

EFFECTIVENESS OF TRIETHANOLAMINE ON GRINDABILITY AND PROPERTIES OF PORTLAND CEMENT IN LABORATORY BALL AND VIBRATING DISK MILLS

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The aim of the present research work is to evaluate the effectiveness of one of the industrially most popular grinding aids (triethanolamine, TEA) on grindability, set and strength behavior of Portland cement in laboratory ball and vibrating disk mills when added at the same amount of 0.06 % by the weight of the cement. The results show that TEA is more effective in ball mill than in vibrating disk mill. It increases the Blaine specific surface area of the mixtures of 95 % clinker and 5 % gypsum by 16 and 7.6 % in ball and vibrating disk mills, respectively, compared to the blank test. The cement samples produced from the two mills were then tested for their initial and final setting times, spread diameter as a consistency measure and compressive strengths after 3, 7 and 28 days of curing. In both mills, addition of TEA increases both initial and final setting times and decreases compressive strengths at 3-, 7- and 28-day curing ages. The effects, however, are more significant in ball mill compared to vibrating disk mill.

INTRODUCTION

The world cement production has been increasing constantly since the early 1950s, especially in developing countries [1]. The Portland cement industry consumes large amounts of energy [2] and a considerable part of this energy (almost 40 % of total electrical energy) is consumed for clinker grinding [3]. This refers to an average specific power consumption of 27 to 43 kWh per ton depending on the mill technology [4]. In cement mill, the cement particles can coat the grinding media, seal the armour plating and agglomerate and form small plates which absorb the impact. The cement particle agglomeration reduces the efficiency of the mill. This phenomenon is characterized by an increase in energy consumption whilst maintaining constant Blaine fineness [5]. The aggregation process essentially depends on clinker nature (chemical composition, crystalline structure), dispersion state of the cement, mill type and grinding system (kinetic energy of the grinding media and their distribution), and the atmosphere within the mill [6, 7]. Grinding aids are the most common types of cement additives widely used to encounter these operational problems, and might consist of glycols, alkanolamines,

aliphatic amines such as triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and phenolic-type compounds. In addition, there are more complex compounds such as aminoethylethanolamine (AEEA) and hydroxyethyl diethylenetriamine (HEDETA) that have been used at low dosage (0.01 - 0.1 % in weight) in order to reduce the energy cost since 1930 [5, 6, 8-10]. Their influence on cement chemico-physical behaviour has been attributed to the reduction of surface energy forces generated on cement grains during comminution and limitation or diminution of ground solid mass aggregation and adhesion effects [5, 7, 11].

The literature on grinding aids and their effects on cement properties is significant. For example, for triethanolamine (TEA) as the most popular grinding aid in cement industry, it has been known that the exact action on cement pastes is very complex and depending on the type of cement and the amount of TEA, it behaves differently. An addition of 0.02 % of TEA to Portland cement, acts as a set accelerator, at 0.25 % it acts as a mild set retarder, at 0.5 % TEA acts as a severe retarder, and at 1 % it behaves as a very strong accelerator [5, 12, 13]. A literature survey, however, shows that no effort has been devoted to the effect of mill type and grinding

mechanism. The very common technology for cement grinding operation at both laboratory and industrial scale is ball mill that is a slow running technique requiring relatively long operating times to achieve the desirable fineness [14]. In contrary, there exist technologies based on fast running technique using relatively high kinetic energy of the grinding media to achieve the desired fineness in a comparatively shorter operating time. An example is vibrating disk mill which is widely used at laboratory scale [15].

All previous studies for the evaluation of grinding aids were performed using laboratory ball mills [4-6]. This work, however, tends to investigate the effectiveness of triethanolamine (TEA) on grindability and properties of Portland cement using the two most common laboratory-scale grinding technologies, i.e. ball and vibrating disk mills. The results of such a comparative study, not only confirm the significant effect brought about by the mill type or the grinding technology, but also clears the uncertainty if ball mills can be replaced with vibrating disk mill for saving time in such laboratory studies.

EXPERIMENTAL

Materials

A relatively fine and dusty Portland cement clinker of type II (in accordance with ASTM standards) was selected as reference. Chemical composition of clinker, expressed in element oxides, is shown in Table 1. Table 2 shows the Bogue's potential phase composition of the clinker. The fineness or dusty form of the clinker helps to reduce the testing time. Figure 1 shows the particle size distribution of the clinker measured with sieve analysis.

