ATLANTIS PRESS
Advances in Engineering Research, volume 173
4th Workshop on Advanced Research and Technology in Industry Applications (WARTIA 2018)

The effect on the Performance of Cement Grinding Aid Components

Guo Yanmei[1, a], Sun Shaofei[2, b, *]

[1]Hohhot Construction Engineering Quality Supervision Station ,Hohhot 010000 ,China ;

[2]Inner Mongolia University of Science &Technology ,Baotou 014010,China

[a]Tel.13314719522, [b]email:1197168195@qq.com

Keywords: cement grinding aid, fineness, compressive strength, size distribution

Abstract: In this paper, By choosing four kinds of grinding aids better one-component, The grinding aid of cement grinding aids is determined by orthogonal optimization. By adding different inorganic reinforcing components, Developed a cement grinding aids. The result turns out, compared with blank sample, the adulteration of grinding aid leads compression strength of 3d, 7d and 28d respectively are improved 17.9%, 17.8% and 16.8%, cement fineness to reduce by 63.1% and specific surface area to increase about 10.6%. Meanwhile, cement particles ranging 3-32 μm is improved 11.3%, which optimizes the grain composition of cement and increases strength of cement. The experimental research to provide technical support for the future development of cement technology.

1. Introduction

With the rapid development of construction industry, people pay much more attention to the quality of cement. As we all know that, the production process of cement can be broadly divided into “two grindings and burn", which means raw meal preparation, clinker calcining and cement grinding, and cement grinding is the most important process in the whole cement production. However the fineness of cement grinding to a certain degree, there will be "reunion" phenomenon”. this is because the cement produce electric charge in the process of grinding, the positive and negative charges on cement particle’s surface attract each other, and cement grinding aid is a good way to avoid the occurrence of this phenomenon. Because of its lower cement fineness, increasing specific surface area, optimizing the grain size distribution of cement particles, reduce gringing enercy, and increasing production, Cement grinding aid is widely used in cement industry[1-4].

Below chemical regent are normally used as cement grinding aid: three isopropanolamine, ethylene glycol, triethanolamine, sorbitol, diethylene glycol, glycerin, etc. Because of the bad adaptability, stability and imperfect function, single-component cement grinding aid is difficult to meet the requirements of grinding aid; Also the macromolecular synthetic grinding agent technology is still not perfect, cannot be applied to the actual production [5-6], So the composite cement grinding aid has become one of the mainstream of the cement industry. Composite cement grinding aid is by a variety of single component and grinding aid distribution, and the interaction of different monomer component, to make composite grinding agent has good grinding effect, good stability, wide adaptability of multiple effect.

2. Experiment

2.1 Experiment Material

2.1.1 Binding Material

In this test, we use clinker from wuhai in Inner Mongolia, natural gypsum. The chemical composition of clinker and gypsum are shown in table 1, the cement clinker without grinding aids’s physical properties such as table 2.

Tab.1 Chemical composition of raw materials /%

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Loss	SO_3	∑
Clinker	24.98	6.42	3.56	60.90	2.42	0.86	0.56	99.7
Gypsum	16.16	2.46	0.82	25.18	2.24	17.75	29.73	94.34

Tab.2 Cement clinker physical properties

	fineness (45μm, %)	specific surface area(m^2/kg)	water requirement of normal consistency(%)	setting time(min)		rupture strength (MPa)		compressive strength (MPa)	
				initial setting time	final setting time	3d	28d	3d	28d
Cement	10.3	450	24.6	128	162	5.4	7.9	24.7	50.0

2.1.2 Grinding Aid

Selection of grinding agent component and its molecular structure as shown in table 3.

