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PREPARATION OF CEMENT GRINDING AIDS BASED ON ALUMINA COMPOUNDS

ALUMİNA BİLEŞİKLERİ ESASLI ÇİMENTO ÖĞÜTME YARDIMCILARININ HAZIRLANMASI

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ABSTRACT

When the cement grinding is performed in the ball mill, the grinding efficiency decreases due to the aggregation of the particles by the electrostatic phenomenon. Therefore, a lot of techniques for preventing agglomeration using various grinding aids have been introduced. In this study, for mineral grinding, the grinding aid composition including a water-soluble aluminate compound and the grinding method in which this grinding aid is used were described. Grinding aids based on aluminate-based compounds not only have high grinding efficiency but are also thermally stable as they are inorganic materials. Compared with the conventional grinding aids based on organic materials such as DEG and TIPA, even if the solid content is half contained, the grinding efficiency is similar and thus the cost can be reduced to half.

Anahtar Sözcükler:
Çimento,
Öğütme yardımcısı,
Alumina bileşiği,
Elektrostatik.

ÖZ

Çimento öğütme bilyalı değirmende gerçekleştirildiğinde, öğütmenin verimliliği tanelerin elektrostatik olaylar sonucu topaklanmasıyla azalır. Bu nedenle, çeşitli öğütme yardımcıları kullanılarak aglomerasyonun önlenmesi için birçok teknik geliştirilmiştir. Bu çalışmada, mineral öğütme için, suda çözünür bir alüminat bileşiği içeren öğütme yardımcısı bileşimi ve bu öğütme yardımcısının kullanıldığı bir öğütme yöntemi açıklanmıştır. Alüminat esaslı bileşiklere dayanan öğütme yardımcıları sadece yüksek öğütme verimliliğine sahip olmakla kalmaz, aynı zamanda inorganik malzemeler oldukları için termal olarak kararlıdırlar. DEG ve TIPA gibi organik maddelere dayanan geleneksel öğütme yardımcıları ile karşılaştırıldığında, katı içerik yarıda olsa bile, öğütme verimliliği benzerdir ve bu nedenle maliyet yarıya indirilebilir.

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INTRODUCTION

In the process of finely grinding minerals such as limestone, cement, slag, and coal, a grinding aid is used to finely grind the raw material and increase the grinding productivity while suppressing the generation of static electricity. (Schneider et al., 2011; Assaad and Issa, 2014; Madlool et al., 2011; Choi et al., 2010; Ding et al., 2004). Grinding process of cement is a dry grinding process with air as medium. When grinding to certain fineness, cement fine particles have a strong tendency to agglomerate. Thus the fine particles easily mutual adhesion, and particle fracture surface easy to heal, so that the small particles will re-combine to form larger particles (Schneider et al., 2011; Imbabi et al., 2012; Sabir et al., 2011; Lee et al., 2003), which can seriously affect the grinding efficiency of cement and miniaturization of particles and particles could not be further ground. In recent years, grinding aids which are used in the cement grinding can improve the characteristics of cement particles and play a role in the dispersion grinding, then grinding aids have become an important means to improve cement grinding efficiency.

Diethylen glycol (DEG) and triisopropanol amine (TIPA), which are most commonly used as grinding aids, are excellent in terms of performance, but even if they have heat resistance of 180ºC or higher. If the friction heat rises instantaneously, there is a problem by which they can be deformed. When grinding, there is a burden to control the frictional heat so that it does not rise above a certain level, but there is also a problem that the production cost increases to a high price (Kucharczyk et al., 2015; Altun et al., 2015; Toprak et al., 2014; Sverak et al., 2013; Teoreanu and Guslicov, 1999; Gao et al., 2011).

Typically, water soluble inorganic compounds have been used only as chemical admixtures for concrete, and in particular, aluminate compounds have been used as hardeners for concrete. Hardeners are compounds used to promote the coagulation of cement for the purpose of increasing the initial strength. In this paper, we have been applied the aluminate compound, a water-soluble inorganic mixture used only as a chemical mixture for concrete, to a grinding aid for the fine grinding of minerals such as limestone, coal, slag, clinker, silica. Inorganic grinding materials compared to organic grinding materials such as DEG and TIPA, they are thermally stable, and cost is not expensive. In addition, the purpose of the present research is to provide a fine grinding aid for grinding minerals by using water-soluble inorganic compounds and organic compounds together.

