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Effects of various grinding aids dosage on comminution efficiency and cement characteristics

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Abstract

Grinding aids are materials that are added to cement mixtures to improve the characteristics of the cement or increase the efficiency of the milling systems or both in the clinker grinding (finish grinding) stage. In this study, the effects of four grinding aids (Triisopropanolamine based (TIPA), Triethanolamine based (TEA), Hydroxylamine based (HA), and Calcium nitrate based (CN) grinding aids) in the clinker grinding process were evaluated on the essential characteristics of the produced cement: namely specific surface area (Blaine number), compressive strength of concrete, and the comminution efficiency-retention time (energy saving) at four different dosage levels. In the first step, the grinding time required to reach the Blaine number of the investigated Cement type (S-OPC: Studied Ordinary Portland Cement) was obtained as 69.75 minutes by kinetic grinding tests. Afterward, 17 laboratory-scale grinding tests were performed utilizing S-OPC cement and four grinding aids at four different doses of 0.02%, 0.05%, 0.08% and 0.11 %. The results indicated that the TIPA-0.11 (Triisopropylamine compound at a dosage level of 0.11%), with a Blaine value of 4069 cm^2/g, and grinding efficiency of 19%, had the most significant effect on the fineness and comminution efficiency. Furthermore, the concrete samples produced from all the grinding aids were tested for their compressive strength at 2, 7, and 28 days. The results showed that compared to control samples, the highest growth of compressive strength were on day 2 and 7 for TIPA-0.11 samples with values of 37.08% and 32.44%, respectively. Meanwhile, the highest increase of compressive strength was after 28 days for TIPA-0.11 samples with a 22.14% increase.

Keywords:
grinding aids; comminution efficiency; Blaine number; compressive strength; cement; concrete

1. Introduction

Cement production is one of the most energy-consuming industries in the world, and in many parts of the world, 50 to 60% of the direct costs of cement production are related to energy costs (**Wang et al., 2009**). Theoretically, at least 1.6 GJ (gigajoules) of heat is required to produce each ton of clinker (**Liu et al., 1995**), but, in practice, the specific energy consumption for factories with modern furnaces is about 2.95 GJ per ton, and in some countries, this figure even reaches 5 GJ per ton (**Khurana et al., 2002**). Also, about 110 to 120 kWh of electricity is consumed to produce each ton of cement (**Alsop, 2007**). **Figure 1** shows the share of energy consumed by each production process of a cement plant.

The clinker grinding or finish grinding stage is the last and most energy-consuming stage of cement production which consumes about 40% of the total energy required to produce one ton of cement. At this stage, the raw materials heated in the cement kiln are ground together with additives such as gypsum in the cement ball mill or tube mill to obtain the final product, which is cement. The purpose of clinker grinding is to achieve a certain amount of fineness in the final product that can provide its desired properties such as hydration rate, compressive strength and water content. A low amount of grinding causes the production of coarser-grained cement than the desired one, and as a result of the cement hydration, the setting time and final concrete strength will be affected. On the other hand, over-grinding will yield fine-grained cement, which will lead to a very rapid setting and possibly incorrect setting of concrete, an increase in the rate of hydration and the rate of heat release, and faster decay of air-exposed concrete. Also, the grinding of smaller particles becomes more complex. This process is associated with higher energy consumption, which leads to increased comminution costs as well as environmental pollution (**Pitt and Wadsworth, 1981**). In order to control quality in the cement industry, it is

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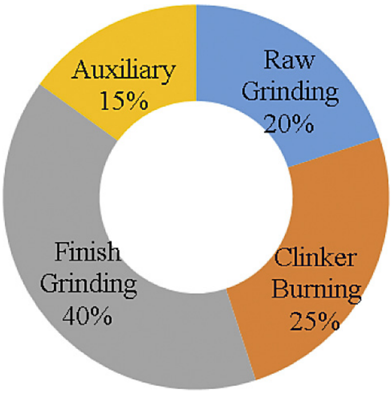

Figure 1: Share of energy consumption of different units of a cement factory (**Khurana et al., 2002**)

necessary to determine the particle size distribution of the product. It is also helpful in predicting cement behaviour in concrete. The retained material percentage on a given sieve is usually utilized in the cement industry. Since the particle size distribution measurement of cement is a problematic and costly practice, another parameter called "cement softness" or "specific surface area" or "Blaine number" is usually utilized (**Mehta and Monteir, 2017**). It is concluded that when comparing the comminution efficiency of several samples, utilizing an index number is more practical than a wide range of dimensions.

The fineness of powdered material, such as cement, as determined by the Blaine apparatus; is usually expressed as a surface area in square centimetres per gram. This parameter is measured using the permeability or air permeability method (**ASTM, 2011; ASTM C150/C150M, 2018**). The basis of this device is the suction of a certain amount of air through a polished surface of cement with a specific porosity. The number and size of the holes depend on the particle size and the intensity of the flow through the surface. Blaine number is imperative in the production and application stages of cement. In order to achieve the desired conditions, the particle surface has a crucial role in the efficiency of physicochemical reactions between cement ingredients, water, and the environment. The importance of this parameter is that the initial reaction rate of cement with water (concrete formation) in the first 24 hours is directly related to the specific surface area, which is also related to the rate of hydration, and due to this matter, fine-grained cement will increase the initial strength of cement and produce heat much faster than coarse-grained cement. In the cement industry, the effect of the Blaine number can be examined from two perspectives:

i) comminution in which the goal is to increase the efficiency of the comminution system due to energy savings or increase mill discharge for the desired Blaine number of the plant;

ii) concrete properties made of the desired cement in which properties such as compressive strength, tensile strength, and setting time are considered.

In many dry mineral comminution industries, some liquid chemicals are added to the milling process to increase milling capacity, reduce specific energy consumption, or increase the fineness of the product. In some cases, these additives are used to facilitate the material transfer or increase some of the product characteristics, such as compressive strength and the setting time of cement (**Lai et al., 2013; Toprak et al., 2014**). Extensive research on the application of additive chemicals, chemical fibres, and mineral additives such as amines, ethylenes, glycols, pozzolans, pumice, and silicates have been conducted to improve the properties of cement and concrete (**Mardulier, 1961; Locher and Seebach, 1972; Scheibe et al., 1974; Sohoni et al., 1991; Mishra and Zurich, 2014; Altun et al., 2015; Oksuzoglu and Ucurum, 2016; Prziwara et al., 2018; Toprak et al., 2018**).

A particular type of these additives is grinding aids. These materials have a significant impact on the quality and final properties of the produced cement and improve the efficiency of the comminution system of cement plants (**Lai et al., 2013; Toprak et al., 2014**). Therefore, the effects of additives in the cement industry can be examined in two separate sections: the first part is related to the stages of cement production, and the second is related to cement application. The primary purpose of using the additives, as grinding aids, is to reduce the specific energy consumption (energy consumed per unit weight) in cement production. This can be achieved using two ways by:

i) increasing the amount of grinding (generation of finer-grained- products) with a fixed flow rate and power;

ii) reducing the milling power by keeping the mill grinding and flow rate constant.

In addition, additives are more important from the standpoint of improving the physicochemical and mechanical properties of the produced concrete, such as compressive strength, tensile strength, and setting time. Since the addition of some chemicals in the production stage can affect the properties of the produced concrete, the effects of the additive in the production-consumption stage should be studied and evaluated simultaneously. Given the importance of these two perspectives in the production and consumption of cement, the need to create an optimal economic point (energy savings or increase the mill discharge) - consumption (estimation of the desired properties of concrete) is imperative.