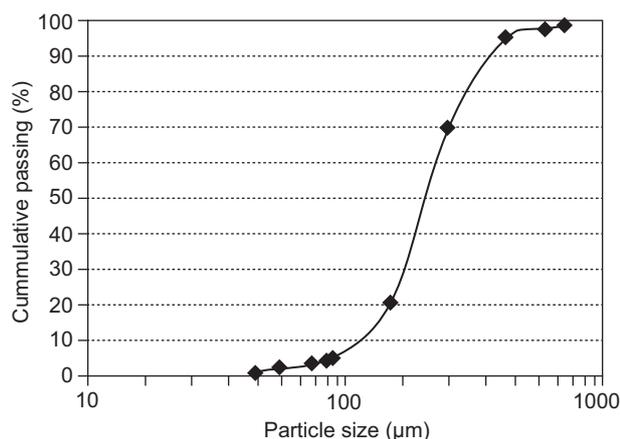


Figure 1. Particle size distribution of type II Portland cement clinker.

Table 2. Bogue's potential phase composition of type II Portland cement clinker.

Phase	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
% weight	50.6	24.6	6.8	9.4

Natural gypsum of more than 98 % purity with a particle size less than 420 µm was also prepared and used. Due to significant cost differences, industrial TEA with a density of 1.124 g/cm³ and a purity of 99 % was prepared and used instead of laboratory grade. For a better distribution of grinding aid with clinker, the weighed amount of TEA was mixed with water at 1:1 ratio prior to the addition. It must be noted that conventionally water itself is believed to be a decent grinding aid [11].

Methods

A laboratory ball mill of 19 cm diameter and 20 cm length was used. 30 % of its volume was filled with steel balls of different sizes ranging from 2.0 to 4.0 cm and almost one-third of its volume was filled with cement (2000 g clinker and gypsum in each experiment). The vibrating disk mill was a Retsch RS 200 model with a continuously adjustable speed of 700 – 1500 min⁻¹ at 50 Hz and a grinding jar size of 250 ml. The clinker samples with gypsum were firstly ground in both mills in the absence of TEA. It almost took 20 h and 30 min for the samples to attain the same Blaine specific surface areas, i.e. 3300 cm²/g, in ball and vibrating disk mills, respectively. In the next step, the same samples (clinker with gypsum) were ground in the presence of TEA for 20 h and 30 min in the ball and vibrating disk mills, respectively. The dosage of TEA has been considered constant at 0.06 % by weight of samples that is within the normal dosages (ranging from 0.04 % to 0.07 %) that are currently being used in cement industry. During the grinding operations, sampling was performed from both mills at different time intervals. The samples were taken after 4, 6, 8, 10, 12, 14, 16, 18, 20 h and 4, 6, 9, 12, 15, 20, 25, 30 min from ball and vibrating disk mills, respectively. The Blaine specific surface areas of the samples were determined using an air-permeability apparatus in accordance with ASTM C204 standard. The fineness of the samples was also determined as the mass percent retained on sieve by simply screening a 2 g sample of ground substance on a standard sieve of 45 µm opening size in accordance with ASTM C430-96 standard. The results of the fineness measurements were compared for evaluating the effect of TEA on clinker grindability and its performance in the two mills.

Table 1. Chemical composition of type II Portland cement clinker.

Oxides	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	Free lime	LOI
% weight	63.02	21.89	4.56	3.10	3.88	0.25	0.51	0.21	0.46	0.25

The produced cement samples were then studied for their properties. The required amount of water for paste normal consistency and the paste spread diameter were determined in accordance with ASTM C187 and ASTM C230 standards, respectively. The produced samples were also characterized by measuring their setting times and compressive strengths. Initial and final setting times were determined using Vicat needle test according to ASTM C191 standard. For compressive strength measurements, fresh pastes of normal consistency were thoroughly mixed in a planetary mixer for 5 minutes and then cast into $2 \times 2 \times 2 \text{ cm}^3$ molds. The molds were stored at an atmosphere of more than 95 % relative humidity at 25°C for the first day and then the specimens were cured in lime-saturated water at 25°C until the time of testing.

