

EFFECT OF GRINDING CHEMICALS AND AIDS ON THE GRINDING  
EFFICIENCY AND THE PERFORMANCE OF PORTLAND CEMENT

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## **ABSTRACT**

### **EFFECT OF GRINDING CHEMICALS AND AIDS ON THE GRINDING EFFICIENCY AND THE PERFORMANCE OF PORTLAND CEMENT**

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Cement production is an energy-intensive process. Cement grinding alone accounts for a third of the total energy used in this process. Improving grinding efficiency is therefore crucial to saving energy. Grinding aids (GA), chemical substances that improve grindability, are adsorbed on the cement surface and reduce its surface energy. As a result, the cement particles agglomerate less during grinding and form a finer cement, leading to increased energy efficiency. In addition, GAs can also affect consistency of the cement mortar and alter the mechanical properties of the cement. This study evaluates the performance of some grinding chemicals (GCs) and GAs, which are mixtures of GCs, on the properties of cement. Amines, polyols, defoamers and polycarboxylate ethers (PCE) are used as GCs. Tests are carried out at constant specific energy consumption (SEC) and their performance at fixed fineness is estimated by regression. Among the GCs, at constant fineness, propyleneglycol (PG) provided the highest energy savings at 9.8%, AF-A provided the highest flow increase at 15.2%, tetrahydroxyethylethylenediamine (THEED) provided the highest early strength increase at 9.4%, and monoethyleneglycol (MEG) provided the highest standard strength increase at 6.7%. Moreover, it was

also shown that GCs can be optimized to obtain GAs. Among the GAs tested, GA-E provided the highest energy savings at 12.1%, GA-A provided the highest flow increase at 17.9% and the highest standard strength increase at 17.5%, and GA-C provided the highest early strength increase at 23.1%.

Keywords: Grinding Aid, Specific Energy Consumption, Surface Energy

## ÖZ

### ÖĞÜTME KİMYASALLARI VE KOLAYLAŞTIRICILARININ PORTLAND ÇİMENTOSUNUN ÖĞÜTME VERİMLİLİĞİ VE PERFORMANSI ÜZERİNE ETKİSİ

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Çimento üretiminde enerji tüketimi oldukça yoğundur. Çimentonun öğütülmesi, tek başına bu süreçte kullanılan toplam enerjinin üçte birini oluşturmaktadır. Bu nedenle öğütme verimliliğinin artırılması enerji tasarrufu için çok önemlidir. Öğütme kolaylaştırıcılar (ÖK), öğütülebilirliği artıran kimyasal maddedir. ÖK'ler çimento yüzeyine adsorbe edilir ve yüzey enerjisini azaltır. Sonuç olarak, çimento partikülleri daha az topaklanır ve çimentonun daha ince olmasını sağlayarak enerji verimliliğini artırır. Ayrıca ÖK'ler çimento harcının kıvamını etkileyebilir ve mekanik özellikleri değiştirebilir. Bu çalışma, bazı öğütme kolaylaştırıcı kimyasalların (ÖKK) ve bunların karışımları olan ÖKK'lerin çimento tozu ve harçlarının özellikleri üzerindeki performansını değerlendirmektedir. ÖK olarak aminler, polioller, köpük kesiciler ve polikarboksilat eterler (PCE) kullanılmıştır. Testler sabit özgül enerji tüketiminde (ÖET) gerçekleştirilmiş ve sabit incelikteki performansları regresyon ile tahmin edilmiştir. ÖKK'ler arasında, sabit incelikte, propilenglikol (PG) %9,8 ile en yüksek enerji tasarrufunu, AF-A %15,2 ile en yüksek akışkanlık artışını, tetrahidsietilendiamin (THEED) %9,4 ile en yüksek erken dayanım artışını ve monoetilenglikol (MEG) %6,7 ile en yüksek standart dayanım artışını sağlamıştır. Ayrıca, ÖK'lerin elde edilmesi için ÖKK'lerin optimize edilebileceği de

gösterilmiştir. Test edilen ÖK'ler arasında GA-E %12,1 ile en yüksek enerji tasarrufunu, GA-A %17,9 ile en yüksek akışkanlık artışını ve %17,5 ile en yüksek standart dayanım artışını, GA-C ise %23,1 ile en yüksek erken dayanım artışını sağlamıştır.

