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# Cement grinding aid based on glycerol-waste antifreeze

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**Abstract.** Grinding aids to increase grinding efficiency in cement production are materials that can produce large amounts of high-quality cement in a short time by reducing surface energy by preventing particle agglomeration and improving fluidity. In the paper, a grinding aid using glycerol-waste antifreeze (GAP) was prepared and its effect on the grinding properties of clinker was investigated in contrast to that without the grinding aid. The results are as follows: The angle of repose of the cement powder added with GAP decreased as the grinding time increased (decreases by 3.8 when the grinding time was 60 minutes), indicating that it increased the flowability of the powder. On the contrary, when GAP was added, the residual amount of 45 µm sieve was also significantly reduced (4.6 % decrease) and the specific surface area increased (30.5 $m^2$/kg), which resulted in an increase in the grinding efficiency. The zeta potential of the cement powder is greatly reduced, which lowers the surface tension of the cement particles. In the size range of 3 to 32 µm, it increases the particle content, makes the particle size distribution uniform, the 7d and 28d activity index of the powder is improved by 5 % and 6 %, respectively, and increases the compressive strength of the cement. In addition, it was confirmed that the performance of the TEA grinding aid and the grinding aid were similar, and were very effective in terms of economy.

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## 1. *Introduction*

Antifreeze is used for the purpose of preventing freezing of cooling water for water-cooled internal combustion engines and preventing corrosion of various devices in internal combustion engines, and its main components are monoethylene glycol or propylene glycol. The antifreeze that is discarded after use is referred to as the waste antifreeze solution. When waste antifreeze solution is treated with waste water, the chemical oxygen demand (COD) reaches about 460.000 ppm, which is equivalent to 10.000 times the discharge standard of normal waste water, so it is impossible to treat waste water. Not only is it expensive to incinerate waste liquid, but it also causes secondary air pollution during incineration.

Cement is one of the most used building materials in our lives, but during its production it consumes a lot of energy and emits carbon dioxide. Clinker baked in a cement kiln is mixed with gypsum and pulverized into powder in a ball mill to make cement. In the production of cement, the amount of energy consumed by the grinding process is almost 50 % of the previous process. When grinding the clinker powder in the ball mill, the cement grinding efficiency decreases due to cohesion between the particles, and it also negatively affects the strength of the cement [1–3].

To solve this problem, a cement grinding aid is added. The grinding aid is adsorbed between the fine cracks of the particles and provides ions or molecules in the functional stage, thereby balancing or shielding the unsaturated charges of the crack part, preventing the surface from being healed, and allowing the crack to expand more easily. In addition, molecules of the grinding aid are adsorbed on the surface of the cement particles to form an adsorption film, thereby reducing the free energy and interfacial tension of the powder surface. This prevents the particles from agglomerating with each other and acts as a dispersion, preventing them from becoming too fine. Therefore, it improves the grinding efficiency and reduces the energy consumption applied in the grinding process [4–10].

Amines such as triethylenetetramine, aminalols such as diethanolamine, glycol compounds such as ethylene glycol, phenol, and phenol derivatives, and also many more complex compounds were used as grinding aids [11–15]. Sohoni et al. reported that grinding aids such as triethanolamine, mono and diethylene glycol, oleic acid, sodium oleate, sulfite waste liquor and dodecylbenzene sulfonic acid have very good effects in grinding limestone and clinker [16]. Jeknavorian and others had identified phenol, 5-glycol, and alkanolamine compounds in cement with the test technique they found [17]. Hasegawa conducted research on grinding aids for use in ultra-fine grinding of limestone, asserting that alcohol and glycol promote ultra-fine grinding of limestone, and that the maximum specific surface area of limestone obtained as an additive is proportional to the amount of additive [18]. Zhenping Su et al conducted an experiment to use glycerol as a grinding aid, and the results showed that GL-C has good compatibility with PCE when the dosage of GL does not exceed 0.02 % [19]. In addition, many researchers have conducted studies on glycerin-based grinding aids and published experimental results for rational addition amounts and grinding properties [20–28]. However, the above-mentioned grinding aids have good grinding effects, but are expensive, so they have limitations in industrial applications.