Despite many studies and research on the benefits of the application of grinding aids and chemical additives in laboratory and industrial scale studies, it is not yet fully understood how the components of commercial grinding aids affect different product characteristics (**Toprak et al., 2014; Prziwara and Kwade, 2020**). Due to this, a thorough understanding of the mechanisms and reactions between the surfaces of particles and grinding aid's molecules has not been established. For this reason, the results of the application of these materials are in the form of case studies (**Hosseinzadeh Ghare-**

hgheshlagh et al., 2021). As a result, various types of research have reported different results and interpretations for similar grinding aids. Therefore, the diversity of the materials used and their different effects have hindered the development of a comprehensive understanding and approach (**Sverak et al., 2013; Hosseinzadeh Gharehgheshlagh et al., 2021**). In general, the impact of grinding aids on the cement industry can be summarized as follows:

i) Reducing van der Waals forces due to the addition of grinding aids increases the fluidity of solids, which also directly affects the retention time of materials inside the mill (**Mardulier, 1961**).

ii) Grinding aids affect the particle fracture process by reducing van der Waals forces (**Locher and Von Seebach, 1972**).

iii) Naturalization of particle surfaces reduces the tendency to agglomerate, making bulk material more fluid and easier to transport inside the mill (**Klimpel and Manfroy, 1978**).

iv) Cement grinding processes are performed in dry mills. The most critical problem is the tendency of fine particles to agglomerate. This phenomenon can be overcome by using grinding aids (**Austin et al., 1984; Toprak and Benzer, 2019**).

v) By adding grinding aids (GAs) to the mill feed, they can increase the system's capacity at constant product fineness or increase the fineness at constant capacity (**Toprak and Benzer, 2019**).

vi) Grinding aids reduce the coating on the mill shell, especially when grinding clinker and limestone, and provide stable operating conditions and therefore reduce the tendency of agglomeration (**Scheible et al., 1974; Sohoni et al., 1991**).

vii) Grinding aids reduce the agglomeration energy, which is inversely proportional to the comminution efficiency (**Weibel and Mishra, 2014**).

viii) the use of a grinding aid reduces the surface energy of limestone. Due to the reduction of surface energy, the agglomeration size (size of aggregation of fine particles and formation of a larger particle) decreases, and this also increases the fluidity of the powder (ground material) (**Sohoni et al., 1991; Prziwara et al., 2018**);

ix) The utilization of grinding aids reduces the specific energy consumption (**Oksuzoglu and Ucurum, 2016; Toprak et al., 2018; Prziwara et al., 2018**).

x) Toprak et al. used three different doses of an amine based grinding aid in a cement milling closed circuit to investigate its effect on material retention time in a mill and the efficiency of the milling circuit. This research showed that using these grinding aids increases the fluidity and transfer of materials. Therefore, the retention time of materials inside the mill is reduced. Consequently, more acceptable sized products are produced with a fixed energy consumption (**Toprak and Benzer, 2019**).

xi) He et al. showed that the use of TEA and PCE base grinding aids reduces the retention time of materials in the cement mill. The use of a PCE-based grinding aid produces a cement with lower water demand, higher fluidity, and higher mechanical strength (**He et al., 2021**).

xii) Ethylene glycol, propylene glycol, triethanolamine, oleic acid, and amino acetate are among the most critical grinding aids used in cement grinding (**Toprak et al., 2014**).

The final stage of cement grinding accounts for about 20 to 30% of the operating costs of cement production, so optimizing this stage by considering the desired quality of concrete will have a significant impact on the cost of cement production. Therefore, the objectives of this study are to investigate the combination of optimal cement grinding and the compressive strength of concrete as an indicator of cement quality utilizing grinding aids available in the market. In this research, the effect of four types of grinding aids (amine – based, nitrate, elemental calcium) at four different dosage levels on three fundamental properties of cement, namely the specific surface area (Blaine number) of the produced cement, compressive strength of the produced concrete and energy saving in the comminution process of clinkers have been evaluated. For this purpose, after industrial sampling and preparation of the samples, kinetic grinding on the reference sample (without a grinding aid) was conducted to obtain the optimal grinding time (t) required to reach the desired Blaine number of the plant. By preparing the ground samples and according to the weight values of the sample – grinding aid, comminution tests with designated grinding time (t) were performed on all raw and grinding aid – containing samples, and therefore, their Blaine number was determined. Subsequently, the grinding efficiency or energy-saving value for different types of grinding aids was calculated. Finally, the standard compressive strength test was performed on concrete samples obtained from all cement samples, and the effect of the type and amount of grinding aid used on the resulting concrete was investigated. In the previous study (**Hosseinzadeh Gharehgheshlagh et al., 2021**), a preliminary examination was made on the same cement using three different doses. The obtained results showed that a more comprehensive examination was necessary and accordingly, this research was carried out by developing the experimental range. All experiments performed in this study have been performed in the laboratories of the Urmia cement plant, Urmia University, and the Urmia University of Technology.

2. Materials and methods

To investigate the effect of adding a grinding aid on the milling efficiency as well as the characteristics of cement, it is necessary to prepare suitable samples for the intended tests. First, the appropriate optimal time to obtain the desired Blaine number should be determined. Then, with the help of proper grinding aid and optimal

Table 1: Chemical composition of Portland cement type 1 of Urmia cement plant

Chemical composition	LOI	Na_2O	K_2O	MgO	SO_3	Fe_2O_3	Al_2O_3	SiO_2	CaO
Amount %	2.08	0.23	1.11	1.70	2.54	3.09	4.89	20.67	63.56

grinding time, milling tests were performed on all the samples and the results obtained for Blaine's number and compressive strength were compared with each other. Furthermore, on each sample, kinetic grinding tests were performed in order to obtain the amount of milling or grinding or comminution efficiency of each sample.

2.1. Specifications of clinker of S-OPC

In the flowsheet of the Urmia cement plant, the clinker enters the clinker mill after adding gypsum and other additives. After leaving the mill, the ground product enters the circuit separators, and the final cement (Portland Type 1) with a specific surface area or Blaine number of 3636 cm^2/gram is produced. General specifications of Portland Type 1 cement produced by the Urmia cement plant are presented in **Table 1**.

2.2. The process of performing experiments

All tests of this research have been performed on the samples prepared from the mixing feed of the Urmia cement plant clinker mill, gypsum, and other additives utilized in the plant. The process of preparing and performing laboratory tests is as follows.

2.2.1. Sample preparing

Seventeen composite samples were used to perform the experiments: one sample for comminution experiments without grinding aids (Blunk Sample) and sixteen samples for comminution experiments utilizing four different grinding aids, each at four different dosage levels. Depending on the capacity of the utilized laboratory-scale mill, the sample amount used for each comminution test is 1 kg. On the other hand, the cement sample required for compressive strength tests at three different times (2, 7, and 28-days concrete) is estimated between 5.5 to 6 kg (taking into account the density of cement and the ratio of cement: aggregate: water). Therefore, six replicate tests are required to provide a sufficient volume of each sample (each cement – grinding aid composite). For the preparation of these six samples, the primary feed and specified doses of grinding aid are used, and then it is ground at the specified time. It is unnecessary to measure the particle size distribution and Blaine number of all six samples. On the other hand, the need for a representative value that expresses the average amount of these six samples was felt. Therefore, three out of every six samples are randomly selected, and the average value of the Blaine numbers of these three samples is accepted as the final Blaine number of that sample. The best way to prepare suitable samples for comminution experiments is to utilize an industrial clinker mill feed. For this purpose, the clinker mill feed of the Urmia cement plant was sampled. Then, according to the chemical composition of Urmia cement, the necessary additives, such as gypsum, oxides, etc., were added with appropriate percentages to obtain a feed similar to the industrial clinker mill feed. In this study, the combination of the materials used precisely matches the one utilized on an industrial scale, but the particle size distribution is smaller than the industrial scale. Industrial mill feed has an F_{100} (100% of materials are smaller) of 50 mm. If this feed is utilized in a laboratory-scale mill, due to the small diameter of the mill and the small size of the balls, the breakage rate of the mentioned coarse feed will be meagre or require a very long grinding time. The long grinding time will cause a significant error in the estimated values and the analysis of the comminution results. Since preparing feed with the same particle size distribution is very difficult, it is necessary to have a characteristic parameter to connect the particle size distribution of industrial and laboratory scales, the most important of which is the top size or the size that all particles are smaller than it, i.e. F_{100}. Therefore, it is best to use the same feed for all experiments so that the combination of the ingredients is similar to the one utilized on an industrial scale, and its size is proportional to the ratio of mill diameters to the F_{100} ratios of mill feed. The diameter of the clinker mill of the Urmia cement plant and the utilized laboratory-scale mill are 460 and 22.4 cm, respectively, and F_{100} of clinker mill feed is 50 mm, therefore the use of feed with F_{100} of approximately 2.44 mm for all tests can yield a more reliable result. The 2.36 mm sieve, the nearest laboratory sieve to 2.44, was selected as the F_{100} sieve to standardize the results.