RESULTS AND DISCUSSION

Effect of TEA on Blaine specific surface area

Fineness is an important quality parameter for cements that significantly influences the rate of hydration and hence the rate of gain of strength, especially at early ages, and also the rate of evolution of heat. Cement manufacturers control this quality parameter by measuring both Blaine specific surface area and residue on sieve. Figures 2 and 3 show the effect of TEA on Blaine specific surface area of samples versus grinding time in vibrating disk and ball mills, respectively. The results indicate that Blaine specific surface area of cement increases with addition of TEA. The general trends of changes in Blaine specific surface area are the same in both mills. The important difference, however, lies in the values of Blaine specific surface areas of the corresponding blank and TEA-incorporating samples. In vibrating disk mill, the differences between the corresponding values are quite less confirming a significantly lower effectiveness for vibrating disk mill than ball mill. This is mainly due to differences in the grinding mechanisms in the two

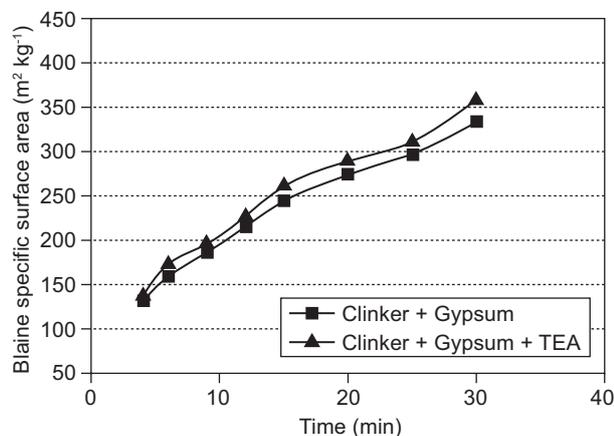


Figure 2. Variations of Blaine specific surface area versus grinding time in vibrating disk mill.

mills. In the case of ball mill, slow grinding over quite longer time periods (40 times longer) provides enough time for effective distribution of grinding aid molecules on particles of the samples being ground. This effective distribution of grinding aid considerably enhances the effectiveness of TEA in ball mill compared to vibrating disk mill.

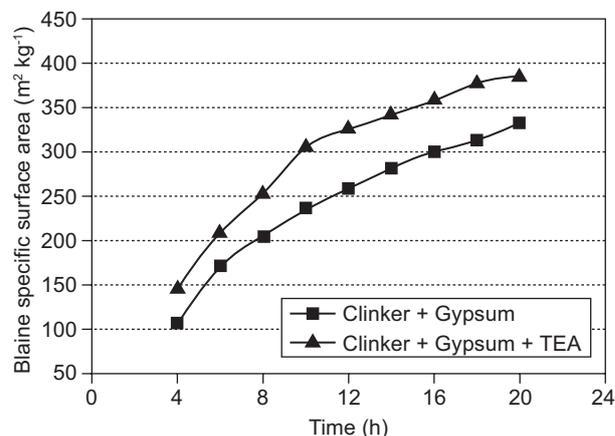


Figure 3. Variations of Blaine specific surface area versus grinding time in ball mill.

Figure 4 compares the effect of TEA on the Blaine specific surface area of the final samples. As seen, with respect to the blank samples, TEA increases the Blaine specific surface area of the samples by 16 and 7.6 % in ball and vibrating disk mills, respectively.

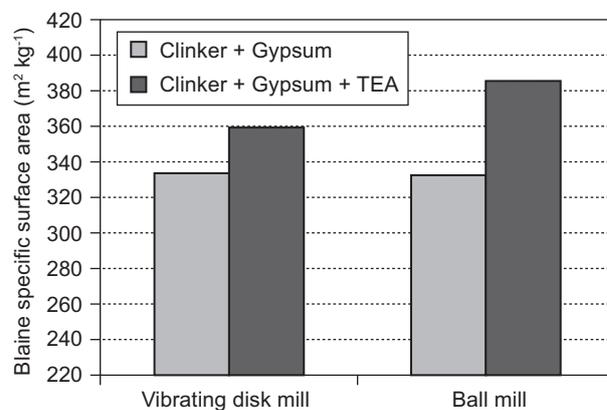


Figure 4. Effectiveness of TEA on Blaine specific surface area in ball and vibrating disk mills.

