .

2.2 Mix proportion of concrete

Based on properties of raw materials, the control mix proportion is given in Table 2 and taken as basic one. The mix proportion for the test is regulated on this basic one.

Table 2: Control mix proportion of concrete

Cement	Sand	Stone	Water	Admixture	Sp (%)
510	612	1140	168	6.12	35
1	1.20	2.24	0.33	0.012	

3. Test Results and Discussions

3.1 Workability and strength of KG powder concrete

Table 3: Workability and strength of KG powder concrete

No.	Initial set h:min	Final set h:min	Slump/spread (mm)			Compressive strength (MPa)		
			Initial	1h	2h	3d	28d	90d
1	7:35	8:28	210/490	200/430	160/350	49.0	67.9	70.2
2	7:52	8:47	210/525	210/472	180/395	46.3	68.2	75.6
3	8:10	9:31	225/530	215/483		43.2	69.8	80.2

Note: Substitution of cement by KG powder for mixes No.1 - 0%, No.2 - 20%, and No.3 - 50%.

The workability and strength of KG powder concrete are given in Table 3.

- Due to the micro filling and dispersing effects of the KG powder, the slump loss for the concrete mix with KG powder is less than that of one without addition. For example, the slump loss for concrete mix without additives at 2 hours reached 50 mm and that for concrete with 20% addition is 30 mm and for 50% addition 15 mm. The reduction of spread has the same character. Such effect is beneficial to the ready mixed concrete.
- Due to the secondary hydration of active additive, in comparison with the concrete without addition, the strength of the concrete with KG powder is decreased at early age with increase of dosage of the gangue powder and about the same at later age. The increment of strength for concrete without addition $(R_{90}-R_3)/R_3 = (70.2-49.0)/49.0 = 40.7\%$; for concrete with 50% addition $(R_{90}-R_3)/R_3 = (80.2-43.2)/43.2 = 85.6\%$.

The authors suggest that a slightly less strength of concrete at early age, in some degree, is beneficial to the durability of the concrete. The development of strength of the KG powder concrete depends on its mix proportion, that is, the mark and type of cement, w/c, content of coal gangue, fineness of additive, type and dosage of admixture, temperature of the environment, curing condition etc. In general, a high-strength concrete can be obtained provided that high quality material is used and a proper mix proportion is chosen. The KG powder concrete will have a high

strength at later age. A careful curing at early age is beneficial to the development of the strength.

3.2 Durability of the KG powder concrete

3.2.1. Permeability of KG powder concrete

Test on permeability of the KG powder concrete was carried out according to the Chinese Standard GBJ82-85, "Test methods for long term properties and durability of ordinary concrete." Due to that the low w/c for high-performance concrete and the pozzolanic and filling effects of the ground KG powder, there is more cementitious material formed with dense structure, therefore, it is easy to prepare a high impermeable concrete in case of using crushed stone with excellent grading and addition of proper admixture [7]. See Table 4.

Table 4: Test results of permeability for KG powder concrete

Compressive strength (MPa)	Impermeable pressure (MPa)	Description	Depth of penetration
67.8	2.0	The pressure up to 2.2 MPa and kept for 10 hours, no leakage found.	On split specimen the depth of penetration at bottom is in average 3-5 cm and maximum 11 cm.

Note: Addition of KG powder 30%.

3.2.2. Resistance of KG powder concrete to sulfate attack

In our tests, the resistance to sulfate attack was studied by storage of specimens cured under standard condition for 28 and 90 days in 5% solutions of sodium sulfate and magnesium sulfate, then, the ratio of flexural to compressive strength of specimens was determined after 28 and 90 days corrosion, the results were compared with those of specimens stored in fresh water.

The mix proportions of mortar specimen are given in Table 5, the forming of specimen was carried out according to the methods for cement mortar specimens.

Table 5: Mix proportions of mortar specimens

No.	Cement (PO425)	KG powder	Sand	Water
1	100	0	300	40
2	80	20	300	40
3	65	35	300	41
4	50	50	300	42

Table 6: Compressive strength of mortar specimen

No.	28-day compressive strength (MPa)	Compressive strength after 28-day storage (MPa)				
		Fresh water	Na ₂ SO ₄	%	MgSO ₄	%
1	51.3	53.7	42.3	0.79	40.1	0.75
2	47.0	54.2	56.1	1.04	53.7	0.99
3	48.3	55.7	57.8	1.04	58.1	1.04
4	53.9	61.3	66.4	1.08	62.9	1.03

Table 7: Compressive strength of mortar specimen

No.	28-day compressive strength (MPa)	Compressive strength after 90-day storage (MPa)				
		Fresh water	Na ₂ SO ₄	%	MgSO ₄	%
1	51.3	55.2	41.0	0.74	36.5	0.66
2	47.0	57.3	57.1	1.00	51.6	0.90
3	48.3	56.6	57.9	1.02	52.6	0.93
4	53.9	62.7	65.9	1.05	60.2	0.96

It can be seen from the test results with storage in 5% sodium sulfate solution and 5% magnesium sulfate solution for 28 days that the corrosion resistance of mortar specimen with KG powder is much better than that of control specimen, the effect is better for those with more additives. This is due to that the active SiO₂ in KG powder can react with the Ca (OH)₂ in concrete to form secondary calcium silicate hydrate and make it chemically stable and structurally dense, the impermeability of concrete is enhanced as well. In addition, the KG powder can reduce the content of calcium aluminate in cementitious material, leading to increase of sulfate resistance of concrete. From the results after 90-day immersion, the mortar specimens with KG powder in 5% sulfate solution have similar effect with those immersed for 28 days, but for those in 5% magnesium sulfate, the influence of addition on anticorrosion factor is not obvious (the test results of flexural strength are similar to those of compressive one).

