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The efficiency analysis on assistant-grinding of lignosulfonate and its modified composites

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Abstract : The method of vibration ball milling is applied in this paper to make research on contents of lignosulfonate and modified composites as cement grinding aids; and studied on the influence of regularity about grinding aids on products fluidity, particle size, specific surface area and powder particle size distribution. The study showed lignosulfonatehas had better effect on the cement grinding function; the cement's particle size and the distribution were improved, the average diameter was decreased, distribution narrowed and ultra-fine grain size increased, of the most importance, the contents of ultra-fine grain size were increased much. Among those, the effect of calcium lignosulfonate was relatively good while its modified composites performed better.

Keywords : Cement; Grinding aids; Lignosulfonate.

INTRODUCTION

The grinding efficiency could be largely improved by cement grinding aids. Promoting the organization of cement particle size distribution and cement quality standard, reducing the cost of cement are the important research subjects in the field of Cement Science and Production Enterprise. During the production of cement, the grinding process is the most energy consuming procedure. (According to the report in America 50 billion kilowatt-hours was consumed in this field per year.) The energy usage was low. About 97% of its energy turned to be heat energy and is in vain. Only little proportion (0.6%-1%) is actually used in increasing surface energy of materials. As the development of dry production, the heat consuming is largely decreased, yet the electricity consuming has been increased. Therefore, how to raise the efficiency of grinding and reduce its electricity consuming are the focus attention for the cement workers and the important energy-saving subject. Add some grinding aids during the process of grinding is a good way to improve its efficiency. It can increase the output with the same cement fineness and the same power consumption. In addition, it can enlarge cement's specific surface area under the condition of the same cement's

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output and power consumption, as while it perfects the distribution of cement's particle size in order to improve cement's strength and quality. Therefore, the application and development of grinding aids have great influence on the cement's industry and worth to make further study.

Since 1930s, cement grinding aids had been used in cement industry[1]. After 1980s, cement additives used to improve the performance of cement's product[2], sucrose and diethylene glycol had been used as cement additives to make cement low temperature stability, waterproof, retardation and grinding aids. After that, there are a large number of patents emerging. At present, the study of grinding aids is widespread in America, Germany, France, Japan and Russia. Rules and checking methods about grinding aids have been also established in those countries. While in China, study and application of grinding aids are underdeveloped; the occupation coefficient of grinding aids is under 5%[3]. The application of lignin is in the form of lignosulfonate[4]. Lignosulfonate is a byproduct produced by the waste liquor of paper pulp after processing sulfonation and spray drying. It is widely used as a normal superplasticizer by most people. Lignosulfonate has better water-reducing property. If added in cement, it can improve its grinding effect and function as the superplasticizer.

EXPERIMENT

Raw material and regent

(1) Done-material: rotary kiln clinker in a factory, mine components in TABLE 1.
(2) Mineral waste residue: copper slag in a certain factory, the quality factor is 1.67.
(3) Gypsum: SO_3 35.48%, crystallized water 17.86%.
(4) Sodium lignosulfonate (SLSF), magnesium lignosulphonate (MLSF) and calcium lignosulfonate (CLSF) provided by Tian Jin Shengfu Jiang Chemical Industry Corp.; modified composite lignosulfonate (self-made)

TABLE 1 : The components of mine [%]

KH	SM	IM	C_3S	C_2S	C_3A	C_4AF	Σ
0.894	2.65	1.58	53.60	24.35	8.27	7.06	93.28

Experiment devices, testers and methods

(a) Experiment devices and testers

Mastersizer 2000 particle size analyzer made in Malvern Corp.; vibrating ball grinder; NRJ-411A cement glue-sand blender; SHBY-20B cement concrete maintaining standard container; the other devices in TABLE 2.

TABLE 2 : Devices used in experiment

Name	Model	Further explanation
jaw crusher		broken to the size of clinker <7[mm]
roll crusher		broken to the size of clinker <3[mm]
shaking table	GZ-85	amplitude 0.85[mm], frequency 50[HZ], vibration time 2[min]
electronic balance		maximum range 600[g], minimum range 0.01[g]
slide caliper		accuracy 0.2[mm]

(b) Analytical methods

(1) 0.08mm square hole sieve used in determination of sieve residue, dry sieve on the basis of GB45-77 Method
(2) The stop-angle was measured by methods of equal height injection
(3) Particle size analyzed by MS2000G laser particle size analyzer, results output by computers
(4) Normal consistency of cement water and setting time measured by GB1346-1999
(5) Cement glue-sand strength test by GBIT1 7671-1999

Test sample preparation

First crush particle size below 2mm by jaw crusher and roll crusher, then the gypsum and slag are sieved to 2mm sizes. The weight of the ball must be calculated according to the ratio 7:1 to decide the weight of raw material, then refer to the ratio done-material 80%: slag 15%: gypsum 5% to get the components and dilute lignosulfonate by water according to the proportion 0.2% and 0.4%. Add 0.05% modified lignosulfonategrinding aids by burette and grind 1 h by ball grinder. The weight and ratio of the ball should be remaining the same each time. LSF will be the shorten form of lignosulfonate in the following descrip-

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tion. The quantity of mixture and test sample code will be found in TABLE 3.