To prepare the initial combination of cement for laboratory tests, first, the industrial mill feed combinations of the Urmia cement plant (clinker, gypsum, and additives) were prepared, and then this mixture was crushed to less than 2.36 mm using a laboratory jaw crusher. Prepared materials below 2.36 mm represent the feed utilized for all laboratory tests. As mentioned, according to the experimental design, 17 composite samples with six repetitions for each are required; therefore, it was necessary to prepare 102 samples, each weighing 1 kg with F_{100} below 2.36 mm. These samples were prepared from raw samples utilizing a riffle separator.

2.2.2. Optimum grinding time test

In this study, to obtain the optimal grinding time (t), the time to reach the Blaine number of 3636 cm^2/g, eight traditional comminution experiments with durations of 3, 7, 15, 30, 50, 70, 90, and 110 minutes were performed on the sample prepared without grinding aids. Afterward, the Blaine number of each grinding time was determined, and the Blaine number-grinding time diagram of the experiments was plotted as shown in **Figure 2**.

These tests were repeated three times to increase the accuracy of the results, and the average value of the Blaine number obtained for each time was considered the representative Blaine number of that time. According to the obtained mathematical relation, the time to reach the Blaine number of 3636 cm^2/g was calculated to be 69.75 minutes.

In this research, for all grinding experiments, a ball mill with the specifications listed in **Table 2** was utilized.

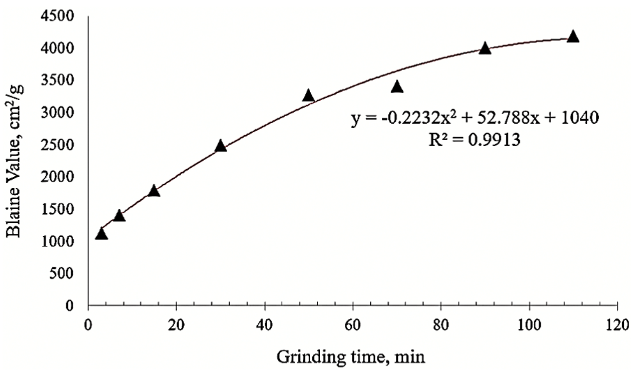

Figure 2: Blaine number – grinding time diagram of the kinetic tests (Blunk Sample)

Table 2: Laboratory mill specifications

Parameter	Unit	Symbol	amount
Diameter	cm	D	22.40
Length	cm	L	30.50
Mill rotational speed	rpm	S	80.00
Fraction of mill critical speed		C_S	90.15
Ball Mass	kg	M_b	11.41
Ball diameter	mm	d_{b1} (40/78%)	30.00
		d_{b2} (32/65%)	25.40
		d_{b3} (13/54%)	19.96
		d_{b4} (8/37 %)	14.95
		d_{b4} (4/66 %)	10.00
Make Up Ball	mm	Dc	20.61
Mill Volume	cm^3	V_m	12011.60
Ball filling	%	J_b	22.61
Material filling	%	J_o	8.31

2.2.3. Comminution experiments and compressive strength tests of grinding aid added samples

By obtaining the grinding time required to reach the desired Blaine number of the factory (t), which is the optimal grinding time, all subsequent tests were ground for 69.75 minutes, and the results obtained for Blaine number, compressive strengths, and energy efficiencies – retention time were compared.

Since the chemical composition of commercial grinding aids are unknown, and on the other hand, there is no thorough information regarding the effects of grinding aids on the properties of cement and concrete; therefore, it is tough to describe and interpret the results of commercial grinding aids, which will bear assumptions. For this reason, applying grinding aids with known chemical compounds such as amines, glycols, alcohols, etc., will be handy for research work. With this in mind, in this study, four types of grinding aids, according to **Table 3**, were utilized to perform comminution and compressive strength tests.

Table 3: Grinding aids and their dosages

Grinding Aid type	Dosage, %	Sample Code
Without the Grinding Aid	0	Blunk
Triisopropanolamine based	0.02	TIPA-0.02
	0.05	TIPA-0.05
	0.08	TIPA-0.08
	0.11	TIPA-0.11
Triethanolamine based	0.02	TEA-0.02
	0.05	TEA-0.05
	0.08	TEA-0.08
	0.11	TEA-0.11
Hydroxylamine based	0.02	HA-0.02
	0.05	HA-0.05
	0.08	HA-0.08
	0.11	HA-0.11
Calcium nitrate based	0.02	CN-0.02
	0.05	CN-0.05
	0.08	CN-0.08
	0.11	CN-0.11

According to the values considered for different levels of grinding aids, which for all are 0.02%, 0.05%, 0.08% and 0.11% of total sample weight, the addition rate of grinding aid to the samples of each level will be 0.2, 0.5, 0.8 and 1.1 gram, respectively (the total weight of each sample is 1 kg).

2.2.4. Comminution efficiency tests

To obtain the comminution efficiency of each sample, it is necessary to perform a kinetic grinding test at different times on the desired sample. After performing each milling test at the specified time, the corresponding Blaine number of that time is obtained. By creating a graphical relationship between time - Blaine's number and obtaining the mathematical model fitted to that

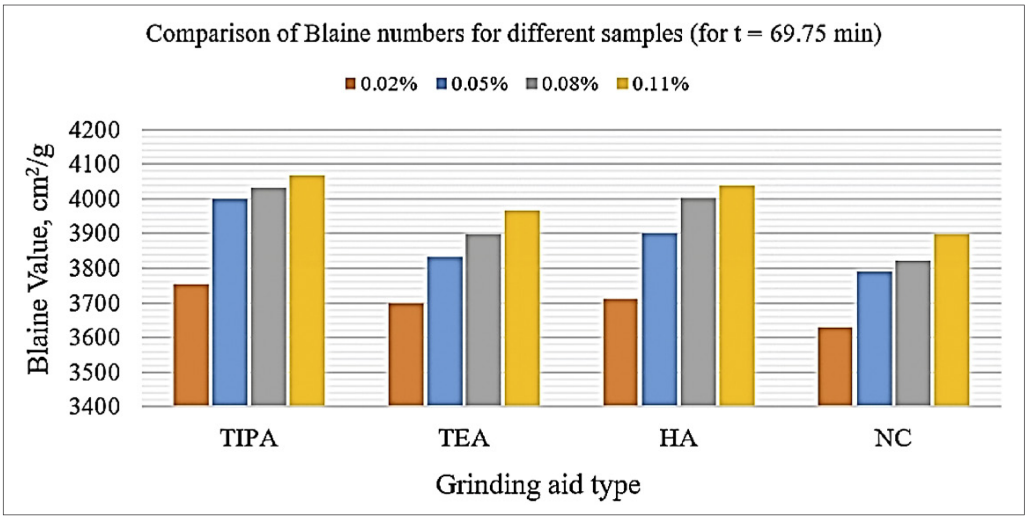

Figure 3: Blaine number comparisons for different combinations samples

graph, it is possible to calculate the time required to obtain the factory's Blaine number (3636 cm^2/g). By comparing this time and the optimal grinding time (t = 69.75 min), the amount of comminution efficiency can be calculated for each sample.

2.2.5. Thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR)

Thermogravimetric analysis (TGA) is used to investigate changes in the chemical and physical behaviour of materials under temperature changes. With this method, it is possible to assess the changes in the mass of the sample due to temperature changes. Often, factors such as loss of moisture, the water of crystallization, release of volatile compounds, combustion of organic compounds (in the presence of air), thermal decomposition, and oxidation alter the mass of the sample. When cement is mixed with water, the cement hydration process begins and hydration products are formed over time. Hydration products include 50-70% hydrated calcium silicate (CSH), 20-25% portlandite, 10-15% ettringite, and other hydration phases. Also, Fourier-transform infrared spectroscopy (FTIR) is used to obtain an infrared spectrum of absorption or emission of each cement – grinding aid sample. The aforementioned analyses were employed to confirm the presence of additives on cement samples (Blunk and TIPA samples) and also the effect of these chemicals on the thermal diagrams of various cement types.