1. MATERIALS AND METHODS

Cement clinker and gypsum are provided from a cement plant in ChangChun city of China. Table 1 shows the chemical composition of clinker and gypsum used in the experiment.

1.1. Preparation of Grinding Aids Based on Aluminate Compounds

1.1.1. Preparation of Sodium Aluminate

20 g of aluminum hydroxide and 22 g of sodium hydroxide were added to 58 g of water, mixed, and heated at 80-100 ºC while stirring to proceed with the reaction. When the reaction solution becomes almost transparent, the reaction is terminated to obtain a 42% aqueous solution of sodium- aluminate (NaAlu). The 42% aqueous solution is further diluted by water to obtain a 30% aqueous solution.

1.1.2. Preparation of Potassium Aluminate

20 g of aluminum hydroxide and 31 g of calcium hydroxide are mixed with 49 g of water and heated to 80-100 ºC while stirring to proceed with

Table 1. Chemical composition of clinker and gypsum

Material	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %
Clinker	21.11	4.88	3.97	64.24	1.15	1.61	0.88	0.23
Gypsum	0.79	0.16	0.19	31.45	0.11	44.22	0.02	0.06

the reaction. When the reaction solution became almost transparent, the reaction was terminated to obtain a 51% aqueous solution of Potassium aluminate (KAlu), followed by dilution with water to obtain a 40% aqueous solution. Again, dilute it with water to form a 30% aqueous solution.

1.1.3. Preparation of NaAlu/GMP and NaAlu/SG

GMP: (2-[(2,3-dihydroxypropoxy)carbonyl]

benzoic acid), purity: 99%

SG: Sodium Gluconate, purity: 99%

Mix evenly at a ratio of NaAlu: GMP = 1: 1 and NaAlu: SG = 1: 1 and stir evenly at 60 ºC using a magnetic stirrer.

1.1.4. Manufacture of Composites of NaAlu and Amine Compounds

A1: N,N-bis(2-hydroxypropl)ethanolamine]

A2:[N,N-bis(2-hydroxyethyl)amino-2-propanol]

A3: [N-Methyl diethanolamine]

purity: 99%

NaAlu and A1, A2, and A3 were mixed at a ratio of 1: 1, respectively, and stirred evenly at 60 ºC using a magnetic stirrer.

1.2. Experimental Methods

Grinding conditions are given in Table 2. Cement is sieved by 0.9 mm square mesh sieve after grinding, and then the characteristics of cement particles group are tested. The test method can be described as follows:

- Cement sieve measured in accordance with GB1345-91,
- Cement particle size distribution used the JL-1166 laser particle size analyzer,
- According to the GB/T 8074-2008, the cement specific surface area was determined using the Blaine air permeability method,
- Strength of cement mortar were measured in accordance with GB/T17671-1999,
- Scanning Electron Microscope (SEM) images tested by German Zeiss LEO- 1450 scanning electron microscope shot.

Table 2. Pilot plant grinding conditions

Parameter	Unit	Value
Mill	Speed (rpm)	55
	Temperature (˚C)	~ 90
Grinding media (balls)	Diameter (mm)	15 – 32
	Ball-filling volume fraction (%)	~ 5
	Balls/material ratio (w/w)	9
	Mass (kg)	36
Material (CK + Gyp + grinding aid)	Mass of CK + Gyp (kg)	4
	Ultrafine CK addition (kg)	0.38
	Feed sizes of CK+Gyp (mm)	≤10
	Grinding aid dosage (ppm)	1000
Grinding process	Grinding time (min)	60
	Sampling time (min)	15

2. RESULTS AND DISCUSSION

2.1 Effect of Grinding Aids on the Particle Size Distribution of Cement Particles

As shown in Table 3, the content of 3-32 μm particles of grinding cement with grinding aids (DEG, TIPA, NaAlu, KAlu) is 6.63%, 5.75%, 4%, 3.33% more than blank cement, 3-32 μm particles play an important role in cement strength.

