

## Grey Connection Analysis between Cement Particle Size Distribution and Compressive Strength

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**Abstract:** This paper studied the effect of triethanolamine(TEA), glycerin(PG) and lignosulphonate(CLS), used as grinding aids respectively, on cement particle size distribution and mortar strength. Grey connection analysis was made between cement particle size distribution and compressive strength. Results showed that TEA and CLS significantly increased the volume proportion of particles with diameter less than 10 $\mu$ m and decreased the volume proportion of particles with diameter larger than 30 $\mu$ m. PG showed opposite effect. According to grey connection index, cement particles with diameter ranging from 10 $\mu$ m to 20 $\mu$ m played a decisive role in the early compressive strength, and particles with diameter between 20 $\mu$ m and 30 $\mu$ m took a major effect on the late compressive strength.

### Introduction

Cement industry, a resource and energy consumption industry, is now facing the increasingly severe challenges of resources and environmental problems. In 2013, according to China's national bureau of statistics released, the cement output reached 2.41 billion tons, accounting for two-thirds of the total output of cement in the world. In the process of cement production, energy consumption during grinding process accounts for 60%-70% of the total energy consumption<sup>[1]</sup>. So some grinding aids are added during grinding process to reduce the energy consumption. At present, the development and application of cement grinding aids have aroused wide attention<sup>[2,3]</sup>.

According to the definition of cement grinding aids, cement fineness should be taken as an important index to evaluate the grinding effects. But cement production enterprises expect that grinding aids can both save energy and increase the strength of cement mortar at the same time. Some scholars indicated that the composite grinding aids showed various grinding effects because of the differences in composition, thus causing different influences on performance of cement products<sup>[4,5]</sup>. It has brought people a lot of technical problems. So it is necessary to study the effect of grinding aids on cement properties, especially on the development of mortar strength.

Screen allowance, specific surface area and average particle size are usually used to reflect cement fineness<sup>[6]</sup>. And the specific surface area is a very important index during the process of cement production. However, cement samples with different grinding aids have different properties, although these cement samples have the same specific surface area<sup>[7]</sup>. So it is of great significance to study the effect of grinding aids on particle size distribution, development of mortar strength and so on.

This paper studied the effect of triethanolamine (TEA), glycerin(PG) and lignosulphonate(CLS) which are used as grinding aids, on cement particle size distribution and compressive strength of cement mortar. Grey connection analysis has been used to analyze the influence of cement particle size distribution on early and late compressive strength of cement mortar.

## Experiments

**Materials.** The clinker of Wan-an ordinary Portland cement is used in this study. The chemical and mineral composition of the clinker is shown in Tab.1 and Fig.1.

Tab.1 Chemical and mineral composition of clinker (by mass)(%)

CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	R <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Other	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
63.1	24.1	3.3	4.3	1.2	0.8	0.9	0.2	2.1	39.8	39.2	6.0	10.0

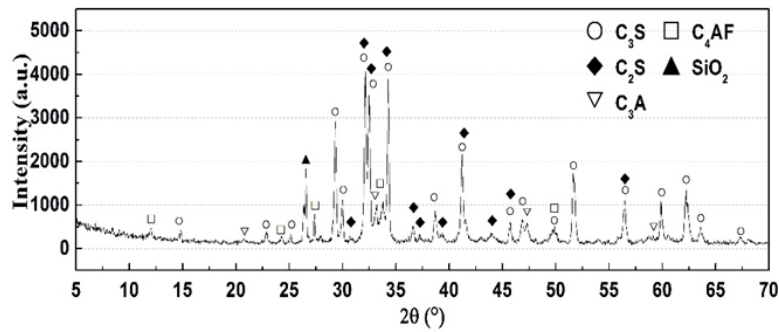


Fig.1 The XRD pattern of cement clinker

Three types of grinding aids used in this study together with their chemical structure are shown in Tab.2.