The aim of the study is to prepare a glycerol-waste antifreeze-based cement grinding aid (GAP) and examine its effect on the grinding properties of the cement powder as compared to the case where a grinding aid is not added to verify its effectiveness.

Objectives:

- Examine the effect of GAP on the angle of repose of the powder and verify the effectiveness of the grinding aid on the flowability of the powder;
- Investigate the effect on the specific surface area and grain size distribution of cement powder;
- Investigate the effect on the surface tension of the powder, the activity index, and the strength of the cement mortar;
- Verifies the effectiveness in contrast to the commonly used TEA grinding aid.

# *2. Materials and Methods*

## *2.1. Materials*

Table 1 shows the chemical composition of clinker and gypsum used in the experiment.

***Table 1. Chemical composition of clinker (by mass)(%).***

| Constituent | Content: mass % |
|---|---|
| Calcium oxide (CaO) | 64.24 |
| Silicon dioxide ($SiO_2$) | 21.11 |
| Iron oxide ($Fe_2O_3$) | 3.97 |
| Aluminium oxide ($Al_2O_3$) | 4.88 |
| Magnesium oxide (MgO) | 1.15 |
| Sulfur trioxide ($SO_3$) | 1.61 |
| R2O (K2O + $Na_2O$) | 1.11 |
| Tricalcium silicate ($C_3S$) | 50.6 |
| Dicalcium silicate ($C_2S$) | 24.6 |
| Tricalcium aluminate ($C_3A$) | 6.8 |
| Tetracalcium aluminoferrite ($C_4AF$) | 9.4 |

## 2.2. Experiment Method

### 2.2.1 Preparation Method of grinding aid GAP

At room temperature, 100 g of waste antifreeze (45 % of antifreeze + 55 % of water), 65 g of glycerin, 5 g of urea, and 55 g of phosphoric acid are added in a mixing container equipped with a stirrer. This solution is stirred evenly for 1 h to make a grinding aid GAP.

### 2.2.2 Test Methods

A mixture of clinker and gypsum (clinker: gypsum = 95: 5) is grinded in the ball mill so that the particle size is < 5 mm. 0.02 % (mass ratio) of grinding aid is added to this mixture and fed to the ball mill (φ600 × φ600). Samples are collected and analyzed at various grinding times. In the experiment, each experimental groups are measured 5 times, and the average value is used as the actual measurement value.

1. The angle of repose is tested according to GB/T11986-1989. After the powder is poured into the funnel, the sample from the funnel is coated the disk under the funnel. At this time, the height h of the powder layer and the radius R of the disk are measured and obtained according to the formula of the powder ($\tan\theta = h / R$).

2. Zeta potential of cement is measured by the zeta potential instrument by the electrophoresis method, and the suspension liquid is prepared by stirring cement and water for 1-3 min.

3. Cement fineness is measured in accordance with GB1345-91.

4. Cement surface area is measured using automatic analyzer of the FBT-5 surface of cement.

5. Cement particle size distribution is tested the JL-1166 laser particle size analyzer determination.

6. SEM images is tested by German Zeiss LEO-1450 scanning electron microscope shot.

7. Strength of cement mortar is measured in accordance with GB/T17671-1999 strength.

8. The activity index of powder in blended cement is measured according to the GB/T 18046-2008.

Then the activity index of cement powder is determined from:

$$A_7 = \left(R_7 / R_{07}\right) \times 100, \quad A_{28} = \left(R_{28} / R_{028}\right) \times 100,$$

where $A_7$ and $A_{28}$ are the activity index of powder at 7 days, and 28 days, respectively, (%); $R_7$ and $R_{28}$ are the 7d and 28d compressive strength of cement mortar, respectively, (MPa); and $R_{07}$ and $R_{028}$ are the 7d and 28d compressive strength of the pure cement mortar, respectively, (MPa).