TABLE 3 : The quantity of mixture and test sample No.

Grinding aids	Blank	SLSF		MLSF		CLSF		modified composites of lignosulfonate		
								SLSF	MLSF	CLSF
Dosage of grinding aids[%]	—	0.2	0.4	0.2	0.4	0.2	0.4	0.05	0.05	0.05
Sample No.	A	B1	B2	C1	C2	D1	D2	E1	E2	E3

RESULTS AND DISCUSSION

Fluidity of cement

The stop-angle is the largest angle formed by free surface layer of powder accumulation in balance with the water surface. It has big influence on the fluidity of powder. The small the stop-angle is, the better powder's fluidity will be. Parameter measure: powder is piled up on the tray naturally. The intersection angle α between powder pile and the bottom of tray is called the stop-angle. It can also be realized in an easy way if there's no specialized device. Get the average value from tests more than once. See the results in TABLE 4

The results of test indicated that different types of grinding aids reduced cement's the stop-angle to 1~6°. After adding lignosulfonate grinding aids, there's no distinctive change in decreasing the stop-angle as it was added more. Big changes about MLSF can be seen in different lignosulfonate. 0.4 % reduced the cement's the stop-angle from 43° to 40.3° was reduced. The fluidity of cement became more powerful because of adding modified composites of lignosulfonate grinding aids. The stop-angle was diminished to 6°. The reason why grinding aids can smooth its fluidity could be explained as follows: when surfactant was absorbed on the surface of powder particles, hydrophilic groups directed arranged on the surface of powder particles, hydrophobic groups were facing to the air forming the surface of one molecule absorbed the thin film on powder particles. The existing of thin film reduced the direct contact area of solid powder particles and the attractive force between each powder particles. In addition, like the lubricant, it reduced friction between solid powder particles and functioned as powder smoother, as a result, the powder slipped easily and its fluidity was changed also.

TABLE 4 : Results of cement powder stop-angle

Sample No.	A	B1	B2	C1	C2	D1	D2	E1	E2	E3
The stop-angle[°]	43	42	40	41	40	41	39	37	37	37

Cement's dispersion

(a) Sieve residue

See the results of sieve residue of 0.08mm square hole sieve in TABLE 5. The cement fineness was raised after adding grinding aids. The sieve residue of 0.08mm square hole sieve was about 6.5% without any grinding aids, but after adding some grinding aids, the sieve residue reduced by 1−2.5%. As more single grinding aids increased with dosage, the sieve residue was reduced afterwards. Among those three single lignosulfonate, CLSF owned the smallest the sieve residue; the sieve residue of SLSF is as much as MLSF. Altogether, there's no big difference among these three. But modified composites of lignosulfonate grinding aids's the sieve residue is much smaller, only 1% the sieve residue, reduced by 5%. It contributed to its good grinding effect and small diameter of powder particles. The results of experiment indicated that adding grinding aids can diminish the contents of coarse particles. Nevertheless, fineness of the sieve residue only showed the contents of coarse particles, the contents of 0−30μm powder particles which affect most the strength can't be tested and the proportion between different powder particles will either be known. So the effect of grinding only could be displayed roughly.

TABLE 5 : The sieve residue of 0.08[mm] square hole sieve[%]

Sample No.	A	B1	B2	C1	C2	D1	D2	E1	E2	E3
>0.08[mm]	6.5	5.6	4.7	5.1	4.4	4.9	4.1	1.0	0.9	0.8

(b) Specific surface area

Figure 1-Figure 4 showed specific surface area of different sample after grinding 1h. From that, we can see the cement's specific surface area was increased after using some grinding aids. Grinding for 1 hour, the

specific surface area of cement was 345m^2/kg without grinding aids. The differences of specific surface area among those threelignosulfonate single grinding aids were not clear. B1, C1, D1 are about 375m^2/kg, raised by 8%; B2, C2, D2 are about 400m^2/kg, raised by 16%. Compared with single grinding aids, the specific surface area of three modified composites of lignosulfonate grinding aids was increased obviously, reached 440m^2/kg, to 30%.