Anahtar Kelimeler: Öğütme Kolaylaştırıcı, Özgül Enerji Tüketimi, Yüzey Enerjisi



To my parents, my very first teachers

To my lovely brother, Tarik

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## LIST OF ABBREVIATIONS

### ABBREVIATIONS

AF:	Antifoam
ANOVA:	Analysis of Variance
ASTM:	American Society for Testing Materials
CA:	Chemical Admixture
DEG:	Diethyleneglycol
DEIPA:	Diethanolisopropanolamine
EN:	European Norms
GA:	Grinding Aid
GC:	Grinding Chemicals
MEA:	Monoethanolamine
MEG:	Monoethyleneglycol
PCE:	Polycarboxylate Ether
PEG:	Polyethyleneglycol
PG:	Propyleneglycol
PSD:	Particle Size Distribution
SEC:	Specific Energy Consumption
SSA:	Specific Surface Area
TEA:	Triethanolamine

THEED:	Tetrahydroxyethylethylenediamine
TIBP:	Triisobutylphosphate
TIPA:	Triisopropanolamine
US\$:	United States Dollar
XRD:	X-Ray Diffraction
XRF:	X-Ray Fluorescence



# CHAPTER 1

## INTRODUCTION

### 1.1 General

The production of Portland cement is responsible for approximately 7% of total CO<sub>2</sub> emissions and is ranked as the fourth most energy-intensive industry worldwide (Pan & Lee, 2018). Notably, the crushing and grinding of the raw material, the clinker, and the fuel accounts for approximately two-thirds of the energy consumed during cement production (Schneider et al., 2011). Grinding aids (GA), which are used to reduce the energy required for cement production, change the particle behavior in grinding media and facilitate the grinding process. Therefore, they increase the cement fineness with enhanced energy efficiency. Moreover, they also provide time efficiency for grinding the same amount of cement with increased production capacity.

GAs are added prior to or during the grinding process as additives. GAs are generally organic substances known for their wetting properties and low surface tension. The adsorption occurs between the GA and the surface of the particles. This is due to the interaction between the non-polar groups present in the GA and the electrostatically charged, hydroxylated surface of the particles that is wetted by the coolant water. As a result, the surface energy of the particles is decreased (Blake, 2006). This reduces the agglomeration of cement particles and avoids ball and wall coating. Furthermore, the powder flowability of cement increases and the grinding process is facilitated. Glycerol, glycols, alkanolamines, antifoams (AF), and polycarboxylate ethers (PCE) are frequently utilized as GAs due to their surface-active properties (Jeknavorian et al., 1998; Mishra & Zurich, 2014; Teoreanu & Guslicov, 1999; Toprak et al., 2014).

GAs are not only beneficial to the cement production process but also to the properties of the cement. As mentioned above, the chemicals in GAs are adsorbed on the surface of the cement particles during grinding. Therefore, cement agglomeration does not occur in fresh mortar as it does in powdered cement. GAs assist in the consistency of the cement paste at constant fineness and water content. On the other hand, adsorbed chemicals affect the hydration reactions. GAs can accelerate or retard hydration. They can enhance AFt to AFm phase transfer, cause different hydration products to be formed, and alter the ultimate strength (He et al., 2021; Heren & Ölmez, 1996; Hewlett et al., 2019; Huang et al., 2016; Huang & Shen, 2014; Katsioti et al., 2009; W. Li et al., 2015; Ma et al., 2015, 2019; Sun et al., 2016; Wang et al., 2022).

## **1.2 Objectives and Scope**

The objective of this study is threefold. First, the effect of various grinding chemicals (GC) on the grinding efficiency of cement clinkers will be established. Later, the effects of these grinding chemicals on the fresh and hardened properties of cement will be sought. Finally, it will be shown that these grinding chemicals can be optimized to obtain various grinding aids that will not only increase the grinding efficiency but also improve certain properties of cement.