Tab.3 Name abbreviation and structural formula of grinding aids components

Component name of grinding aids	Abbreviation in this paper	Structural formula
Triethanolamine	TEA	$N(CH_2CH_2OH)_3$
Triisopropanolamine	TIPA	$C_9H_{22}NO_3$
Glycerin	GLY	$HOCH_2CHOHCH_2OH$
Sorbitol	MDBS	$C_6H_{14}O_6$
Ethylene glycol	EG	$HOCH_2CH_2OH$
Sodium sulfate	Na_2SO_4	Na_2SO_4
Sodium thiosulfate	$Na_2S_2O_3$	$Na_2S_2O_3$
Sodium chloride	NaCl	NaCl
Sodium carbonate	Na_2CO_3	Na_2CO_3
Sodium hydroxide	NaOH	NaOH

2.2 Experimental Method

2.2.1 Grinding Method

According to the 95% clinker + 5% gypsum cement mixing ratio, when the grinding clinker (1-7 mm), gypsum and grinding agent to join together Φ 500 x 500 national cement plant in the unified test standard laboratory mill grinding together, each time grinding 5 kg, grinding time for 40 min, the release time for 5 min.

2.2.2 Performance Test

(1) The cement fineness determination basis of(GB/T1345-2005)《Cement fineness testing method Sieve analysis method》;Specific surface area measurement basis of(GB/T8074-2008)《Cement specific surface area measurement method (Bertrand method)》;Cement strength measurement basis of(GB/T17671-1999)《Cement mortar strength testing method(ISO method)》.

(2) Cement particle size distribution with BT - 2001 laser particle size analyzer (dry).

2.2.3 Cement Grinding Aid Compound Process

Choose 5 kinds of single-component grinding agent which are commonly used in market for experiment, determine the scope of the content; Choose single-component grinding agent with good effect for orthogonal optimization, determine the best mix proportion and amount. In the composite grinding aid system, keep the same of grinding components, redistribute the grinding components with different kinds of inorganic enhancement composition, Study the influence that different inorganic components affect of cement performance, to determine the proportion of cement grinding aid.

3. Results and Discussion

3.1 Effect of monocomponent grinding aid on cement performance

All information show that, Organic alcohol amine especially triethanolamine and three isopropanolamine, they have significant effect on cement grinding and enhancement; Polyol molecules has good grinding effect, but slightly of enhance effect; Inorganic salt is helpless for grinding function, strengthen effect is good[4] [7]. Therefore, select of triethanolamine, three isopropanolamine, ethylene glycol, glycerol and sorbitol as grinding components, Study of 5 kinds of grinding components, Grinding dosage control components from 0.01% to 0.04% (according to the quality of cement, similarly here in after), The result is shown below.

3.1.1 Effect of monocomponent grinding aid on cement fineness and specific area

Effect of monocomponent grinding aid on cement fineness and specific area, As shown in figure 1:

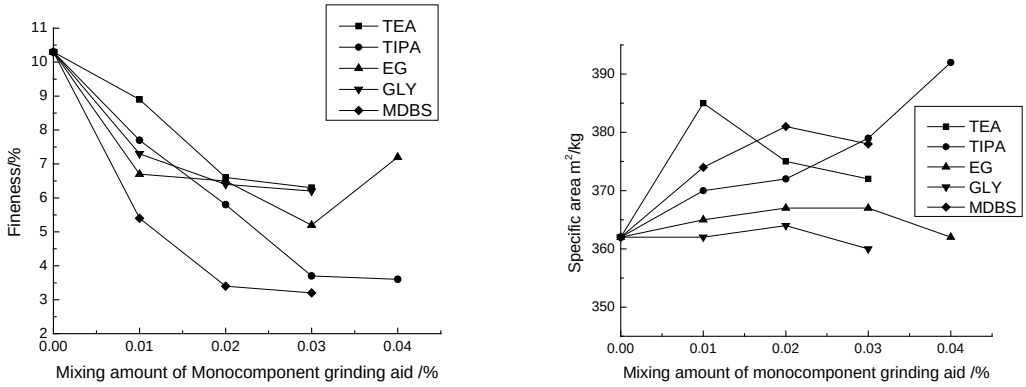


Fig.1 Effect of monocomponent grinding aid on cement fineness and specific area

As shown in figure 1, the one-component grinding agent of cement fineness and specific surface area has a certain effect. Compared with the blank group, dosage of triethanolamine was 0.02%, cement fineness is 38.4% lower, specific surface area increased by 3.9%; Three isopropyl alcohol amine content was 0.04%, 65.0% lower cement fineness, specific surface area increased by 8.9%; Ethylene glycol content was 0.03%, 50.0% lower cement fineness, specific surface area increased by 1.3%; Glycerin content was 0.02%, 38.2% lower cement fineness, specific surface area increased by 1.9%; Sorbitol content was 0.02%, 66.6% lower cement fineness, specific surface area increased by 5.1%. Test data shows that above one-component grinding agents have certain effect of improving cement fineness and specific surface area , has a positive effect for the preparation of the composite cement grinding aid.

3.1.2 Effect of monocomponent grinding aid on compressive strength

Effect of monocomponent grinding aid on compressive strength, As shown in figure 2:

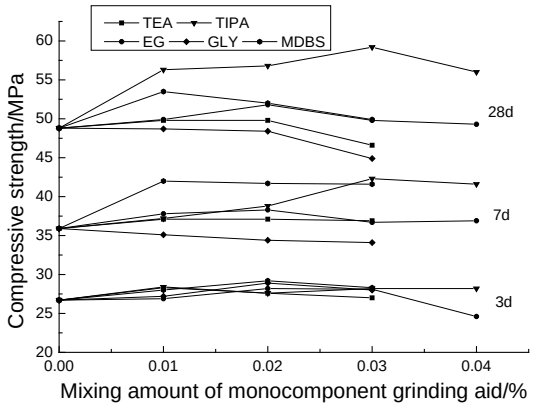


Fig.2 Effect of monocomponent grinding aid on compressive strength

As shown in figure 2, Every single-component grinding aid on growth of compressive strength of cement has a certain effect. Compared with the blank group, dosage of triethanolamine was 0.01%, 3 d, 7 d and 28 d compressive strength increased by 6.0%, 3.3% and 2.0%; Three isopropyl alcohol amine content was 0.03%, 3 d, 7 d and 28 d compressive strength increased by 5.6%, 17.8% and 21.3%; Ethylene glycol content was 0.02%, 3 d, 7 d and 28 d compressive strength increased by 5.6%, 6.7% and 6.1%; Glycerin content was 0.02%, 3 d compressive strength increased by 8.2%, but the 7 d and 28 d compressive strength with the increase of the content gradually reduced; Sorbitol content was 0.01%, 3 d, 7 d and 28 d compressive strength increased by 4.9%, 17.0% and 9.6%.

To sum up, triethanolamine, three isopropanolamine, ethylene glycol and sorbitol have certain effect on cement fineness decreased, the improvement of specific surface area and the improvement of compressive strength of mortar, So according to the test results and economic cost, control components content in 0.01%, 0.01%, 0.02% and 0.01% respectively; Although glycerin has some effect of reduce the cement fineness, and the improvement of specific surface area, it has no improvement of compressive strength of mortar, even has a tendency to pour shrinkage, So the glycerin has a little contribution to the development of the cement strength.

3.2 Grinding Aid Orthogonal Optimization Design

3.2.1 The Choice of factors Orthogonal Optimization Test

In order to develop grinding agent, On the basis of the single component test, Choose triethanolamine (A), Three isopropyl alcohol amine (B), ethylene glycol (C) and sorbitol (D) 4 kinds of grinding aid as influence factors in the orthogonal experiment. The specific factors and levels as shown in table 4.

Tab.4 Orthogonal experimental factors and their levels

factors / levels	A/%	B/%	C/%	D/%
1	0.008	0.010	0.018	0.008
2	0.010	0.012	0.020	0.010
3	0.012	0.014	0.022	0.012

3.2.2 Orthogonal Test Results

According to orthogonal design of experiment to test the 1-9 set of sample for adding grinding agent, the 10th groups of blank sample without adding grinding agent, Orthogonal test table and different age compressive strength and compressive strength ratio as shown in table 5.