3. Results and Discussions

3.1. Comminution experiments and Blaine number results

Dry comminution tests were performed on all the prepared samples containing different amounts of various grinding aids at a grinding time of 69.75 minutes. Due to the minimal amount of grinding aids used in each sample (maximum of 1.1 grams), the direct addition of these substances to the sample and its grinding can cause errors due to the absence of the added chemicals in some parts of the mill. Therefore, a general solution is to produce an aqueous compound from the grinding aid required for each sample so that the amount of water in it has minimal effect on the rheological properties of the materials in the mill. After preparing the desired aqueous compound for each sample, the material first entered the mill, then according to the amount of grinding aid considered, the aqueous compound was sprayed on the material. Finally, the mill hatch was closed, and the comminution operation was carried out at the desired time. Six repeated tests were performed for each sample, to provide the required sample volume for compressive strength tests. To increase the accuracy of the data and eliminate possible errors, three samples of these six samples were randomly selected, and their Blaine number was determined, and then the average value of these three numbers was introduced as the Blaine index of that composite sample. A total of 102 comminution tests were performed, and 17 representative Blaine numbers were obtained for all composite samples prepared from cement and grinding aid mixtures. The summary of the results is shown in **Figure 3**.

3.2. Compressive strength tests of concrete samples

The compressive strength test is the most important test performed on concrete because of its convenience and economic price (**Mindess et al., 2003**). Samples of different shapes and sizes can be utilized to test the compressive strength of concrete. The most critical shapes used for this experiment are cylindrical specimens with a diameter and height of 150 and 300 mm, respectively, and cubic specimens with dimensions of 150 mm. The second shape is mostly used in Europe and the UK and

 pp. 69-82, DOI: 10.17794/rgn.2023.1.7

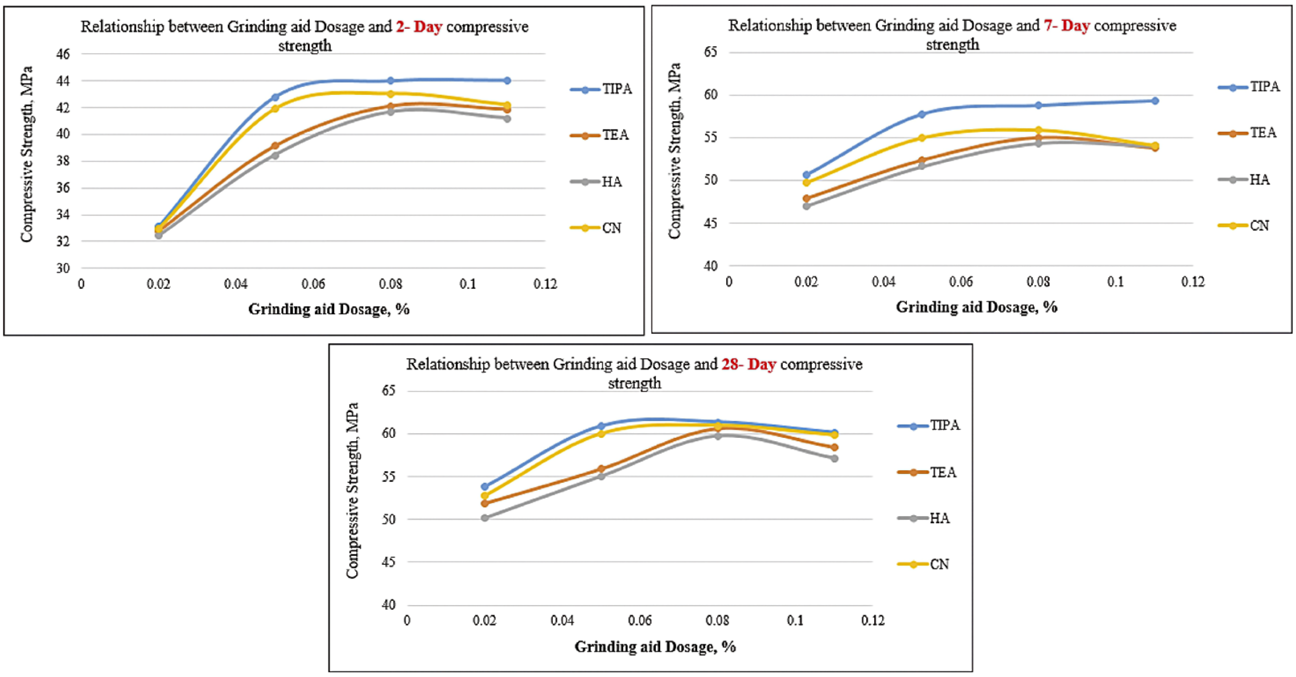

Figure 4: Comparison of 2-day, 7- day and 28- day compressive strength tests of different samples

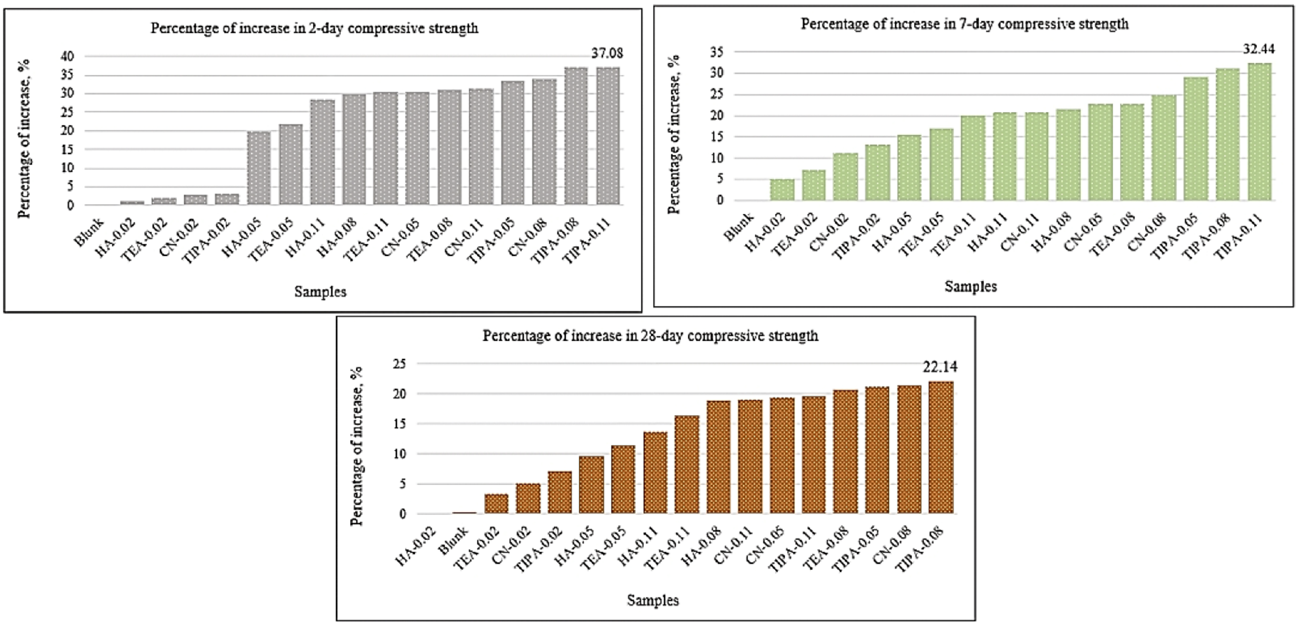

Figure 5: Percentage of increases in 2, 7 and 28-day compressive strength tests of different samples

the first in the USA (**Kim and Yi, 2002**). In this research, cubic samples with dimensions of 15 cm and an aggregate-cement-water mixing ratio of 3:1:0.5 were used. Due to having 17 composite samples and considering durations of 2, 7, and 28 days for compressive strength tests, a total of 51 concrete blocks which are obtained from different composite samples (combination of cement and different grinding aids) were made, and compressive strength tests were carried out. The compressive strength test results are shown in **Figures 4** and **5**.