In the first phase, four types of GCs are used: amines, polyols, antifoams, and PCEs. Each GC is used to grind a pre-selected Portland cement clinker at a fixed grinding time, i.e., fixed grinding energy, and the effects of each GC on the fineness, consistency, and strength properties of the cement are determined. Later, the effects of each GC were sought for a fixed fineness. However, since each GC affects the fineness differently, and the number of GCs and the number of grinding times will form a large number of grindings, a different approach is used. In this approach, in the absence of the GCs, the same clinker is ground at different grinding times and the energy requirements for each grinding time and the corresponding properties of each cement at these grinding times are determined. Later, regression analysis is



used to obtain the specific energy consumption, consistency, and early and standard strength. Using the established regression analysis, a comparison could be made between the cement without GC and the cement with GC of the same fineness. The comparisons include the energy savings obtained, the consistency, and the early and standard strengths of the cements.

In order to examine the effects of each GC on the consistency and the strength of cement, in the absence of grinding, a CEM I 42.5R type OPC is obtained and each GC is used as a chemical admixture (CA). The fresh and hardened properties of cement are then determined and the effects of the GCs on the consistency and the strength of cement were obtained.

Finally, commercially available GAs that were prepared by using two or more GCs in varying amounts were obtained and these GAs were used to grind the same pre-selected Portland cement clinker at a fixed grinding time, i.e., fixed grinding energy, and the effects of each GA on the fineness and consistency and strength properties of the cement are determined. The aim was to show that the GCs can be optimized to obtain a synergetic effect.

Chapter 2 includes a literature review on energy efficiency in cement grinding, the working mechanisms of GAs, their historical development, and the chemicals used in GAs. Chapter 3 discusses the materials and methods used in the study. In Chapter 4, the results of the experiments are analyzed in 3 phases. In Phase 1, the effects of GCs on cement properties at constant energy consumption and constant fineness are investigated separately. In Phase 2, GCs are used as CAs in mortars prepared with Portland cement. And in Phase 3, the effects of GAs on cement properties at constant energy consumption and constant fineness are evaluated. In the 5th and last chapter, all conclusions are summarized and recommendations for future studies are given.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Energy Efficiency in Cement Production

Concrete, with an annual consumption of 30 billion tons, is the most extensively utilized material globally after water (Monteiro et al., 2017). The key ingredient of the concrete is the cement, the binder. The cement industry accounts for approximately 7% of global carbon dioxide emissions. This emission stems from burning fossil fuel for energy supply and the calcination of raw materials utilized during production. Furthermore, it stands as the fourth-largest consumer of energy within the industrial sector (Pan & Lee, 2018). The shares of the industrial sectors in energy consumption are shown in Figure 2.1.

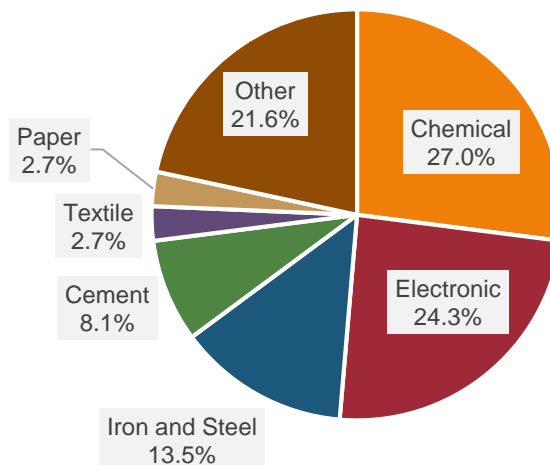


Figure 2.1. Energy consumption of industrial sectors (Pan & Lee, 2018)

### 2.1.1 Cement Production

Ordinary Portland cement basically includes two constituents: clinker and gypsum. Clinker, the base ingredient of Portland cement, comprises of mainly four oxides: silicon, calcium, aluminum, and iron oxides, which are supplied by raw materials. Limestone, shale, marl, sand, clays, iron ore, etc., are used as raw materials in clinker production (Carpio et al., 2008).