Tab.2 The molecular formula and structural formula of grinding aids

Name	Abbreviation	Molecular formula	Structural formula
Triethanolamine	TEA	C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub>	
Glycerine	PG	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	
Calcium lignosulfonate	CLS	C <sub>20</sub> H <sub>24</sub> CaO <sub>10</sub> S <sub>2</sub>	

**Cement samples preparation.** Portland cement samples were produced by intergrinding 96% clinker and 4% gypsum in a ball mill, with (370±5) m<sup>2</sup>/kg Blaine fineness. Every 5kg cement samples were produced after one grinding circle. At the beginning of a grinding process, the grinding aid, accounting for four dosage levels (0.01%, 0.02%, 0.03% and 0.04%) of binder (clinker+gypsum), was added into the clinker-gypsum system. The proportions of grinding materials were listed in Tab.3.

Tab. 3 Proportions of cement samples

Samples	Cement composition(g/5kg)				
	Cement clinker	Gypsum	TEA solution (50% by mass)	PG solution (50% by mass)	CLS solution (50% by mass)
PC	4800	200	-	-	-
PCT1	4800	200	1	-	-
PCT2	4800	200	2	-	-
PCT3	4800	200	3	-	-
PCT4	4800	200	4	-	-
PCP1	4800	200	-	1	-
PCP2	4800	200	-	2	-
PCP3	4800	200	-	3	-
PCP4	4800	200	-	4	-
PCC1	4800	200	-	-	1
PCC2	4800	200	-	-	2
PCC3	4800	200	-	-	3
PCC4	4800	200	-	-	4

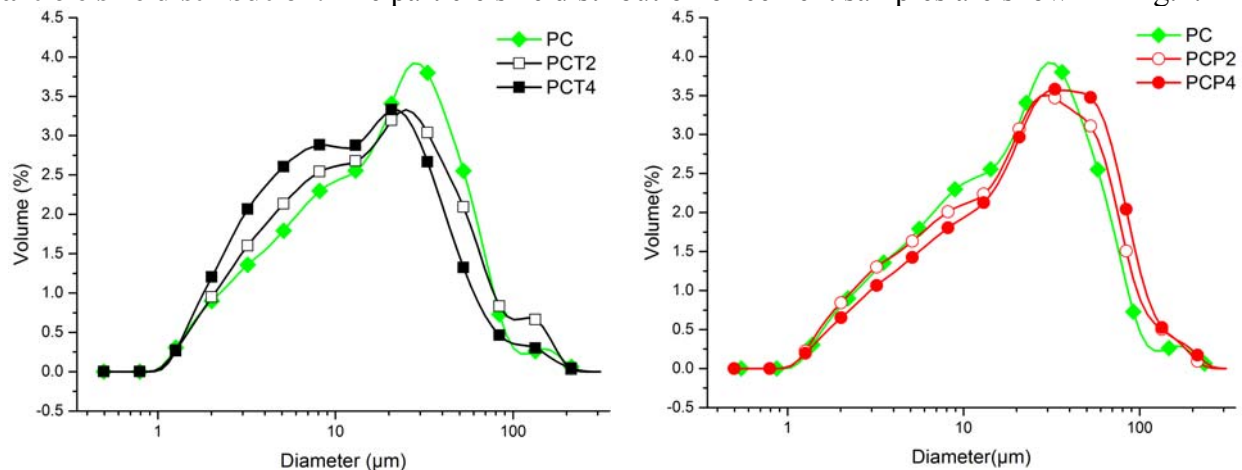
**Testing procedure and specimen preparation.** The particle size distribution of cements was measured by Beckman Coulter LS230 Laser Particle Analyzer. The scattering light and refracted light may obtain the information of particle size and distribution by detecting the relative energy scattered by the particles, with the continuous range of the wavelength, so it could be used as a rapid method to determine the characteristic parameter and particle size distribution of the grinded cement samples. The test scope of the analyzer ranges from 0.04 $\mu\text{m}$  to 2000 $\mu\text{m}$ .

The calculation and judgment of grey connection analysis were carried out based on the references [8] and [9]. The grey connection index reflects the contribution degree of sub-array (sub-factor) to the main-array (main-factor). That is to say, sub-array with higher absolute index value shows greater effect on the main-array. Positive index means that the sub-array is favorable to the main-array, while negative index means the opposite effect.