The results of the concrete compressive strength tests for all ages showed that the compressive strength of all samples (except TIPA) increased at doses from 0.02 to 0.08%, and decreased after the 0.08 point (see **Figure 4**). The same trend is seen in the 28-day compressive strength tests using the TIPA reagent, but the 2 and 7-day compressive strength values always increase, albeit with a low slope (see **Figure 4**). The comparison of the percentage increase in compressive strength of different ages of all samples shows that the highest increase for

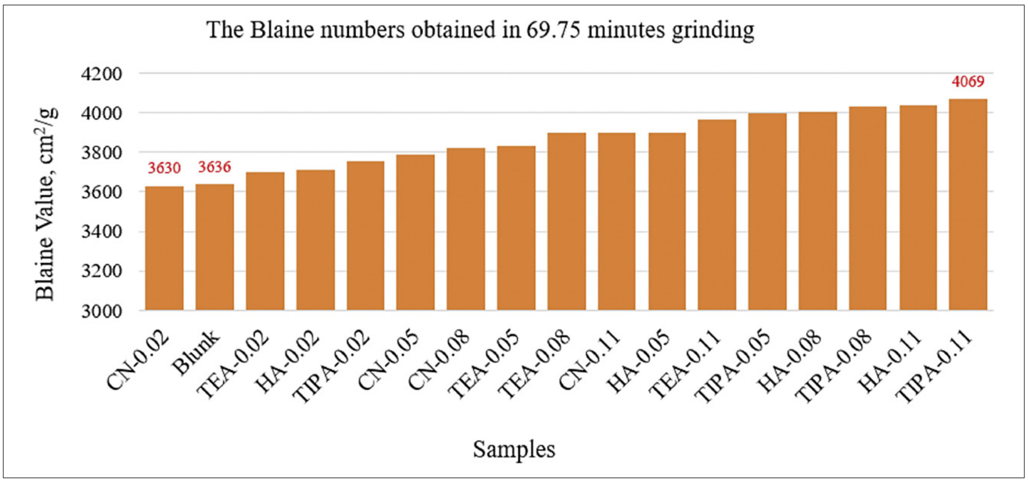

Figure 6: The Blaine numbers were obtained in 69.75 minutes grinding

the ages of 2, 7, and 28 days belonged to the TIPA-0.11 (37.08%), TIPA-0.11 (32.44%) and TIPA-0.08 (22.14%), respectively (see **Figure 5**).

These results indicate the existence of an optimal point in the amount of grinding aids from the point of view of compressive strength. Deciding to choose the optimal point for the amount of used grinding aid depends on satisfying the minimum standard compressive strength required for the prepared concrete and then maximizing the amount of energy savings.

It is noteworthy that the effect of TIPA on increasing the compressive strength of concrete at low levels is small, this is probably due to the volume of pores and air permeability (**Ma et al., 2018**). TIPA can increase the volume of harmful pores (in micro and nanometre dimensions), hurting compressive strength. On the other hand, the effect of TIPA on the compressive strength of 2 and 7 days is greater than the 28-day strength, and an even more significant increase is observed in younger concretes, which is attributed to the acceleration of the cement minerals hydration by TIP. By further increasing the amount of TIPA, the effect of air to accelerate the hydration of the concrete system can also be enhanced. Another reason is that TIPA can also accelerate the dissolution of silicates, iron, and aluminates, accelerating the formation of calcium hydro aluminate hydrate to fill concrete pores and help with compressive strength (**Ma et al., 2018**).

3.3. Comminution efficiency tests results

The effect of grinding aid on comminution efficiency can be examined in three general forms:

a) increasing grinding rate (production of finer grained-product) with a constant flow rate and mill power;
b) increasing flow rate with a constant grinding rate and mill power; and
c) reducing mill power by keeping the mill grinding and flow rate constant.

In the batch grinding experiments performed in this study, in the first stage, the weight of all samples and their grinding time was constant and equal to 1 kg and 69.75 minutes, respectively. In addition, the power supplied to the mill was kept constant in all experiments. This means, in this stage, the mill feed (mass flow rate and size distribution), mill power, and grinding time were kept constant. Therefore, the comminution efficiency in this mill can be examined from the perspective of grinding rate (production of finer grained-product). The results of the grinding tests performed on all samples (Cement - Grinding aid type) are given in **Figure 6**.

The results of **Figure 6** show that keeping the grinding time constant causes differences in the fineness of products in different samples. For example, grinding the Blunk sample for 69.75 minutes gives a Blaine amount of 3636 while grinding at the same time gives the Blaine values of 3660, 3897, and 4069 for the CN-02, TEA-08, and TIPA-011 samples, respectively. Therefore, these results show that in order to reach a constant Blaine number of 3636, for samples whose Blaine values are greater than 3636, it is possible to reduce the sample's grinding times.

The solid volumetric flow rate in the dry industrial mills is given roughly with equality, where and are the volume of materials in the mill and material retention time, respectively. The solid volumetric flow rate is equal to the solid mass divided by the solid density (). Therefore, taking into account that the material density is constant, it is understood that is inversely proportional to . In industrial mills, the grinding time (t) is known as the material retention time (), therefore, since t and are equivalent, it can be said that and t also have an inverse relationship (i.e. or). Therefore, for a certain comminution size or a fixed grinding degree (Blaine value), reducing the retention time of the materials in the mill means increasing the solid flow rate.

For each sample, a series of kinetic grinding tests are needed to obtain a logical relationship between Blaine

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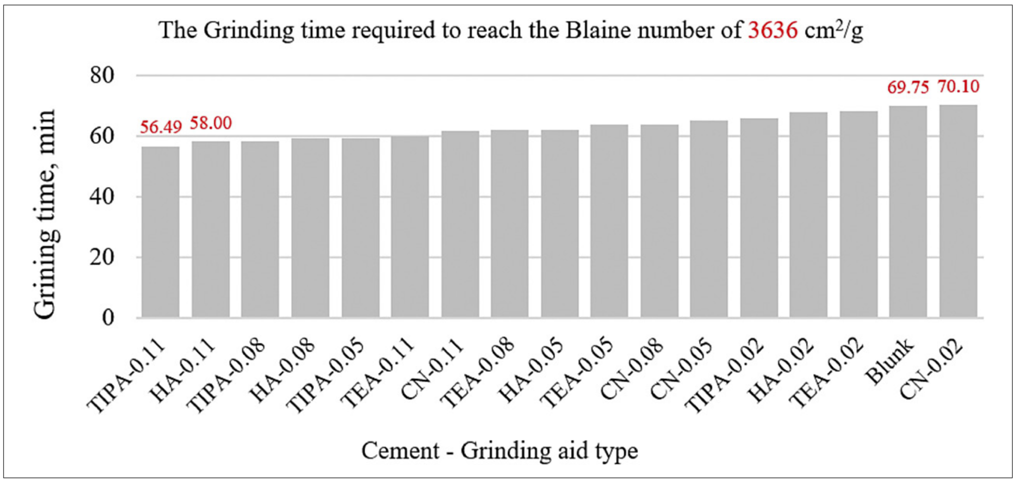