Raw materials are ground, mixed in prescribed ratios, homogenized, and burnt at about 1450 °C in rotary kilns. In the kiln, powdered raw material partially melts, and oxides react to form alite ( $C_3S$ ), belite ( $C_2S$ ), tricalcium aluminate ( $C_3A$ ), and ferrite ( $C_4AF$ ), the main components of clinker (Bullard, 2015; Carpio et al., 2008; Kang et al., 2023). The clinker is cooled rapidly, facilitating the formation of the desired phases in precise proportions (Bullard, 2015; Dolenc et al., 2020; Ono, 1981). The clinker is transferred to silos for storage until grinding (Figure 2.2).

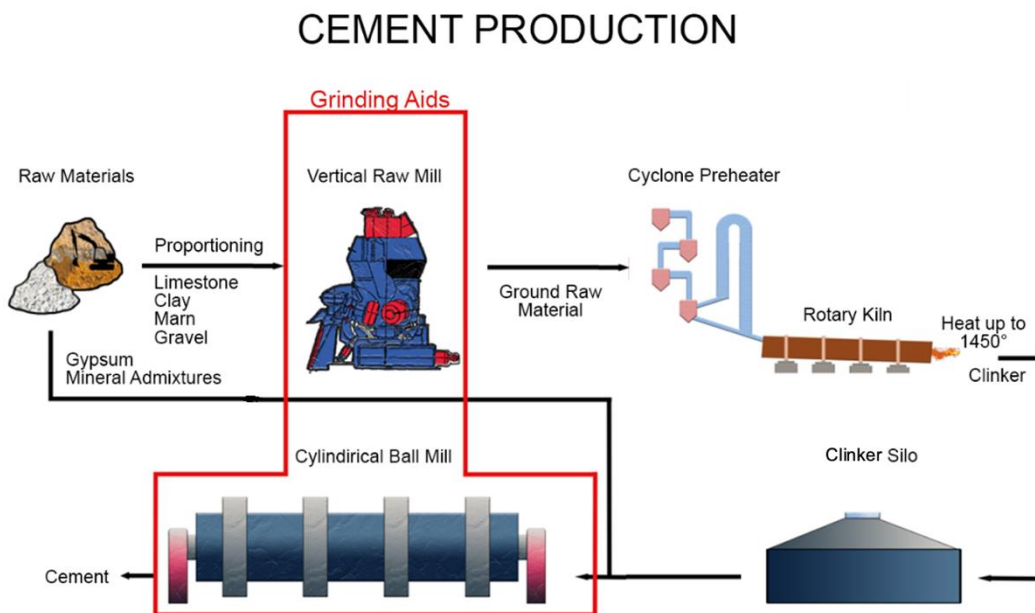


Figure 2.2. Schematic description of cement production

### 2.1.2 Grinding Process

Grinding is one the most vital processes of cement production. Two-thirds of the electrical energy used in cement production is spent on crushing and grinding of raw materials, clinker, and coal, as can be seen in Figure 2.3 (Schneider et al., 2011). The cement should be fine enough to react with water. The clinker is mixed with gypsum and ground together inside the grinding mill. Several types of mills are used in the cement industry: grinding media mills, roller mills, high-pressure mills, etc. (Aydođan & Benzer, 2011; Jankovic et al., 2004; L. Li et al., 2023; Pareek & Sankhla, 2021). Grinding media mills, in other words, cylindrical ball mills, are the most widely used mill type (V. K. Singh, 2023).