# 3. Results and Discussion

## 3.1. Effect of Grinding Aids on the Fluidity of Cement Powder

The angle of repose is a factor that reflects the friction characteristics between the powder particles and characterizes the flow properties of the cement powder [4, 6]. In other words, a large angle of repose means that the fluidity of the powder is deteriorated.

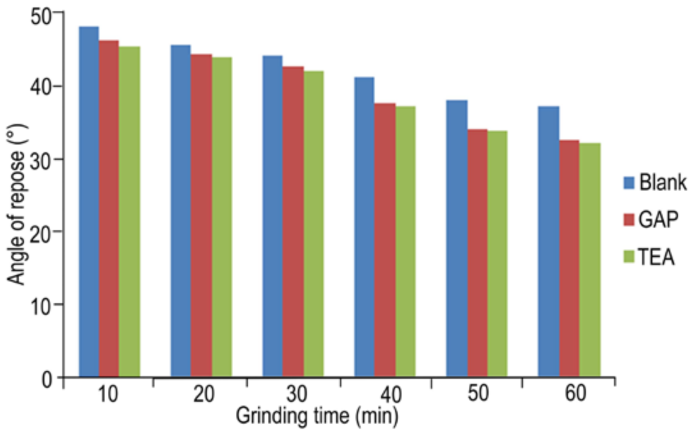



**Figure 1. Effect of GAP on the repose angle of ground powder.**

As shown in Fig. 1, as the grinding time increases, the repose angle of GAP and TEA tend to decrease compared to Blank. In particular, when the grinding time was 60 min, the repose angle of GAP and TEA decreased by 3.8° and 4.0°, respectively, compared to Blank. This is because the polishing aid adsorbed on the surface of the cement particles forms a single-molecule adsorption layer to reduce the contact area and surface agglomeration between the particles, thereby facilitating sliding between cement powders. Therefore, the flowability of the cement is increased and the grinding efficiency is increased.

### *3.2. Effect of Grinding Aids on the Fineness of Cement*

In general, as the pulverization time increases, agglomeration between the cement powders occurs violently, which greatly reduces the specific surface area of the powder [5, 8, 10].

As shown in Fig. 2, as the grinding time increases, the Blaine specific surface area of GAP and TEA significantly increase compared to the blank. This is because the grinding aid prevented agglomeration between the cement particles and increased the fluidity.

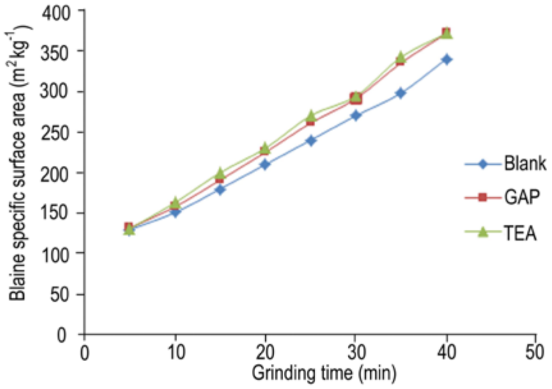



**Figure 2. Effect of grinding aid on Blaine specific surface area.**

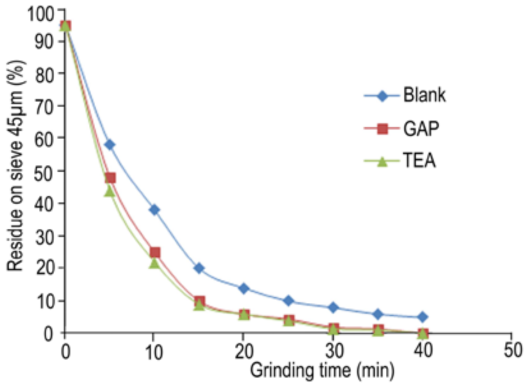



**Figure 3. The effect of grinding aids on 45 µm sieve.**

Fig. 3 shows the effect of grinding aid on a 45 µm sieve. As can be seen from the figure, as the grinding time increases, the residual amounts of GAP and TEA tend to be significantly less than that of Blank. This shows that the grinding aid has improved the grinding properties of the cement powder.