Figure 7: The Grinding time required to reach the Blaine number of 3636 cm²/g

Table 4: The Models fitted to the kinetic grinding tests

Blaine = a.t² + b.t + c				
Samples	**Model parameters**			
	a	**b**	**c**	**R^2**
TIPA-0.02	-0.2629	58.087	955.79	0.9995
TIPA-0.05	-0.3355	68.127	777.38	0.992
TIPA-0.08	-0.3353	67.679	838.18	0.9917
TIPA-0.11	-0.3476	69.38	825.83	0.9933
TEA-0.02	-0.2392	54.954	1003.9	0.9997
TEA-0.05	-0.2784	60.458	915.05	0.9977
TEA-0.08	-0.2956	62.682	892.26	0.9963
TEA-0.11	-0.3183	65.743	844.31	0.9944
HA-0.02	-0.2417	55.417	991.8	0.9994
HA-0.05	-0.2983	63.105	871.76	0.9955
HA-0.08	-0.3266	66.696	835.68	0.9919
HA-0.11	-0.3353	67.932	824.02	0.9912
CN-0.02	-0.2175	52.009	1059	1
CN-0.05	-0.2679	58.953	935.33	0.9986
CN-0.08	-0.2756	59.901	936.54	0.9984
CN-0.11	-0.2954	62.622	896.71	0.9964

values - grinding times and grinding times - energy efficiencies. The following steps were applied to all samples to perform the kinetic grinding tests:

i. Firstly, 20, 50, 69.75, and 110 minutes grinding tests were performed on each sample.

ii. At the end of each grinding process, the Blaine value of the obtained product was determined.

iii. After completing the four grinding stages and obtaining four Blaine numbers for each sample, a quadratic polynomial relationship (Blaine = $a.t^2 + b.t + c$) was established between the times and the Blaine values.

iv. Using the obtained model for each sample, the grinding time required to reach the Plant Blaine number (3636 cm²/g) was obtained. In fact, this time is the material retention time of each sample ().

These models and the retention times are given in **Table 4** and **Figure 7**.

When the amount of grinding of the materials in the mill is kept constant, reducing the grinding time means reducing the energy consumption required for comminution. Now, assuming the power entering the mill is constant, then, reducing the retention time means increasing the flow rate of the materials entering the mill which means reducing the energy consumption per unit weight of materials in the mill (). **Figure 8** shows the time saving and power saving of all samples to reach the Blaine number of 3636 cm²/g. **Figure 9** shows the ratio of the specific comminution energy of each sample to the Blunk sample (). This ratio indicates energy efficiency, and the smaller its value, the less energy is consumed to grind the unit weight of the material.

The results of the comminution experiments indicate an increase in the comminution efficiency of the laboratory ball mill by up to 19% for various types of grinding aids at different levels (see **Figure 8**). Except for calcium nitrate 0.02% (NA-0.02) in other cases, the addition of a grinding aid has led to a finer-grained final product, and with an increase in the dosage level, the product was also more refined (see **Figures 3** and **8**). This trend is not linear, and after a certain level, the amount and trend of the impact of the grinding aid decreases. At all four dosages (0.02, 0.05, 0.08 and 0.11%) of grinding aids used, the most ground material was obtained with the TIPA grinding aid, followed by HA, TEA, and NC, respectively (see **Figure 10**). The most significant increase in fineness is attributed to the TriIsoPropanolAmine compound at 0.11% dosage level (TIPA-0.11) in which the Blaine number increased to 4069 cm²/gram. This may be due to the superiority of TIPA-based grinding aids in reducing the polarity of the clinker surface and, as a result, reducing the clinker surface energy (**Altun et al., 2015**). On the other hand, with an increase in the amount of the grinding aid, the rate of reduction of surface energy also

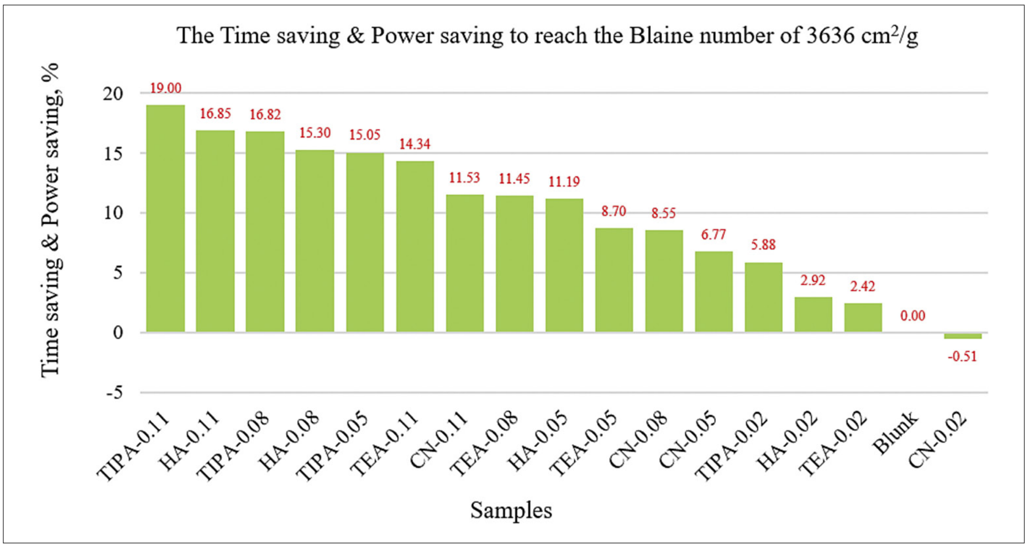

Figure 8: The time saving and power saving of all samples to reach the Blaine number of 3636 cm²/g

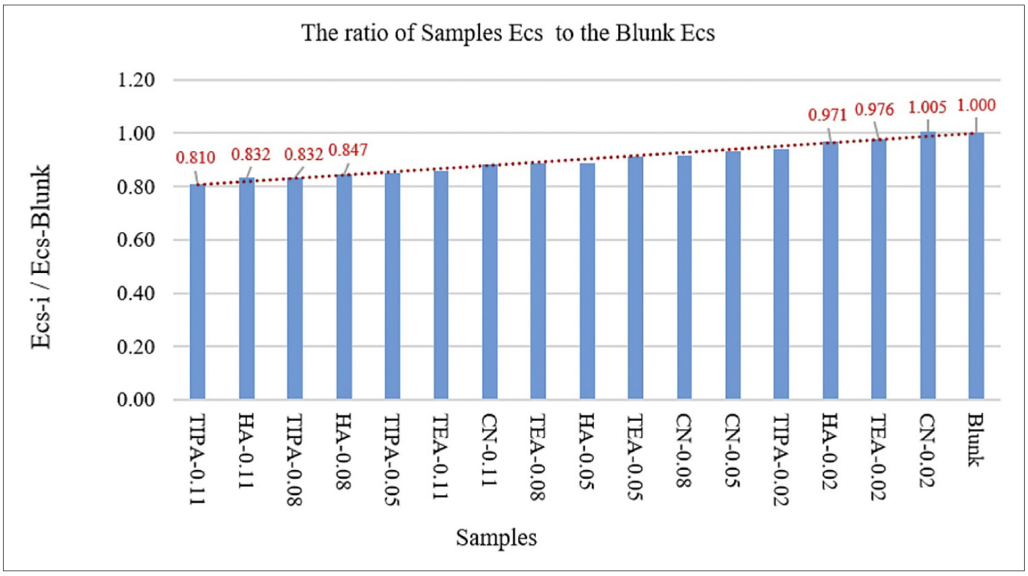

Figure 9: Ratio of specific comminution energy of each sample to the Blunk sample (E_{CS-i}/E_{CS})

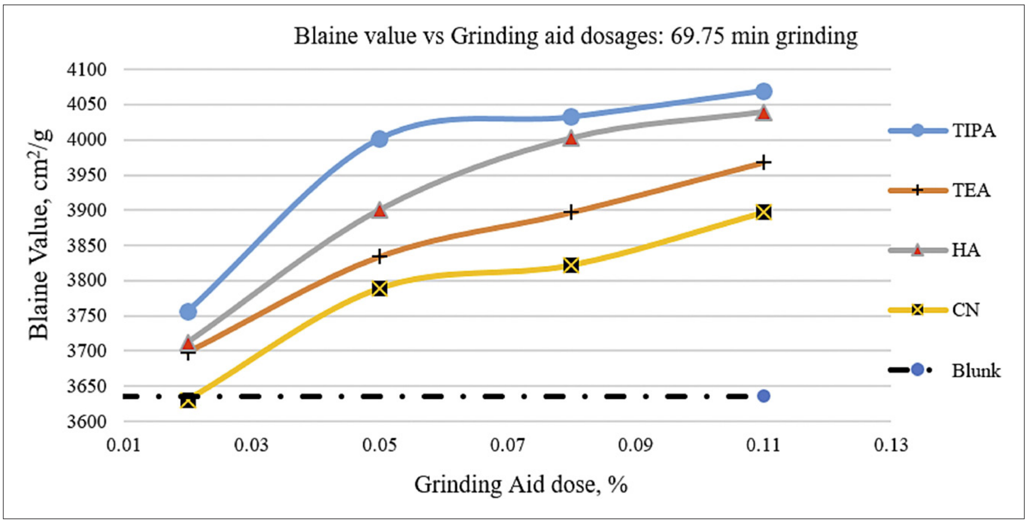

Figure 10: Blaine numbers of all ground composite samples at the optimal time (69.75 min)