3.2.3 Resistance of KG powder concrete to acid rain

According to the monitoring data from Chongqing Bureau of Environmental Protection [8], the weighted means of pH value for annual precipitation (rain, snow) in Chongqing was in range of 4.09-4.70. The frequency of acid rain was over 70%. The minimum pH value reached 2.85 in 1990. In precipitation of Chongqing, the polluting component anion is mainly the sulfate ion, which takes about 75% of all measured anions. So the acid rain attack is characterized by sulfuric acid one and in laboratory the resistance of concrete to acid corrosion is carried out in diluted solution of sulfuric acid.

Table 8: Mix proportion of cement mortar

No.	Cement (PO525)	KG powder	w/c ratio	c/s ratio
1	100	0	0.4	1:3
2	90	10	0.4	1:3
3	80	20	0.4	1:3
4	70	30	0.4	1:3
5	50	50	0.4	1:3

Table 9: Mix proportion of concrete

No.	OPC : KG powder : W : admixture	Sand percentage (%)	28-day (MPa)
1	1 : 0 : 0.35 : 1.0%	38	61.1
2	1 : 0.3 : 0.35 : 0.8%	38	67.3
3	1 : 0.45 : 0.36 : 1.1%	38	71.2

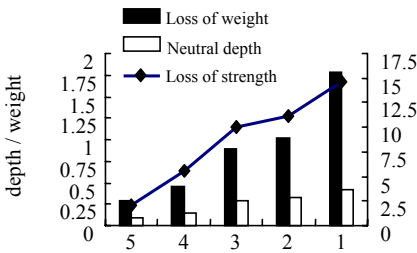


Fig. 1: Neutral depth, loss of strength, and weight of mortar attacked by sulfuric acid

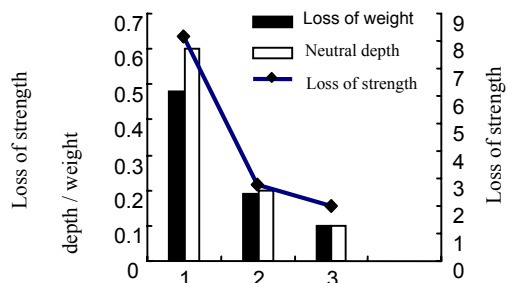


Fig. 2: Neutral depth, loss of strength, and weight of concrete attacked by sulfuric acid

The mortar and concrete specimens were cured for 28 days in sulfuric acid solution with pH value of 3.0 for corrosion test. During storage, the color of specimen surface changed into yellow, then white. There were loss in weight and strength of specimen occurred, the depth of neutralization varied with the additives. After washing the loose material covered on the surface, there was some cement paste on the surface fallen off and part of the aggregate exposed, which is similar to that found in concrete structure attacked by the acid rain in Chongqing [8].

From Figs. 1 and 2 it can be seen that the resistance of OPC to acid corrosion is rather poor, the strength loss of mortar specimen reached 14.6% after immersion in sulfuric acid solution with pH value of 3.0 for 90 days and the strength loss for concrete specimens is 8.15%. For specimens with additives, those with KG powder have good performance in acid resistance and better than specimens without additives both in the depth of neutralization and loss in weight and strength. As for mortar and concrete, the depth of neutralization is in linear relationship with the loss in weight and strength.

It can be seen from the test results that the KG powder concrete is better than ordinary Portland cement concrete. This is due to that there is more active component in KG powder. In addition, due to less cement content, the amount of Ca (OH)₂ in KG powder concrete mix reduced by 30%-50% in comparison with that in OPC paste, the CSH gel in paste at later stage of hydration is much more than that for OPC. The rate of formation of Ca (OH)₂ during hydration is low with fewer amounts than that for OPC. Consequently, it will have more strength and better stability, the composition of cementitious material in cement paste and the interface between cement paste and aggregate are improved. Thus, the stability of the concrete in respect of resistance to acid corrosion is enhanced.

4. Conclusion

The fully calcined coal gangue ground in mix with slag and fly ash can serve as additives for high performance concrete. Piling up of coal gangue in large amount

seriously caused the pollution of environment and there is latent danger of self-combustion. However, the utilization of coal gangue fell behind that of other industrial wastes such as fly ash, slag etc. the authors carried out a series of experiments and it is verified that like other similar industrial wastes, the coal gangue can be used for concrete, provided that the proper mix proportion is chosen and high quality admixture is used to improve the properties of concrete, even the high performance concrete can be prepared with the characteristics of green concrete.

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