### *3.3. Effect of grinding aid on the particle size distribution of cement powder*

Generally, 3–32 µm particles which play a major role in increasing the strength of cement are the optimum particle size distribution of cement [17–19].

As shown in Fig. 4, the volume of 3 to 32 µm particulates in the GAP and TEA samples is greater than that of the blank sample. This shows that the grinding aid narrows the particle size distribution by reducing the content of excessive fine particles and large particles. Therefore, it is shown that the grinding aid plays a role in rational control of the particle size distribution.

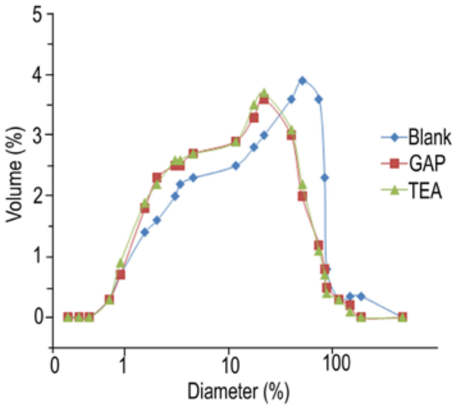
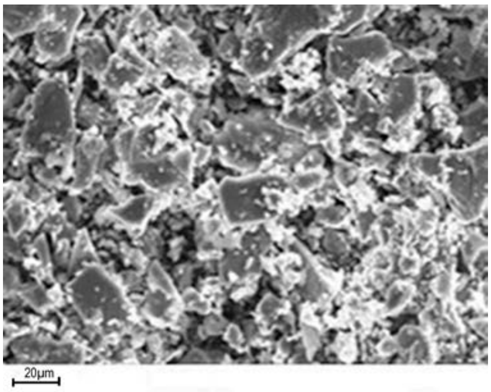
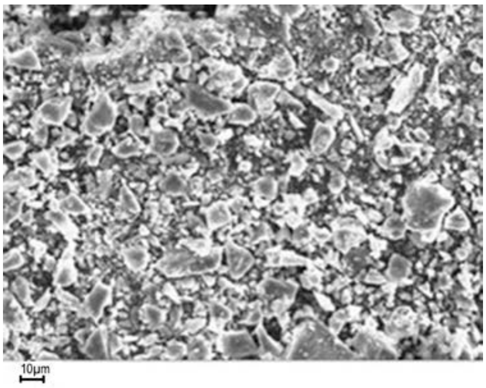



**Figure 4. Particle size distribution of cement powder.**

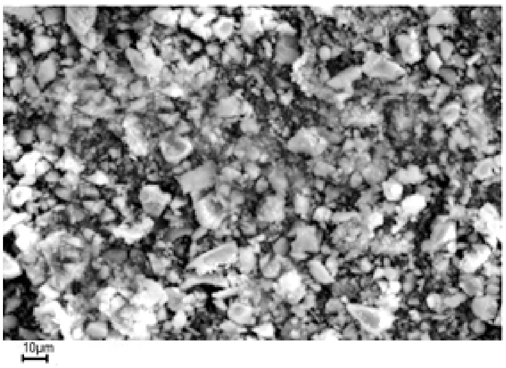
As can be seen in Fig. 5, there are many coarse grains (more than 20 µm in diameter) in the blank. With the addition of grinding aids, the particle size is relatively uniform and almost less than 10 µm.

Therefore, it was confirmed that the GAP and TEA grinding aid has a good effect on suppressing the agglomeration of the cement powder after grinding and making the grain size distribution even.