Tab.5 Orthogonal experimental table and results

Test no.	A(TEA)	B(TIPA)	C(EG)	D(MDBS)	compressive strength /MPa			compressive strength ratio /%		
					3d	7d	28d	3d	7d	28d
1	1(0.008)	1(0.010)	1(0.018)	1(0.008)	30.9	42.3	57.2	105.8	106.5	106.7
2	1(0.008)	2(0.012)	2(0.020)	2(0.010)	29.8	42.5	58.8	102.1	107.1	109.7
3	1(0.008)	3(0.014)	3(0.022)	3(0.012)	29.5	42.5	56.4	101.0	107.1	105.2
4	2(0.010)	1(0.010)	2(0.020)	3(0.012)	30.6	39.3	54.8	104.8	99.0	102.2
5	2(0.010)	2(0.012)	3(0.022)	1(0.008)	28.1	39.5	51.6	96.2	99.5	96.3
6	2(0.010)	3(0.014)	1(0.018)	2(0.010)	25.2	40.0	48.6	86.3	100.8	90.7
7	3(0.012)	1(0.010)	3(0.022)	2(0.010)	30.0	39.8	52.5	102.7	100.3	97.9
8	3(0.012)	2(0.012)	1(0.018)	3(0.012)	29.1	40.0	51.5	99.7	100.8	96.1
9	3(0.012)	3(0.014)	2(0.020)	1(0.008)	30.6	39.8	48.5	104.8	100.3	90.5
10	/	/	/	/	29.2	39.7	53.6	100	100	100

3.2.3 Experimental Result

This experiment use the method of range analysis, The results of the analysis as shown in table 6.

Tab.6 The range analysis results

	Sum of 3 d compressive strength of various factors and range				Sum of 7 d compressive strength of various factors and range				Sum of 28 d compressive strength of various factors and range			
	A	B	C	D	A	B	C	D	A	B	C	D
I_i	90.2	91.5	85.2	89.6	127.3	121.4	122.3	121.6	172.4	164.5	157.3	157.3
II_j	83.9	87	91	85	118.8	122	121.6	122.3	155	161.9	162.1	159.9
III_i	89.7	85.3	87.6	89.2	119.6	122.3	121.8	121.8	152.5	153.5	160.5	162.7
K_i	3	3	3	3	3	3	3	3	3	3	3	3
I_j/K_i	30.07	30.50	28.40	29.87	42.43	40.47	40.77	40.53	57.47	54.83	52.43	52.40
II_j/K_j	27.97	29.00	30.33	28.33	39.60	40.67	40.53	40.77	51.67	53.97	54.03	53.30
III_j/K_j	29.90	28.43	29.20	29.73	39.87	40.77	40.60	40.60	50.83	51.17	53.50	54.23
D_j	2.10	2.07	1.93	1.54	2.83	0.3	0.24	0.24	6.64	3.66	1.60	1.83

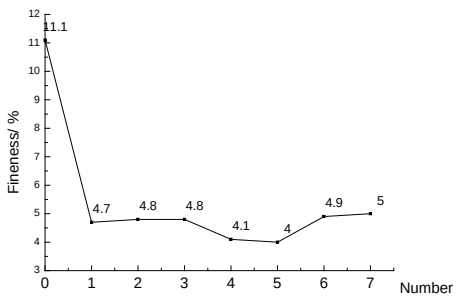
As shown in table 6, 4 kinds of single component grinding aid for 3d the factors influencing the compressive strength of the size of A > B > C > D, The 7d the factors influencing the compressive strength of the size of A > B > C =D, the 28d the factors influencing the compressive strength of the size of A > B > D > C. In range analysis, the greater of range D_j, The greater the influence of the factors on the test. In orthogonal experiment, we can clearly see that the influence of grinding aids composition in the 4 factors. Based on analyzed of test results of 3 d, 7 d, 28 d compressive strength, Finally confirmed of A dosage of 0.008%, B dosage of 0.01%, C dosage of 0.02%, D dosage of 0.01%,it is the optimal ratio of grinding components.