Table 3. Particle size distribution of cement powder

Sample	Particles size distribution of cement, %				D50 (Median diameter) / μm
	≤3 μm	3-32 μm	32-65 μm	≥65 μm	
Blank	4.17	60.23	32.82	2.78	24.23
With DEG	3.03	66.86	29.05	1.06	22.48
With TIPA	2.87	65.98	29.01	2.14	22.98
With NaAlu	3.82	64.23	30.91	1.04	23.08
With KAlu	3.95	63.56	31.05	1.44	23.76

The median diameter of cement particles is less than the blank. So the results show that cement particles are effectively refined after adding grinding aids in the grinding process, and the particle size distribution become narrow by reducing over-grinding of cement and the content of large-size particles of cement, especially the particles concentrate in the range of 3-32 μm, so grinding aids play an optimal role on particle size distribution.

2.2. Effect of Grinding Aids on Blaine Fineness of Cement

It can be seen from Figure 1 that the specific surface area of sample with grinding aids is larger than blank sample. In addition, it can be found from Figure 1 that Blaine fineness of the cement with grinding aids at the grinding time for 30 min and the blank cement without grinding aids are respectively close at the grinding time for 45 min. Blaine fineness of the cement with grinding aids at the grinding time for 45 minutes also respectively reach to the level of blank cement. It also shows that the grinding aids added in the grinding process of cement can reduce the grinding time and power consumption for grinding and improve efficiency of grinding. In addition, it can be seen that the grinding aid NaAlu shows better grinding efficiency than KAlu.

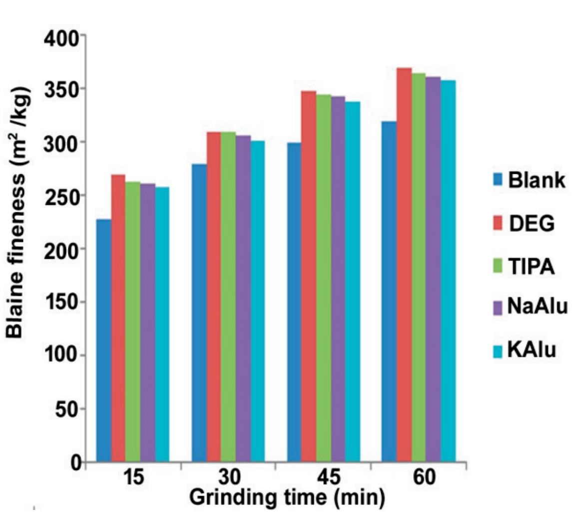


Figure 1. Effect of grinding aids on Blaine fineness of cement

As shown in Figure 2, it can be seen that the specific surface area of the cement powder with the addition of NaAlu/GMP and NaAlu/ SG is much higher than with the addition of GMP and SG alone. At the same time while lowering the manufacturing cost of the grinding aids, it is possible to increase productivity by accelerating the grinding time.

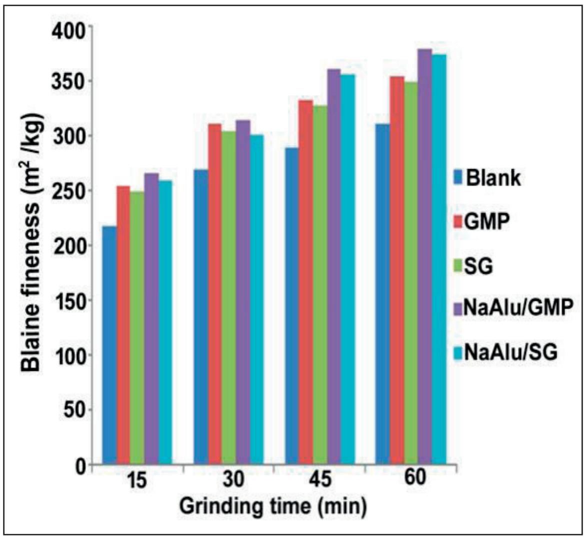


Figure 2. Effect of grinding aids on Blaine fineness of cement

2.3. Effect of Grinding Aids on Compressive Strength of Cement

As shown in Figure 3, the three-days strength and the 28-days strength of the cement with NaAlu / GMP and NaAlu / SG were 1.2~1.5 MPa and 2.6~3.1 MPa respectively, compared to the compressive strength of the cement with GMP and SG. This is because aluminate-based grinding aids not only increase the grinding efficiency, but also promote the cement hydration reaction.

SEM images of hydration products for cement paste at 3 and 28 days are shown in Figure 4 and Figure 5, respectively.

It can be seen from Figure 4 that hydration product structure of blank cement at 3 days is relatively loose and has more pores.