**a) Blank** **b) With GAP**



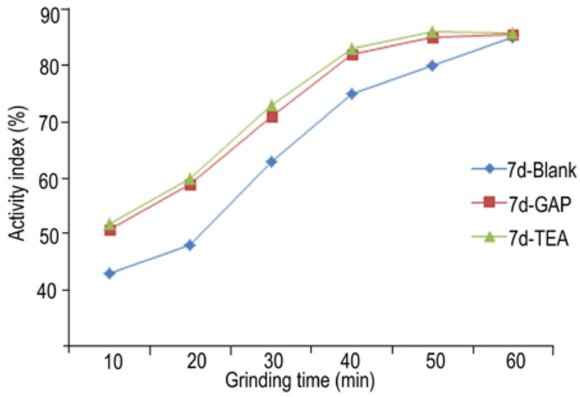

**c) With TEA**

**Figure 5. SEM images of the particles distribution of ground cement.**

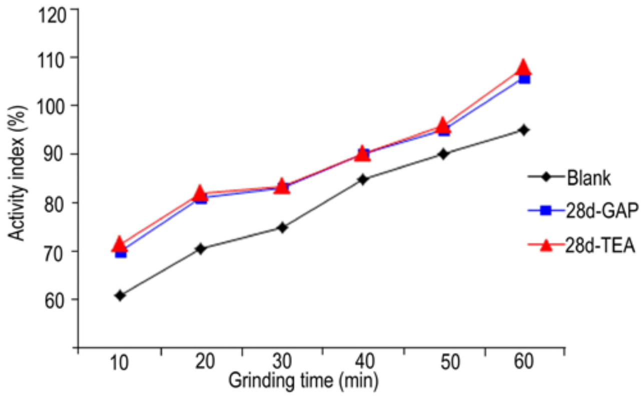
## *3.4. Effect of grinding aid on the activity index of cement powder*

The activity index is a characteristic index that defines the hydration activity of cement [12–15].

As shown Fig. 6, the activity index of the powder is improved by GAP compared to the Blank sample during the same grinding time. With the increasing of grinding time, the improvement of GAP on the 7d activity index of cement powder gradually becomes weak, while for 28d, the improvement gradually intensifies. This is because the initial activity of the powder is low, so when the particle size decreases to some extent, the initial active growth of the powder is in equilibrium. As the curing time increases, the activity increases thereafter, and as the powder particle size decreases, the increase in the activity index becomes more pronounced. During 50 minutes of grinding time, the 7d and 28d activity index of the powder is improved by 5 % and 6 %, respectively. It can be seen that the GAP grinding aid has a good effect on improving the hydration activity of the cement powder.




**(a)**




**(b)**

**Figure 6. Effect of GAP on the activity index of cement powder.**

## *3.5. Analysis of zeta potential of cement*

Zeta potential is commonly used to characterize the adsorption properties of chemical mixtures.

When the grinding aid is adsorbed on the cement particles, the electric charge distribution on the surface of the particles is changed [20–28]. Therefore, the change in zeta potential can reflect the adsorption characteristics of the grinding aid on the surface of the cement particles. The effect of grinding aids on the zeta potential of cement is shown in Table 2. As can be seen in Table 2, the absolute value of the zeta potential for cement with GAP and TEA is significantly reduced compared to blank cements. In other words, it shows that the negative charge on the surface of the cement particles containing the polishing aid is reduced. This may be because GAP is easily adsorbed to the particle surface by functional groups (hydroxyl groups) and positively charged hydrophobic alkyl chains neutralize the charged portion of the cement particles.

***Table 2. Surface tension and Zeta potential of cement powder.***

| Sample | Dosages of grinding aids / % | Zeta potential / mV |
|---|---|---|
| Blank | | –10.68 |
| With GAP | 0.02 | –6.07 |
| With TEA | 0.02 | –6.01 |

## *3.6. Effect of grinding aid on the compressive strength of cement*

According to the literature [6–10], the hydration reaction of cement is highly dependent on the size of the cement powder. Fig.7 shows the effect of grinding aid on the compressive strength of cement mortar samples. As shown in the figure, the 7d intensity and 28d intensity of GAP and TEA tended to be significantly higher than that of Blank. This can be attributed to the fact that the grain size was reduced to some extent by the grinding aid, and as a result, the cement hydration reaction was promoted.