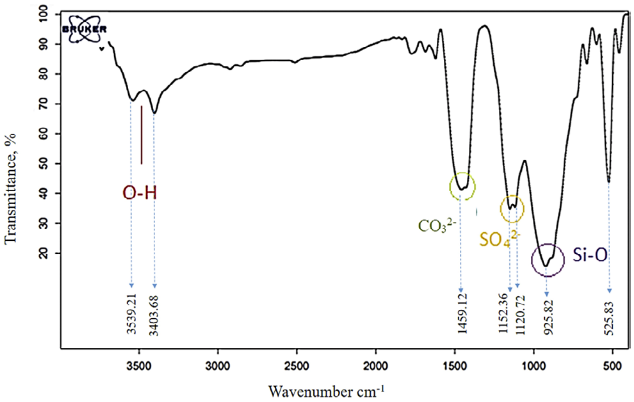

Figure 11: FTIR spectrum of reference cement

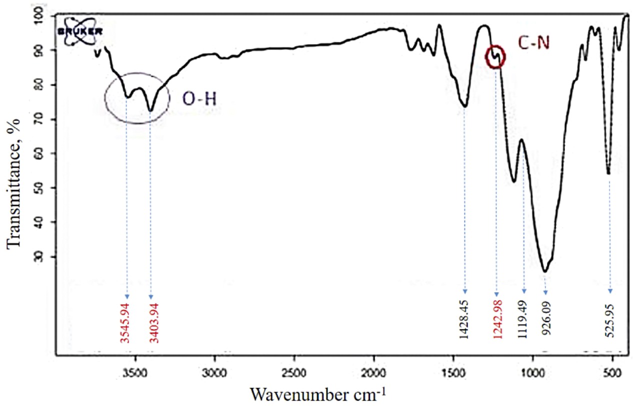

Figure 12: FTIR spectrum reference cement with grinding aid TIPA (Amine)

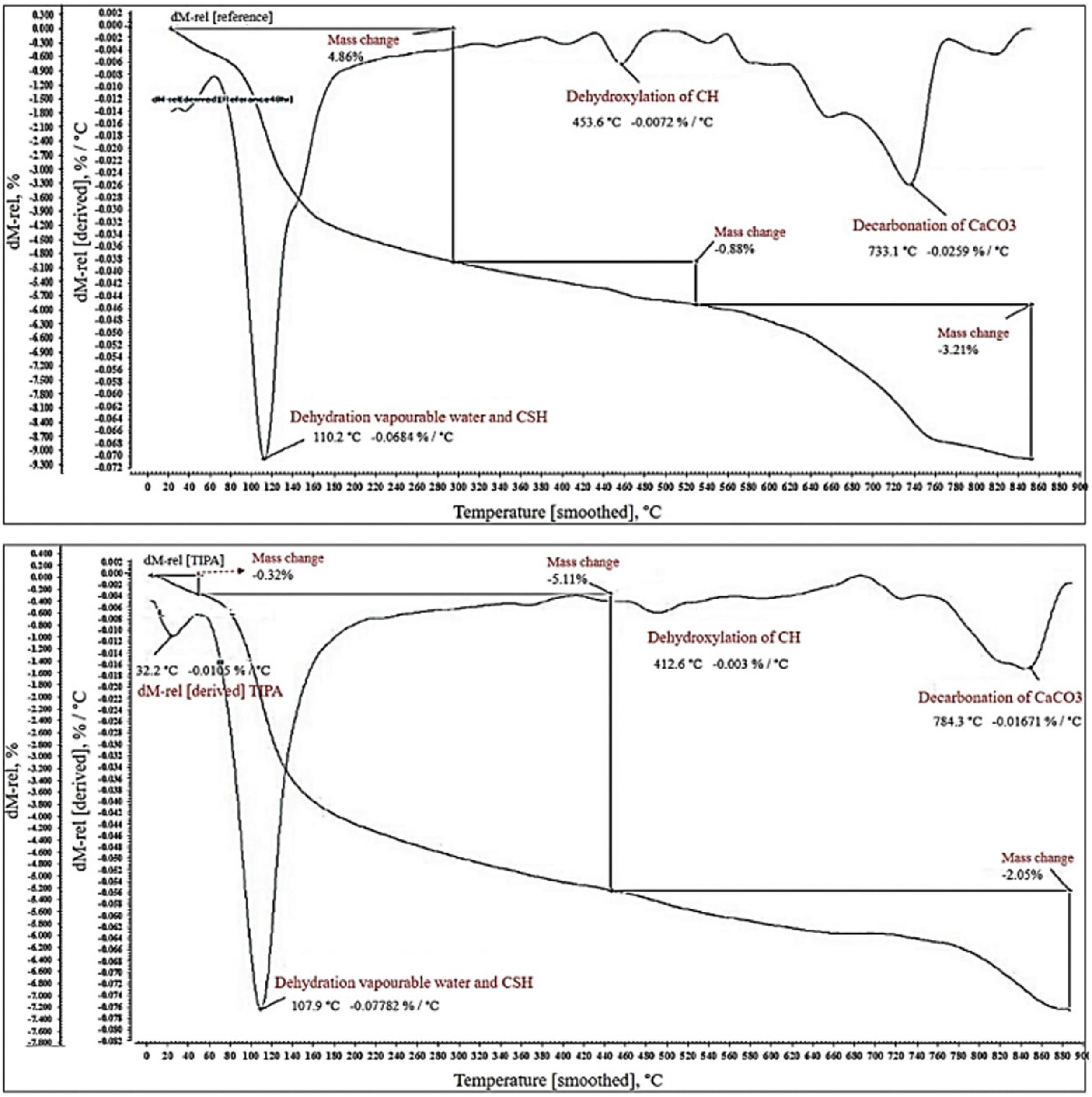

Figure 13: TGA/DTG diagrams of Two-day; a) reference cement b) TIPA cement

increases. Therefore, the comminution efficiency also increases (**Sverak et al., 2013**).

3.4. TGA/DTA analysis and FTIR diagrams results

The reference cement is a mixture of clinker, lime, and gypsum. The O-H peaks and the peaks of the carbonate, sulphate, and silicate groups (several peaks overlap) can be seen in the FTIR diagrams. The reference cement was ground along with the addition of grinding aid TIPA (amine group) for a certain duration of time. As presented in **Figures 11** and **12**, the peak in the range of 1242.98 cm^{-1} indicates the presence of C-N in the amine grinding aid (due to the small amount of added grinding aid, a small peak has appeared in the spectrum). The peak in the range of 3403.94 -3545.94 cm^{-1} indicates the presence of the O-H group (intensity has increased in this spectrum) in the amine grinding aids and water and caused an increase in absorption.