Amorphous C-S-H gel is unevenly distributed in hydration structure and a small amount of layered $Ca(OH)_2$ is fuzzy visible. Although hydration product structure of cement with NaAlu/GMP at 3 days also is relatively loose, its structure has more hydration product, and C-S-H gel and $Ca(OH)_2$ in hydration structure overlap with each other to form a more stable microstructure. It can be seen from Figure 5 that hydration products of blank cement at 28 days have a large number of flocculent amorphous C-S-H gel, the morphology of which has been unable to identify, and the structure is relatively dense. The hydration of cement paste with NaAlu/GMP is more thoroughly and paste structure is filled fully with hydration product. The cement stone, pore of which is very few, is formed integrally, and then the structure of hydration product is firm. The uniformity and compactness of structure is ideal and there is almost no weak link. This is because the alumina compound not only enhances the grinding effect but also promotes the hydration reaction of the cement.

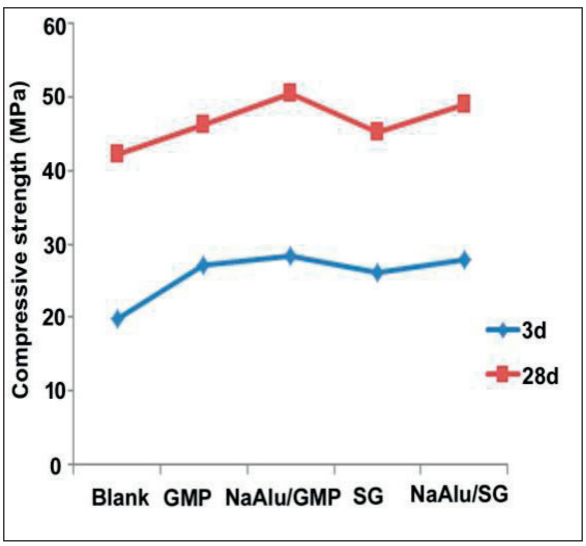
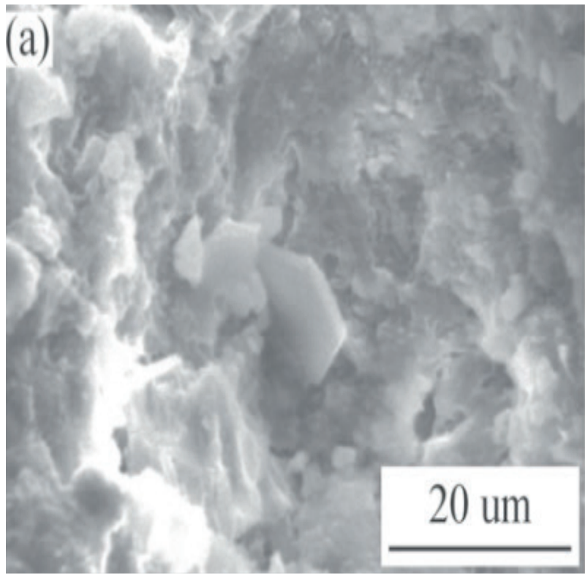


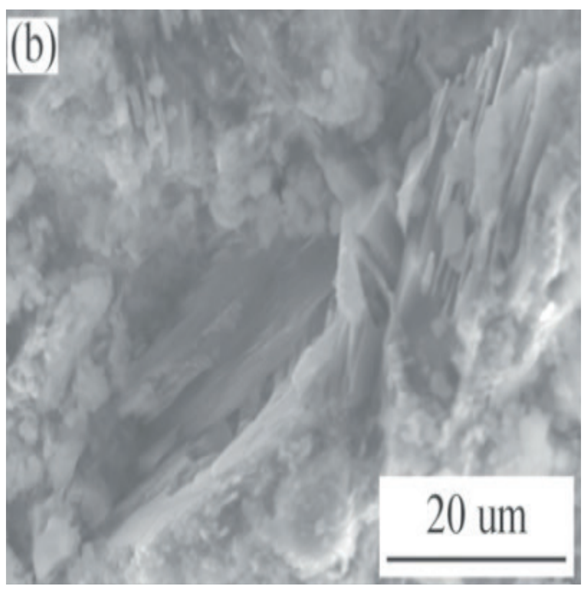
Figure 3. Compressive strength according to different grinding aids

In order to confirm the effect of the grinding aid composition prepared from the alumina compound on the amine compound, a typical amine compound grinding aid was tested. As comparative grinding aids, [N, N-bis (2-hydrox-ypropyl) ethanolamine], [N, N-bis (2-hydroxyethy-l) amino-2-propanol] and [N-methyl diethanol amine] were used. 40% aqueous solution of NaAlu was mixed with A1, A2 and A3 in a weight ratio of 1: 1.