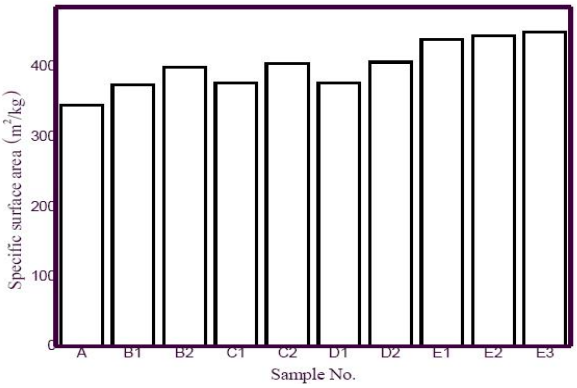

Figure 1 : Comparison of specific surface area after grinding 1h

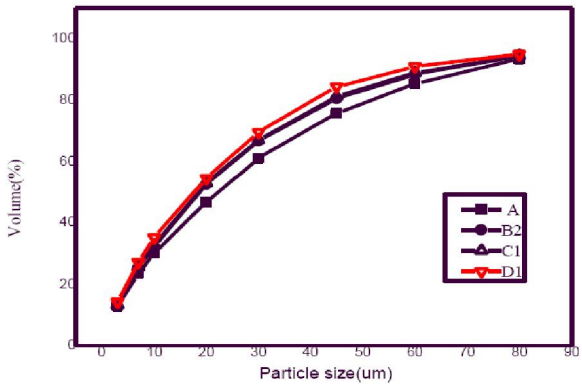

Figure 2 : The comparison of cumulative distribution of 0.2% dosage LSF

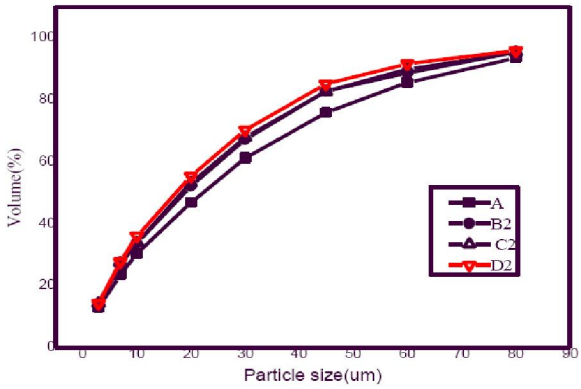

Figure 3 : The comparison of cumulative distribution of 0.4% dosage LSF

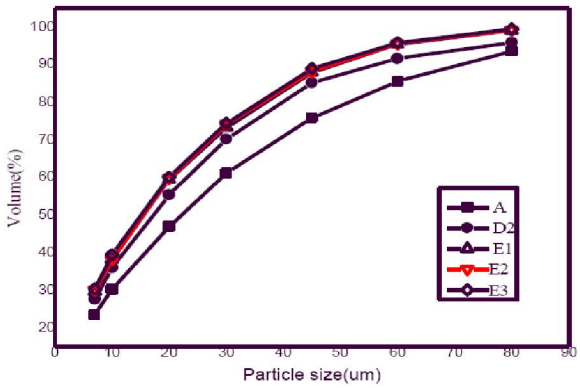

Figure 4 : The comparison of cumulative distribution of modified composites grinding aids

(c) The average diameter of cement's powder particles and its distribution

The average diameter of cement's powder particles and particle distribution were changed various after adding grinding aids. Figure 2 to Figure 4 are comparison about distribution of different LSF with diverse dosage, modified composites of lignosulfonate and particle size of blank sample. After adding grinding aids, the average diameter of powder particles (D_{50}) was decreased. Without grinding aids, D_{50} was 22.3 μm, but after adding single lignosulfonate for 0.2%, D_{50} decreased to about 19μm, and when the dosage increased to 0.4%, D_{50} reached to 18μm. However, because of using modified composites grinding aids, D_{50} decrease to 15μm. It can be showed from the distribution of powder particles, after using grinding aids, the percentage in each parts of cement was decreased. For lignosulfonate single grinding aids, cement's particle of 0.4% dosage got thinner one than that of 0.2%.

Compared with these three LSF, CLSF had better assistant-grinding performance, while no significant difference between SLSF and MLSF. The contents of powder particles 45μm for three LSF are almost the same. The main difference is about their particle size, that's 3-45μm, the cement's particle size was 3-45μm with adding 0.2% MLSF and SLSF. It occupied 67%. The percentage was 69% with 0.2% CLSF and particle size 3-45μm. With0.4% SLSF and CLSF's particle size was3-45μm. The percentage was 68%, and it was the same about dosage to be 70% CLSF. Figure 4 told that modified composites grinding aids had better grinding effect than single grinding aids. Powder particles with more than 60μm particle size was only less

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than 5%, while there was 9% of powder particles 0.4% CLSF and its particle size was 60μm. Modified composites grinding aids particle size was 3-45μm with about 74% powder particles which was 70% higher than CLSF. Modified composites grinding aids about every particle size's cumulative distribution was much higher than LSF. It illustrated that modified composites grinding aids's fine particles were more than LSF during every period of time.

CONCLUSION

lignosulfonate single grinding aids and its modified composites grinding aids can show an evident increasing fluidity of cement. The particle size of powder particles was raised to a new height, the cement's specific surface area was enlarged and especially the proportion of particle size between 3-30μm which played an important role in the strength of cement was enhanced. What's more, the cement particle size distribution of cement was improved a lot. As the increasing of dosage, lignosulfonate's grinding effect was more efficient accordingly. The best dosage was 0.3%-0.4%. Among those three lignosulfonate single grinding aids, CLSF got the best grinding effect; the grinding effect of modified composites grinding aids was better than single grinding aids. The modified composites of CLSF got the best grinding effect.

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