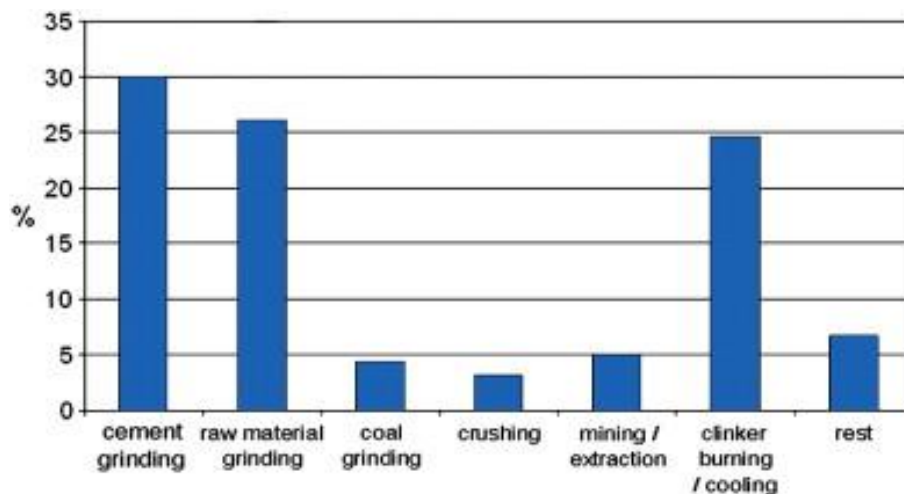


Figure 2.3. Electrical energy consumption during cement production (Schneider et al., 2011)

Cylindrical-shaped ball mills are hollow and have metal balls in different shapes and sizes. They also have multiple chambers inside. In the first chamber, larger steel balls are used for grinding because the raw meal is initially coarse. A diaphragm, shown in Figure 2.4, separates the chambers and allows finely ground particles to pass the second chamber but keeps the coarser ones until they can pass through. The second

chamber includes smaller balls to further grind the particles that pass through the diaphragm. The number of chambers can be more than two (V. K. Singh, 2023). Because the material is classified inside the mill, continuous feeding can be possible. Therefore, the grinding can be maintained as a continuous process (Aydoğan & Benzer, 2011).

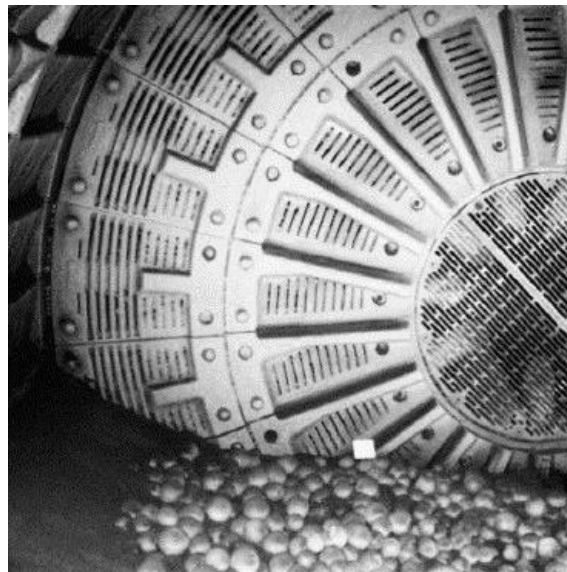


Figure 2.4. The diaphragm divides two chambers (Jankovic et al., 2004)

The clinker grinding stage is responsible for one-third of the energy consumption during cement production (Schneider et al., 2011). Thus, saving energy in this stage is vital to reduce energy consumption in cement production. Engineers have worked on optimizing the cement grinding stage (Jankovic et al., 2004; Touil et al., 2006; Tsamatsoulis & Lungoci, 2010). In addition, GAs can be used to ease the grinding process.

Clinker compounds have different mechanical properties (Campbell, 1999). Consequently, the grindability of the clinker is directly linked to the mineralogical composition (Frigione et al., 1983; Gouda, 1979). The composition of the clinker can

be deliberately manipulated to enhance the grinding process. However, this method would change other properties of the cement, the final product, such as grindability, the heat of hydration, and early and standard strengths (Erdoğan & Erdoğan, 2014). On the other hand, in most conditions, available raw materials from the economic point of view are the limiting factor for cement's chemical constitution.

GAs, other facilitators, are also used to modify the particle behavior of ingredients of grinding materials, especially the clinker (Katsioti et al., 2009; Mishra & Zurich, 2014; Prziwara et al., 2018; Prziwara & Kwade, 2020, 2021).

## **2.2 Cement Grinding Aids**

GAs are needed for dry grinding in many industries, such as ceramics as well as cement production. These substances provide finer grinding using the same energy, increased production capacity, and energy saving in the same grain fineness. It is also exhibited that GAs avoid agglomeration inside the grinding mill, so avoid coating chamber walls, diaphragm, and balls (Figure 2.5).