Effect of TEA on the amount of residue on sieve

Figures 5 and 6 show the effect of TEA on the amount of residue on 45 μm sieve of the samples versus grinding time in vibrating disk and ball mills, respectively. The general trends of the changes in the residue on sieve is the same for both mills. The important difference, however, lies in the values of the residue on the sieve of the

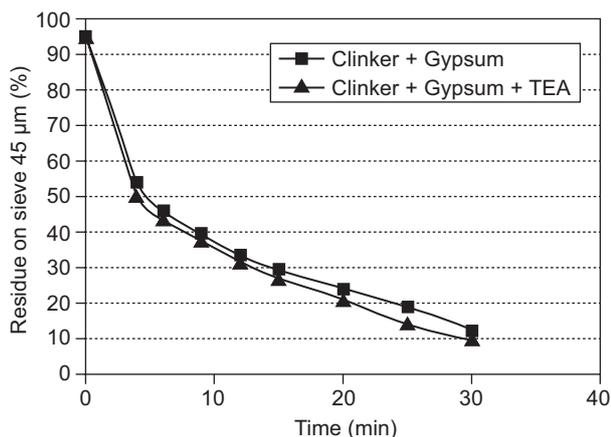


Figure 5. Variations of residue on 45 µm sieve versus grinding time in vibrating disk mill.

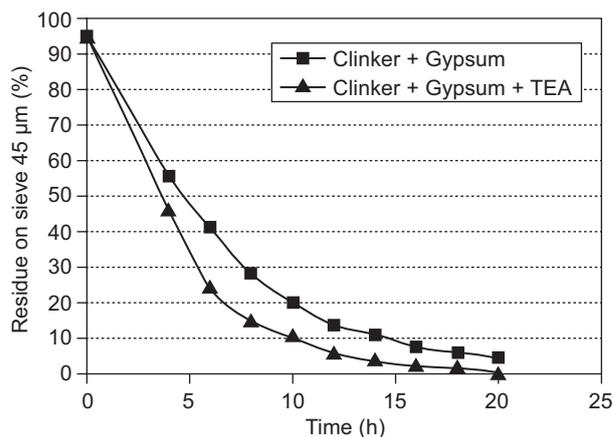


Figure 6. Variations of residue on 45 µm sieve versus grinding time in ball mill.

corresponding blank and TEA-incorporating samples. As seen, in vibrating disk mill, the presence of TEA only slightly decreases the amount of coarse fraction greater than 45 µm, whereas in the ball mill the effect is considerable resulting in quite lower coarse fraction. The results therefore again clearly confirm a stronger effect for TEA in ball mill compared to vibrating disk mill. The differences in both Blaine specific surface area and residue on sieve confirm the difference between the particle size distribution of the cement samples ground in the two mills. These differences along with the chemical effects brought about by the presence of TEA may significantly affect the main engineering properties of the produced cements.

Effects of TEA on main engineering properties of cement

Setting times describe the stiffening behavior of the cement paste. The results of setting time measurements for produced cement samples with and without TEA in ball and vibrating disk mills are given in Table 2. At an addition rate of 0.06 %, TEA increases both initial and final setting times in both mills. Samples with higher Blaine specific surface area have more reaction surface; thus if TEA didn't have any effect on cement hydration, setting times would reduce instead of increasing. The increase in both initial and final setting times with the addition of TEA in both mills, therefore, confirm a retardation effect for TEA at this level of addition. In a

previous study [16], it is claimed that TEA can drastically alter the setting characteristics of Portland cement paste by providing retardation effect. As seen, the retardation effect of TEA is more pronounced in ball mill than in vibrating disk mill. Experimental results given in table 2 show that initial setting time has increased by 53 and 13 % and final setting time by 29 and 10 % in ball and vibrating disk mills, respectively. This again confirms that TEA in ball mill is more effective than in vibrating disk mill due to the grinding mechanism of the ball mill, which provides enough time for effective distribution of TEA.

Water consistency refers to the relative mobility of a freshly mixed cement paste or mortar or its ability to flow. Figure 7 shows the values of spread diameter for the produced cement samples measured at the same w/c ratio of 0.26. Blaine specific surface area of the samples in m²/kg were also written above each column. V and B are related to the samples ground in vibrating disk and ball mills, respectively. The spread diameter that is a measure of flowability is connected with the size and shape of cement particles, which are always agglomerated in water suspensions. At constant w/c ratio, this can lead to a viscosity increase by an apparent particle volume increase. In fact, a part of water is trapped in the porosity of the particles and does not contribute to the flowability. The interesting point in the experimental results is the relatively higher values of spread diameter for cement samples produced in ball mill. As seen, the cement sample produced in ball mill

Table 3. Initial and final setting times of cement samples.