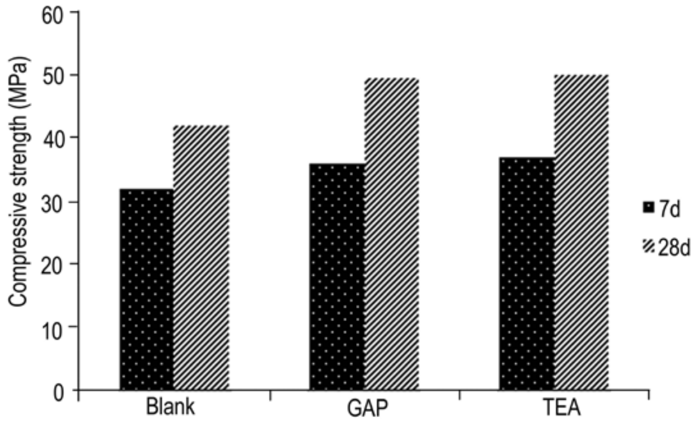



**Figure 7. The impact of grinding aids on compressive strength of cement mortar.**

### *3.7. Performance comparison of GAP and TEA*

The most commonly used cement grinding aid is TEA (triethanolamine), and its effectiveness is very good, but it is expensive, so it is limited in industrial introduction [1–3] Table 3 shows the effect of the prepared GAP grinding aid and the most commonly used TEA grinding aid on the grinding performance and hydration properties of the cement powder. Compared to the blank, when GAP and TEA were added, the sieve residue of the pulverized powder decreased by 4.6 % and 5.2 %, and the specific surface areas increased by 30.5 $m^2$/kg and 33.7 $m^2$/kg, respectively. In addition, the particle content in the range of less than 32 μm was improved by 7.94 % and 9.03 %, respectively, by Blank. The results show that the grinding aid effects of GAP and TEA are almost similar. After all, compared to TEA, GAP shows that the grinding aid effect is not bad. On the other hand, GAP costs only 15/1 compared to TEA. Therefore, the use of GAP as a grinding aid provides a number of economic benefits.

***Table 3. Particle characteristics and hydration activity of cement powder with different grinding aids.***

| Type of grinding aids | Sieve residue (%) | Specific surface area ($m^2$/g) | Particle size distribution (%) | | | Activity index (%) | |
|---|---|---|---|---|---|---|---|
| | | | ≤ 32 μm | 32-65 μm | ≥ 65 μm | 7d | 28d |
| Blank | 12.7 | 340.5 | 75.18 | 16.24 | 8.58 | 76 | 85 |
| GAP | 8.1 | 371.0 | 83.12 | 11.82 | 5.06 | 81 | 91 |
| TEA | 7.5 | 374.2 | 84.21 | 10.62 | 5.17 | 82 | 91 |

## *4. Conclusions*

By studying the influence of expanded perlite cement grinding aid (GAP) prepared from Glycerol, Waste Antifreeze on the grinding performance and physical properties of cement, we can get the following conclusions:

1. Angle of repose for cement was reduced for the same grinding time for the specimens with the addition of the GAP grinding aid, compared to Blank. Therefore, the fluidity of the cement powder is greatly improved.

2. The sieve residue of the pulverized powder decreased by 4.6 % and the specific surface area increased by 30.5 $m^2$/kg. This shows that the manufactured GAP increases the grinding efficiency of the cement powder.

3. The particle size distribution of the cement powder was more uniform than that of the Blank, and the use of the grinding aid GAP increased the content of fine particles in the range of 3 ~ 32 μm compared to the Blank.

4. GAP grinding aid has a good effect on improving the hydration activity of cement powder and increases the compressive strength of cement mortar.

5. The effectiveness of the grinding aid of GAP is similar to that of TEA and is very economical in terms of cost.

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