The water requirement of normal consistency of cement, the setting time of cement, and the development of mortar strength were measured according to the methods specified by GB/T 1346-2011, GB/T 1346-2011 and GB/T 17671-1999 respectively.

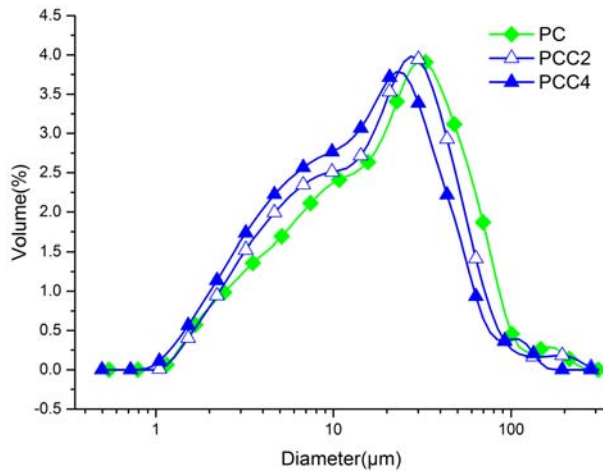
## Results and discussion

**Particle size distribution.** The particle size distribution of cement samples are shown in Fig.2.

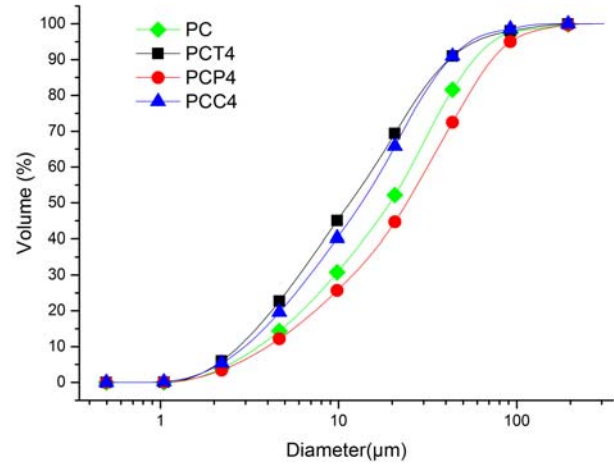


(a) Particle size distribution of PCTs

(b) Particle size distribution of PCPs



(c) Particle size distribution of PCCs



(d) Cumulative distribution of cement samples

Fig.2 Particle size distribution and cumulative distribution

With the same Blaine fineness, Fig.2 demonstrated that TEA, PG and CLS significantly changed the particle size distribution of cement samples. Comparing with PC, PCTs and PCCs showed a higher volume proportion of fine particles with diameter ranging from 10μm to 30μm. Meanwhile, the volume proportions of coarse particles of PCTs and PCCs, with diameter ranging from 60μm to 160μm, were lower than that of PC. But there was no obvious difference in volume proportion of particles with diameter range of (10-30) μm among PC, PCTs and PCCs. On contrary to PCTs and PCCs, PCPs had a lower volume proportion of fine particles with diameter ranging from 10μm to 30μm and a higher volume proportion of coarse particles with diameter ranging from 60μm to 160μm.

**Water requirement for normal consistency and setting time of cement samples.** The experimental results of water requirement for normal consistency and setting time of the cement samples were shown in Tab.4.

Tab.4 Water requirement for normal consistency and setting time of cement pastes

Samples	Water requirement for normal consistency(%)	Setting time(min)	
		Initial	Final
PC	26.0	120	150
PCT1	26.2	100	150
PCT2	26.3	90	140
PCT3	26.4	80	120
PCT4	26.4	75	115
PCP1	25.6	130	170
PCP2	25.7	130	185
PCP3	25.7	125	195
PCP4	25.6	120	205
PCC1	25.4	110	145
PCC2	25.4	100	150
PCC3	25.2	90	135
PCC4	25.0	80	125

Tab.4 illustrated that the three kinds of grinding aids all had slight effects on water requirement for normal consistency. Comparing with PC paste, PCTs pastes had a larger water requirement, while PCP pastes and PCC pastes showed a lower water requirement. With increased dosage of grinding aids, water requirement of PCT pastes slightly ascended, while water requirement of PCP pastes slightly declined. But there was no obvious evidence showing the difference in water requirement of PCP pastes.