Cement samples	Blaine specific surface area (m ² /kg)	Initial setting times (min)	Final setting times (min)
Blank- Vibrating disk mill	334	230	418
Blank- Ball mill	333	178	333
TEA 0.06 %- Vibrating disk mill	359	262	462
TEA 0.06 % - Ball mill	386	274	430

in the absence of TEA exhibits a significantly higher spread diameter compared to the corresponding cement sample produced in vibrating disk mill. Also, the cement sample produced in ball mill in the presence of TEA, in spite of its higher Blaine specific surface area, shows a considerably higher spread diameter compared to the corresponding cement sample produced in vibrating disk mill. The differences between the vibrating disk and the ball mills in terms of grinding mechanism and grinding time, therefore, can significantly affect the rheological properties of the produced cements. In addition, cement samples produced in vibrating disk mill with and without TEA show the same value of spread diameter. Neglecting the effects due to relatively small difference between their Blaine specific surface areas, this shows that the presence of TEA does not significantly affect the rheological properties of the cement produced in vibrating disk mill.

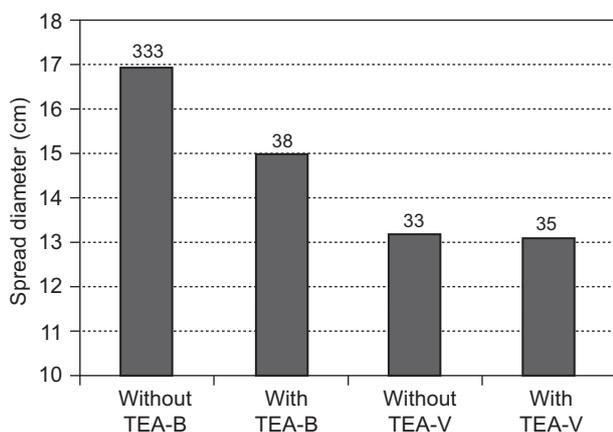


Figure 7. The effect of TEA on spread diameter ($w/C = 0.26$).

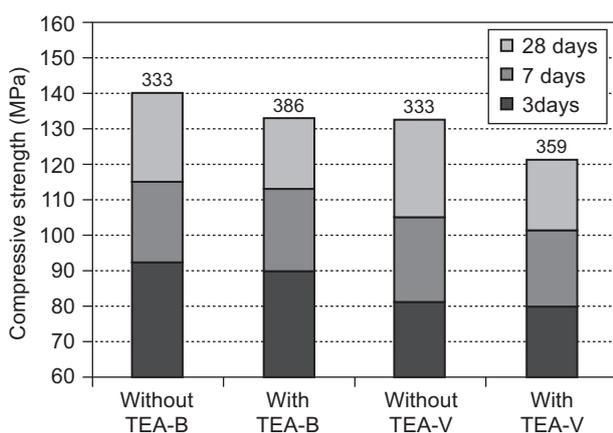


Figure 8. The effect of TEA on compressive strength ($w/C = 0.26$).

The produced cement samples were also tested for their compressive strengths at the same w/c ratio of 0.26 after 3, 7 and 28 days of curing. The obtained

results are represented graphically in Figure 8. Blaine specific surface area of the samples in m^2/kg were also written above each column. V and B are again related to the samples ground in vibrating disk and ball mills, respectively. As seen, in the absence of TEA, the cement sample produced in ball mill exhibits the highest 3-, 7- and 28-day compressive strengths. In the presence of TEA, compressive strengths at all the three curing ages decrease, in spite of the significant increase achieved in Blaine specific surface area. The same behaviour is seen for the samples produced in vibrating disk mill. These small losses in compressive strengths can be attributed to the retardation effect of TEA on hydration reactions. Similar results have also been reported by others [16, 17]. Ramachandran et al [16] claimed that in portland cement paste, TEA decreased the strength at all ages, especially at higher TEA contents.

CONCLUSIONS

Experimental results confirm that TEA as a grinding aid is considerably more effective in ball mill than in vibrating disk mill when added at the same amount of 0.06 % by the weight of the cement. It increases the Blaine specific surface area of the mixtures of 95 % clinker and 5 % gypsum by 16 and 7.6 % in ball and vibrating disk mills, respectively, compared to the blank test. In both ball and vibrating disk mills, addition of TEA increases both initial and final setting times and decreases compressive strengths at 3-, 7- and 28-day curing ages. The effects, however, are more significant in ball mill compared to vibrating disk mill. This is mainly due to differences in the grinding mechanisms in the two mills. In the case of ball mill, slow grinding over quite longer time periods (40 times longer) provides enough time for effective distribution of grinding aid molecules on particles of the samples being ground. This effective distribution of grinding aid considerably enhances the effectiveness of TEA in ball mill compared to vibrating disk mill.

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