3.3 Effect of grinding aid of enhance component on cement performance

On the basis on confirming of grinding components of grinding aids, study the composite cement grinding aid effect on the physical properties of cement by changing different inorganic reinforced components (as shown in table 7), The various components in proportion to configure form a homogeneous solution, Content is 0.1% (according to the quality of cement). Effect of different combinations on cement fineness, specific surface area and the influence of the compressive strength is shown in figure 3, 4, 5.

Tab.7 Composite grinding aid of enhance component combination design /%

NO.	Grinding combination	Na_2SO_4	$Na_2S_2O_3$	Na_2CO_3	NaOH	other
0	/	/	/	/	/	/
1	48					52
2	48	10			10	32
3	48	20			10	22
4	48		5		10	37
5	48		10		10	32
6	48			5	10	37
7	48			10	10	32



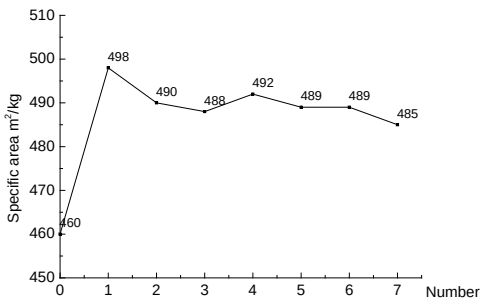


Fig.3 Effect of different combinations of cement fineness Fig.4 Effect of different combinations of specific area

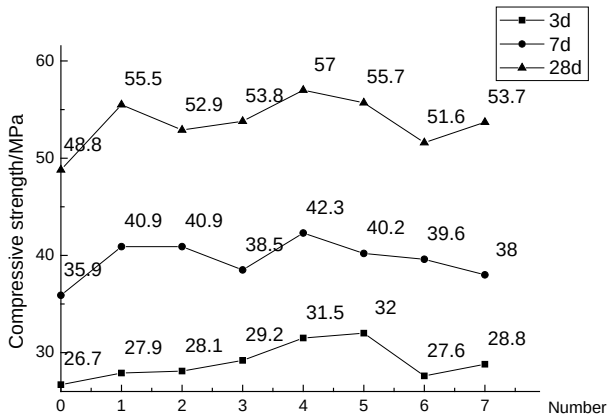


Fig.5 Effect of different combinations of cement compressive strength

From Figure 3, 4 and 5,Compared with no addition of inorganic enhancement component No.1(Sample No. 0 not included, Cement fineness and specific surface area have no significantly change. The compressive strength of cement mortar at various ages is increased, Among them, the compressive strength of the No.4 cement samples increased a lot at different ages. The analysis shows, There was no obvious change in cement fineness and specific surface area after the addition of inorganic components, The results show that the inorganic strengthening component has no significant effect on the reduction of cement fineness and the increase of specific surface area. The best combination of compound grinding aids is grinding aids.$Na_2S_2SO_3$ and NaOH. From the test results, The $Na_2S_2SO_3$ optimum dosage was 0.005%(According to cement quality), NaOH optimum dosage was 0.001%(According to cement quality),Compared with the No.0 cement samples , No. 4 cement samples make cement fineness decreased 63.1%,The compressive strength of 3d, 7d and 28d increased by 17.9%, 17.8% and 16.8%, respectively, Specific surface area increased by 10.6%.

3.4 Effect of Grinding Aids on Cement Particle Size Distribution

Through the research on the preparation of cement composite cement fineness and specific surface area and compressive strength had a good effect of grinding aids. The cement particle size distribution of No. 4 cement sample with adding cement grinding aid and No. 0 cement sample without adding cement grinding aid was tested. The results are shown in Table 8 and Figure 6.