According to Schiller and Ellerbrock <sup>[10,11]</sup>, water demand is composed of three fractions: low proportion of chemical water needed to form the initial hydration products, the second proportion needed to lubricate the initial hydration products, and a large amount of water to lubricate the surfaces of the cement grains. PG and CLS are usually used as retarder and water reducer, respectively, so both of them can help lubricate the surface of cement grains. The water demand of PCPs and PCCs are certainly lower than that of PC.

The results also indicated that the setting time of PCT pastes and PCC pastes were shorter than that of PC paste. With increased dosage of the two grinding aids, both the initial setting time and final setting time of cement pastes were getting shorter. PG showed no effect on initial setting time of cement pastes. The initial setting time of PCP pastes were almost the same as PC. However, PG remarkably delayed the final setting time of cement pastes. The higher the dosage was, the longer the final setting time would be.

**Compressive strength and flexural strength of cement mortars.** Tab.5 showed the compressive and flexural strength values at 3 and 28 days for all cement samples. As expected, the compressive and flexural strength values of all mortar specimens increased with curing time.

Tab. 5 The development of mortar strength

No.	Compressive strength (MPa)		Flexural strength (MPa)	
	3d	28d	3d	28d
PC	27.2	50.9	6.0	7.7
PCT1	29.6	49.7	5.7	7.6
PCT2	30.7	47.2	6.3	7.6
PCT3	33.8	51.8	6.6	8.0
PCT4	31.8	51.2	6.4	8.0
PCP1	31.1	55.8	6.8	8.7
PCP2	23.7	44.9	5.9	8.1
PCP3	20.8	42.5	5.5	7.8
PCP4	24.3	46.3	5.4	8.4
PCC1	29.9	45.6	5.4	7.4
PCC2	30.6	55.9	6.8	8.3
PCC3	31.2	55.0	5.7	7.5
PCC4	32.2	52.7	7.3	8.0

Tab.5 showed the significant influence of TEA, PG and CLS on mortar strength. Comparing with PC mortar, compressive strength values of PCT and PCC mortars at 3 days increased by 8.8%-24.3% and 9.9%-18.4%, respectively. The compressive and flexural strength of PCP1 mortar at 3 days were higher than that of PC. While PCP2, PCP3 and PCPP4 mortars presented much lower compressive and flexural strength than PC. After 28 days of curing time, PCT1 and PCT2 mortars showed a little lower compressive and flexural strength than PC, while PCT3 and PCT4 had a contrary tendency. The flexural strength of PCP mortars were all higher than that of PC mortars. As for the compressive strength, PCP mortars shared the same change rule as PCP mortars cured for 3 days. There was a 9.0%-16.5% compressive strength loss for PCP2, PCP3 and PCP4. For PCC mortars, the compressive strength of PCC1 mortar was 10% lower than that of PC mortar, but the compressive strength increased by 3.5%-9.8% for PCC2, PCC3 and PCC4 mortars.

**Grey connection analysis between particle size distribution and compressive strength.**

According to Fig.2, TEA, PG and CLS showed different effects on the particle size distribution of cement samples, thus indirectly influencing some basic properties of cement samples, such as water requirement for normal consistency of cement, setting time of cement, mortar strength and so on. In order to clarify the effect of cement particle size distribution on compressive strength of cement mortar, this paper intended to establish grey connection analysis between cement particle size distribution and compressive strength of mortar. Seven cement samples (shown in Tab.6), with different size distribution, were taken for grey connection analysis. The early compressive strength

(3d) and late compressive strength (28d) are taken as main-arrays (named as  $y_{early}$  and  $y_{late}$ ), and the volume fraction of cement particles in each specified particle size range are taken as the Sub-arrays (named as  $y_1$ ,  $y_2$ ,  $y_3$ ,  $y_4$ ,  $y_5$  and  $y_6$ ). The calculation and judgment of grey connection method consult the references [8] and [9]. And  $r_{early}$  and  $r_{late}$  are taken as the connection indexes. The result was presented in Tab.6 and Tab.7.