Studies also have demonstrated that GAs can manipulate the chemical behavior of the cement and affect the mechanical properties of cement paste (Anitha et al., 2016; Çallı & Pehlivan, 2019; Gartner & Myers, 1993; Han et al., 2015; He et al., 2021; Heren & Ölmez, 1996; Hewlett et al., 2019; Huang et al., 2016; Huang & Shen, 2014; Katsioti et al., 2009; W. Li et al., 2015; Ma et al., 2015, 2019; Mishra & Zurich, 2014; Prziwara & Kwade, 2020; Riding et al., 2010; Roskopf et al., 1975; Sun et al., 2016; Wang et al., 2022). On the other hand, the dispersion of cement particles in the fresh matrix enhances the workability because the water requirement is reduced to gain sufficient lubrication (Assaad & Issa, 2015).

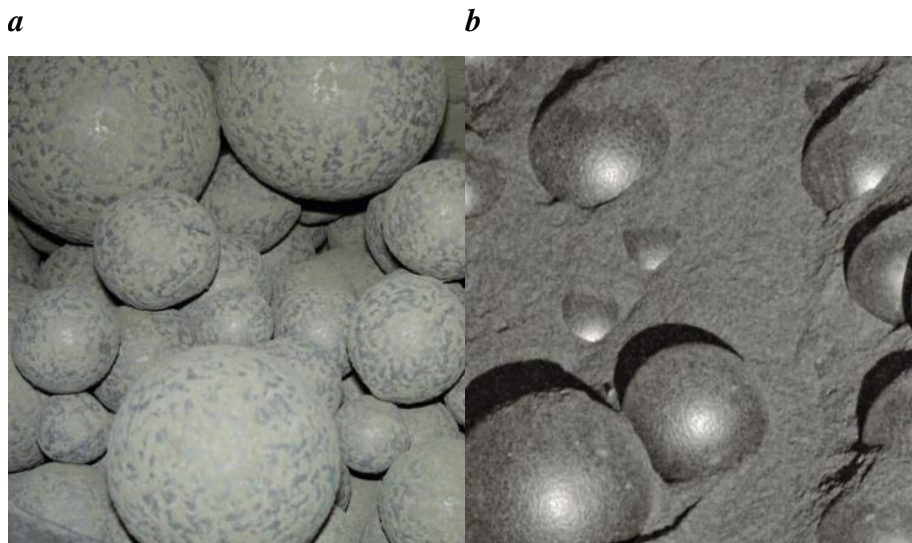


Figure 2.5. Ball coating a) without and b) with GAs (Mishra & Zurich, 2014)

### 2.2.1 History

The history of the invention of the GAs dates back to the 1930s (Rehbinder, 1931). Many scientists have put forward various theories about the working mechanisms of GAs since their industrial use. This section discusses the historical development of these studies chronologically. In the early 1930s, Rehbinder's (1931) theory was accepted. In the 1960s, Mendular and Wightman (1961) and Westwood (1966) proposed a theory about the working mechanisms of GAs that differed from Rehbinder's theory. In the following years, both theories were refuted by some indirect studies. Finally, the computer models developed in recent years have changed the way the working mechanisms of GAs are understood.

The facilitating effect of GAs is initially explained by liquid GAs altering the surface charges (Rockwood, 1939). However, the effectiveness of non-ionic GAs disproved this idea. Besides, the impact of surface-active substances, in other words, surfactants, is studied by Rehbinder (1931), who claimed that the surfactants adsorb onto the surface and reduce the surface hardness of the milling material, which is named the “Rehbinder effect” (Boozer et al., 1963; El-Shall & Somasundaran, 1984; Prziwara & Kwade, 2020; Rehbinder, 1931).



It is proven and patented that GAs increase the formation of powder form during grinding. The fineness increases with particle dispersion and agglomeration reduction is described (Kennedy & Mark, 1935). GAs also prevent ball coating, as can be seen in Figure 2.5. Thus, they keep the grinding media clean, which increases the grinding effectiveness (Boozer et al., 1963; El-Shall & Somasundaran, 1984; Prziwara & Kwade, 2020; Rehbinder, 1931).