As shown in Table 4, even when used alone, A1, A2, and A3 showed excellent grinding efficiency compared to DEG. However, when mixed with sodium aluminate (NaAlu), even when the amount used was 50%, the grinding efficiency was similar to that of DEG. Sodium aluminate is economical because the raw material cost or production cost is much less than the amine compound and the grinding time is short to improve productivity.

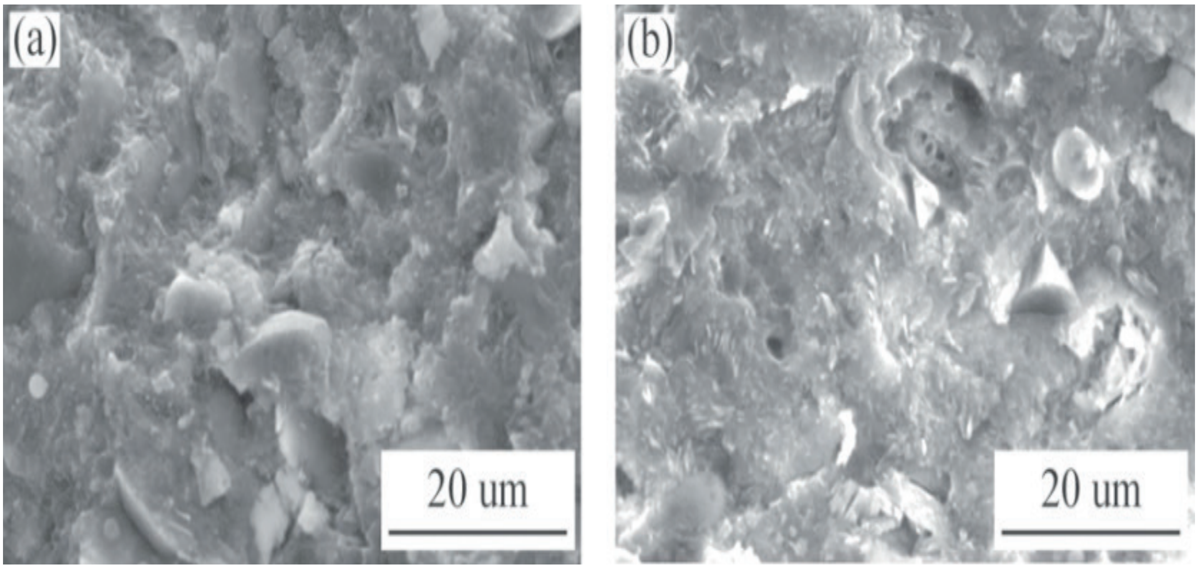


(a) Blank sample



(b) Sample with NaAlu/GMP

Figure 4. SEM images of hydration product of cement paste at 3 days



(a) Blank sample (b) Sample with NaAlu/GMP

Figure 5. SEM images of hydration product of cement paste at 28 days

Table 4. Effect of grinding aids based on alumina compounds on amine compounds

Grinding aids	Rate (%)	Grinding Time (min)	Blaine Fineness (m^2/kg)	Emission (kg)
DEG	100	42	343.2	3.9
A1	100	41	354.7	4.2
A2	100	40	350.8	3.9
A3	100	40	359.2	4.2
NaAlu/A1	50/50	39	341.2	3.9
NaAlu/A2	50/50	40	342.5	3.9
NaAlu/A3	50/50	38	342.9	3.9

CONCLUSION

The process of NaAlu, KNaAlu grinding aids can effectively reduce the sieve margin of particles and grinding time of cement. Then the fluidity of powder and specific surface area of particles are also improved. Grinding aids play an optimal role on cement particles size distribution by improving the particles content in the range of 3-32 μm particle size.

Compared to GMP and SG grinding aids were used alone, the grinding aid made by NaAlu/GMP, NaAlu/SG not only had a good grinding effect but also improved the hydration characteristics of the cement.

Though the alumina compound and the amine grinding aids are mixed in a 1: 1 ratio, the grinding efficiency does not decrease, and the cost can be reduced to 1/2.

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