Tab.6 Sub-array and main-array of mortar strength

No.	Main-array		Sub-array					
	$y_{early}$	$y_{late}$	$y_1$	$y_2$	$y_3$	$y_4$	$y_5$	$y_6$
			(0-5) ( $\mu\text{m}$ )	(5-10) ( $\mu\text{m}$ )	(10-20) ( $\mu\text{m}$ )	(20-30) ( $\mu\text{m}$ )	(30-40) ( $\mu\text{m}$ )	( $>40$ ) ( $\mu\text{m}$ )
PC	27.20	50.90	16.07	14.68	21.40	14.79	11.31	21.76
PCT2	30.70	47.20	20.20	17.17	22.68	13.09	8.57	18.29
PCT4	31.80	51.20	25.28	19.75	24.31	12.56	7.20	10.89
PCP2	23.70	44.90	16.55	13.48	19.90	13.67	10.21	26.18
PCP4	24.30	46.30	13.59	12.07	18.99	13.58	10.71	31.06
PCC2	30.60	55.90	18.46	16.67	23.14	15.58	10.65	15.50
PCC4	32.20	52.70	21.93	18.28	25.58	14.55	8.42	11.24

Tab.7 Grey connection index between particle size distribution and mortar strength

Connection index	$y_1$ (0-5) ( $\mu\text{m}$ )	$y_2$ (5-10) ( $\mu\text{m}$ )	$y_3$ (10-20) ( $\mu\text{m}$ )	$y_4$ (20-30) ( $\mu\text{m}$ )	$y_5$ (30-40) ( $\mu\text{m}$ )	$y_6$ ( $>40$ ) ( $\mu\text{m}$ )
$r_{early}$	0.82	0.90	0.93	0.76	-0.65	-0.51
$r_{late}$	0.71	0.75	0.84	0.89	-0.72	-0.55

According to the connection index, cement particles with diameter less than  $30\mu\text{m}$  was helpful to the development of mortar strength (for the positive connection index), while cement particles with diameter larger than  $30\mu\text{m}$  did harm to the development of mortar strength (for the negative connection index). The ability for different diameter range of cement particles to enhance early compressive strength (3d) was as follows:  $(10-20)\mu\text{m} > (5-10)\mu\text{m} > (0-5)\mu\text{m} > (20-30)\mu\text{m}$ . For late compressive strength, the ability order was as follows:  $(20-30)\mu\text{m} > (10-20)\mu\text{m} > (5-10)\mu\text{m} > (0-5)\mu\text{m}$ . That is to say, the mortar strength could be improved by reducing the volume fraction of cement particles with diameter more than  $30\mu\text{m}$  and increasing the volume fraction of cement particles with diameter larger than  $30\mu\text{m}$  at the same time.

## Conclusion

Based on the test results and analysis above, the following conclusions were made.

Three kinds of grinding aids showed significant influence on cement particle size distribution. As for the same specific surface area, PCTs and PCCs had higher proportion fine particles, while PCPs showed opposite result.

TEA increased the water demand and shortened the setting time of cement samples. PG decreased the water demand and extended the setting time of cement samples. In addition, CLS decreased the water demand and reduced the setting time of cement samples.

The results of mortar strength Indicated that TEA and CLS improved both the early strength and late strength of mortars. PG decreased the early strength of mortar, but it obviously increased the late strength.

According to the grey connection analysis, cement particles with diameter about  $(10-20)\mu\text{m}$  affected most on the early compressive strength of mortar, while the  $20-30\mu\text{m}$  ones had maximum effect on the late compressive strength of mortar.

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