Tab.8 Test result of two kind cement particle size distribution

Sample number	Particles size distribution of cement/%						
	<1μm	1-3μm	3-10μm	10-32μm	32-60μm	>60μm	3-32μm
0	3.45	10.43	22.59	34.94	21.44	7.15	57.53
4	4.93	13.92	26.62	37.41	16.23	0.89	64.03

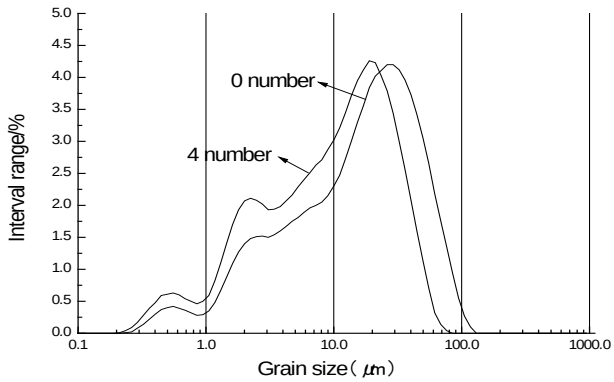


Fig.6 size distribution curve of cement

Hydration rate of cement mainly depends on the size of cement particle.. 0-10 um particle is close to full hydration at 28d; 10-32 microns particles is half hydration at 7d ; 32-60 um particle is half hydration at 28d, The particles larger than 60 m were less than half hydration even after 3 months. As can be seen from table 8 and figure 6, The size range of cement 0-10 um increased by 24.68% with the composite grinding aid, The size range of 1-3 um increased by 33.46%,The early compressive strength increased significantly. The content of cement particles is lower than 60 um, Improve the utilization ratio of cement; 3-32 um size range increased by 11.30%,Cement hydration reaction, The 28d compressive strength of cement mortar is improved, The particle size distribution of cement particles was optimized.

4. Grinding and Enhancement Mechanism

Cement grinding aid used in cement grinding process,Grinding agent in the molecular adsorption on cement particle surface[9-10], between the micro cracks,Can reduce the cement particle surface free energy, and crackle Ca-O ionic bond and covalent bond rupture after Si-O produce unsaturated charge, Stop Ca^{2+} and O^{2-} back together (theoretical model shown in figure 7), improve the dispersion of fine particles, improve the material liquid inside the mill, improve grinding efficiency. However, the molecular structure of the different grinding agent is different, it leads to the different grinding aid grinding dispersion effect., And cement in different mineral compositions during grinding with different grinding mechanism, Such as C_2S mineral need depolymerization, And mineral C_3S need crack stress corrosion crack propagation. So in the process of cement grinding, using only a molecular structure of grinding aid can appear the function is not perfect, the effect of one sector[11]. So you need to different molecular structure of grinding aid distribution in use, you will get very significant results.

Add inorganic salt and NaOH in grinding agent system can promote the precipitation of Ca^{2+} in the cement mortar system, In the system of colloidal Ca^{2+} fast saturated state, Silicate ions can produce C-S-H combined with Ca^{2+} , promote the cement hydration reaction, improve the strength of cement at early stage..