The TGA/DTG diagrams of the reference cement at the ages of 2, 7, and 28 days generally indicate an increase in the production of hydration products and a decrease in the amount of carbonate (it should be noted that calcium carbonate in clinker and lime participate in the formation of hydration products during the hydration process and the amount of calcium carbonate decreases). From the age of 2-28 days, the formation of hydration products such as C-H increased and the peaks in the range of 100-400°C appear over time, which indicates the formation of products such as CSH, ettringite, and other hydrates. The rate of hydration of the phases that make up cement is different, as a result, with increasing time, more phases are hydrated and more products are formed. It was found that with an increase in age, the degree of hydration also increases. Based on the TGA/DTG diagrams, the number of hydration products (such as CSH and ettringite) in the reference cement with grinding aid TIPA at the ages of 2, 7, and 28 days have increased compared to the reference cement. As the conductometric analysis suggests grinding aid B is chelated with iron and aluminum ions, and this indicates that TIPA increased the dissolution of these phases through chelation with C4AF and C3A phase ions. As a result, the hydration products (CSH and ettringite) increase, consequently the degree of hydration has also increased. Also, at the age of 28 days, the non-carbonated portion in the sample containing TIPA is lower than the reference sample, which indicates that the hydration is more advanced in this sample (**Figure 13** indicates the results for 2-day).

In this research, the effect of four types of grinding aids at four different levels of 0.02, 0.05, 0.08 and 0.11% on the compressive strength of concrete and the amount of energy saved in clinker grinding has been investigated. In this study, by obtaining the optimal grinding time, comminution operations were performed on all composite samples, and subsequently, their Blaine number was determined.

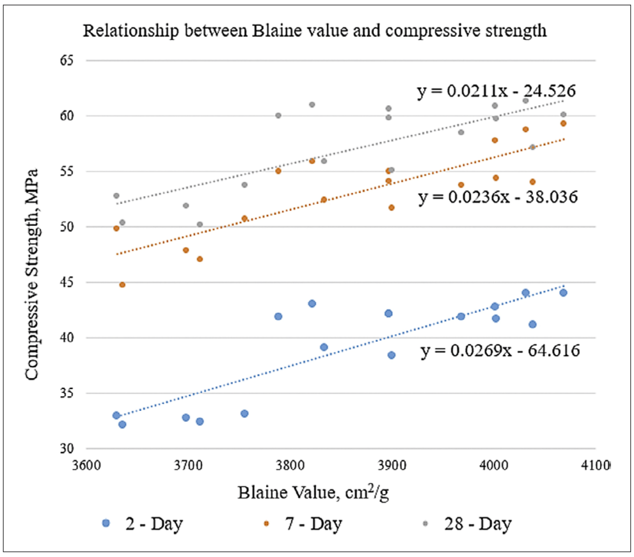

Figure 14: The relationship between Blaine number and compressive strength of concrete in 2-7-28 days

The results of the comminution and compressive strength tests of concrete showed a relative agreement between comminution efficiency and compressive strength of concrete, and as shown in **Figure 14**, a decrease in particle size (increasing Blaine value) increased compressive strength at all ages of concrete. However, the extent of this effect in 2 and 7-day strength is more than the 28-day one (by comparing the slopes of the fitted lines).

The results indicate that adding these chemical compounds increased the compressive strength of all samples and thus improved the quality criterion of cement. On the other hand, an increase in the comminution efficiency of all samples (except NC-0.02) was observed. In this study, the highest efficiency is related to the application of TIPA-0.11, which caused a 19% increase in comminution efficiency and a 37.08% increase in 2-day compressive strength.

4. Conclusion

In this research, the effect of four types of grinding aids at four different levels of 0.02, 0.05, 0.08 and 0.11% on the compressive strength of concrete and the amount of energy saved in clinker grinding has been investigated. The results show that adding a grinding aid reduces the agglomeration of fine particles and removes the coating of balls (grinding media) inside the clinker mill. The results indicated that:

i. Using grinding aids increased the amount of grinding or the capacity of a mill per given power consumption, which means a reduction in the specific grinding energy. In all samples (except NC-0.02), an increase in the comminution efficiency was observed.

ii. Adding a grinding aid made the milling product more acceptable and increased the specific surface area of the product or the Blaine number, increasing the mill comminution efficiency.

iii. The results of the comminution and compressive strength tests of concrete showed a relative agreement between comminution efficiency and the compressive strength of concrete. On the other hand, decreasing the particle size (increasing Blaine value) increased the compressive strength at all ages of concrete. However, the extent of this effect in 2 and 7-day strength is higher than the 28-day one (by comparing the slopes of the fitted lines).

iv. In any case, it should be noted that in addition to the Blaine number of types of cement, the presence of various chemical compounds in various types of grinding aids and the effect of the reaction of these components with cement and water components are also effective on compressive strength.

v. Adding these chemical compounds increased the compressive strength of all samples and thus improved the quality criterion of cement.

vi. The comparison of the percentage increase in compressive strength of different ages of all samples shows that the highest increase for the ages of 2, 7, and 28 days belonged to the TIPA-0.11 (37.08%), TIPA-0.11 (32.44%) and TIPA-0.08 (22.14%), respectively.

vii. At all four dosages (0.02, 0.05, 0.08 and 0.11%) of grinding aids used, the most ground material was obtained with the TIPA grinding aid, followed by HA, TEA, and NC, respectively.

viii. In this study, the highest efficiency is related to the application of TIPA-0.11, which caused a 19% increase in comminution efficiency and a 37.08% increase in 2-day compressive strength.

Due to the increase in the Blaine number of samples by these chemicals, it can be concluded that increasing these materials on the quality of cement, comminution costs, and consequently the cost of cement is very high and requires the development of relevant studies. Considering the very high energy costs, it is very important to optimize energy consumption in the cement production process while maintaining the required characteristics of concrete. Therefore, by obtaining the optimal amounts of each of these additives on a laboratory scale, future studies will continue on a semi-industrial scale and finally on an industrial scale.

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SAŽETAK

Učinci različitih doziranja pomoćnih sredstava za mljevenje na učinkovitost sitnjenja i karakteristike cementa

Pomoćna sredstva za mljevenje jesu materijali koji se dodaju cementnoj smjesi kako bi se poboljšala svojstva cementa i/ili povećala učinkovitost sustava sitnjenja u fazi mljevenja klinkera (završno mljevenje). U ovoj studiji proučavani su učinci četiriju pomoćnih sredstava za mljevenje (na bazi triizopropanolamina (TIPA), na bazi trietanolamina (TEA), na bazi hidroksilamina (HA) i na bazi kalcijeva nitrata (CN)) na bitna svojstva proizvedenoga cementa, a to su specifična površina (Blaineov broj), tlačna čvrstoća betona i učinkovitost sitnjenja, tj. vrijeme zadržavanja (ušteda energije) za četiri različite razine doziranja. U prvome je koraku kinetičkim testovima mljevenja vrijeme mljevenja potrebno za postizanje Blaineova broja ispitivane vrste cementa (S-OPC: obični portlandski cement) iznosilo 69,75 minuta. Nakon toga provedeno je 17 laboratorijskih ispitivanja mljevenja S-OPC cementa i četiri pomoćna sredstva za mljevenje u četiri različite doze od 0,02 %, 0,05 %, 0,08 % i 0,11 %. Rezultati su pokazali da TIPA-0,11 (triizopropilaminski spoj u dozi od 0,11 %) s Blaineovim brojem od 4069 cm^2/g i učinkovitošću mljevenja od 19 % ima najveći učinak na finoću i učinkovitost sitnjenja. Nadalje, nakon 2, 7 i 28 dana ispitana je tlačna čvrstoća uzoraka betona koji su napravljeni od cementa i pojedinih pomoćnih sredstava za mljevenje. Rezultati su pokazali da je, u usporedbi s kontrolnim uzorcima, najveći porast tlačne čvrstoće zabilježen nakon 2. i 7. dana kod uzoraka TIPA-0,11 s vrijednostima od 37,08 % odnosno 32,44 %. Uzorci stari 28 dana pokazali su najveće povećanje tlačne čvrstoće kod TIPA-0,11, koje je iznosilo 22,14 %.

Ključne riječi:
pomoćna sredstva za mljevenje, učinkovitost sitnjenja, Blaineov broj, tlačna čvrstoća, cement, beton

Author's contribution

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[2]**Sajjad Chehreghani,** Assistant Professor of Mineral Processing Engineering, collaborated on the literature review, data collection and analysis procedure of this manuscript.
[3]**Behnam Seyyedi**, Assistant Professor of Chemical Engineering, collaborated on the description of the chemistry of the manuscript.