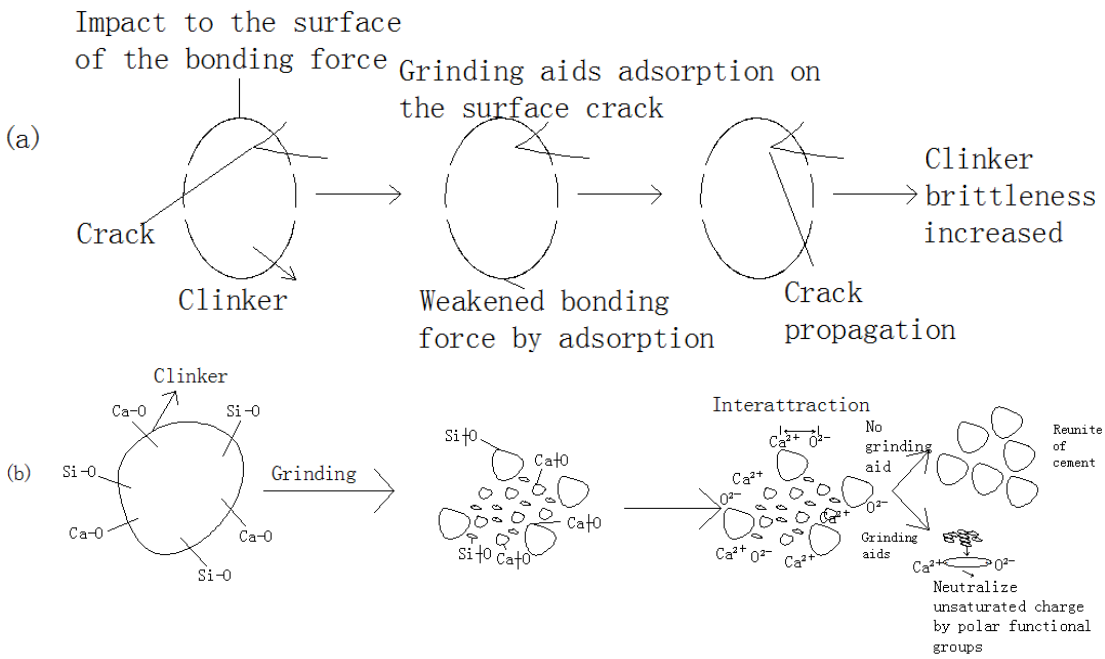


Fig.7 Grinding mechanism (a) adsorption model (b) split valence bond theory model

5. Conclusion

(1) The ratio of grinding aids was determined by experiment: TEA was 0.008%, TIPA was 0.01%, EG was0.02%, MDBS was 0.02%, $Na_2S_2O_3$ was 0.005%, NaOH was 0.01%.

(2) Compared with black sample, Development of grinding aids can reduce 63.1% cement fineness, specific surface area increased by 10.6%; cement particles ranging 3-32 μm is improved 11.3%, which optimizes the grain composition of cement.

(3) Compared with blank sample, The developed grinding aids have the effect of promoting hydration, 3d, 7d and 28d respectively are improved 17.9%, 17.8% and 16.8%, increases strength of compression cement.

References

[1] Jiang C X. Study on high performance grinding aids of cement [J].Journal of the Chinese Ceramic Society, 2001, 29(6):508-511.

[2] Gao X J,Yang Y Z,Deng H W.Utilization of beet molasses as a grinding aid in blended cements[J]. Construction and Building Materials, 2011, 25(9):3782- 3789.

[3] Shao H J, Zhang D C. Study on high performance recombination grinding aids of cement [J]. Building Materials of Shandong, 2000, (6):1-3.

[4] Wang Y P. Zhang T S, Tong G Q. Study on recombination grinding aids of cement[J].Cement, 2002,(8):8-10.

[5] Teoreanu I,Guslicoy G.Mechanisms and effects of additives from the dihydroxy- compound class on Portland cement grinding[J]. Cement and Concrete Research, 1999, 29(1):9- 15.

[6] Choi H,Lee W.Kim D U,et al. Effect of grinding aids on the grinding energy consumed during grinding of calcite in a stirred ball mill[J].Minerals Engineering,2010,23(1)54- 57.

[7] Zhao J H, Wang D M. Wang X G. Formulation Design of Grinding Aids and It is Effect on the properties of Cement [J]. Bulletin of the Chinese Ceramic Society, 2014, 33(4):724-730.

[8] Chen S L. Application Guide of Cement Grinding Aids [M]. Bei Jing, Chinese building materials industry publication.2014:200.

[9] Zhang X P, Huang C Y. The progress of cement grinding aid in China and the development tendency[J].Cement,2014,(9):17-20.

[10] Qian H, Fang Y, Li Z. The research and development situation of cement grinding aid[J]. New Chemical Materials, 2014,42(1):27-29.

[11] Jiang C H. New type of grinding aid and the process research of under the action of cement ultra-micronization model [D].Nan Jing: Phd thesis of nan jing university of technology,2001.

*Sun shaofei , Master Dergree Candidate , Mainly engaged in the research of high performance concrete.Tel:15049209157