In subsequent studies, the polarity of the GA is attributed to its grinding performance. It is shown that polar molecules surpass non-polar GAs (Mardulier & Wightman, 1961). It is also shown that in contrast to the Rehbinder effect, polar molecules cover the particle surface and reduce the surface energy. Thus, the interparticle adhesion forces reduce, which leads to dispersion and flowability effectiveness in powder form through a decrease in agglomeration (Prziwara & Kwade, 2020).

Another theory has claimed that the grinding aid molecules manipulate the plastic behavior of solid particle surfaces, blocking the dislocation motion (Westwood & Goldheim, 1970; Westwood & Stoloff, 1966). This theory contrasts with the Rehbinder effect. In contrast to the Rehbinder effect, the Westwood effect explains the underlying mechanisms of GAs that reduce the plasticity of the solid surface. Since its inception, this theory has raised doubts among scientists. This is because brittle material behavior is common in most grinding processes in ball mills. However, this theory has claimed that GAs manipulate the plastic behavior of the material (Prziwara & Kwade, 2020).

During the grinding, particles are subjected to dynamic forces instead of static forces. In another study, crack propagation velocities due to the impact are measured (Schonert, 1972). The Rehbinder and Westwood effects were indirectly disproved because the propagation velocity of surfactants (Blake, 2006) cannot reach the crack propagation velocity and cover the crack surface (Prziwara & Kwade, 2020).

The clinker minerals have different crystal dimension ranges (Campbell, 1999). On the other hand, agglomeration increases as the fineness increases. Thus, clinker can be ground until it reaches a specific fineness. That phenomenon is called the grinding

limit. In subsequent studies (Dombrowe et al., 1982; Scheibe, 1978), it is exhibited that GAs can shift the grinding limit toward a finer product and avoid coating of the grinding media mill balls (Figure 2.5) and interior walls by the reduction of agglomeration (Prziwara et al., 2018; Prziwara & Kwade, 2020).

More recent studies (Mishra, 2012; Mishra et al., 2013) have verified this effect. Mishra (2012) and Mishra et al. (2013) developed computer models to simulate the molecular behavior of GAs on cement surfaces. The models showcase that GAs cover the surface and reduce adhesion forces, decreasing the inter-particle agglomeration energy. Thus, it facilitates the pulverization of cement (Mishra & Zurich, 2014; Prziwara & Kwade, 2020).

### **2.2.2 Underlying Mechanisms**

The critical function of the GA should be known to determine its dosage. The adsorption of GAs was modeled (Mishra, 2012; Mishra et al., 2014). Mishra (2012) and Mishra et al. (2014) suggested that the dosage of the GA is essential in terms of the molecular adsorption layer thickness. According to their model, the surface coverage should be 50-100% (at least 50% of the surface should be surrounded to prevent the contact of two uncovered points in two particles) (Mishra & Zurich, 2014).

The performance of GAs from various points of view is tested in different dosage ranges (Fraser, 2003; Heren & Ölmez, 1996; Katsioti et al., 2009; Kobya et al., 2022; W. Li et al., 2015; Ma et al., 2019; Mishra et al., 2012; Sun & Liu, 2016; Teoreanu & Guslicov, 1999; Toprak et al., 2020; Wang et al., 2022). It cannot be inferred from these studies that there are strict limits or optimum dosages. However, the under dosage can be insufficient, and the overdosage results in the lubrication effect. GAs reduce friction enormously. Thus, abrasive grinding is not able to take place owing to the reason that raw material and mill balls glide on each other's surface (Deckers & Stettner, 1979; Mishra & Zurich, 2014).

### **2.2.2.1 Dispersion**

Grinding media mills are fed with clinker, gypsum and, if used, other ingredients such as limestone and additives such as GAs. Ball mills supply a homogenous blend alongside grinding. The dispersion of GAs in the grinding media mills happens in that way. In addition, the high frictional heat generated by abrasive grinding increases the temperature in the mill. Therefore, some amount of the GA inside the mill evaporates with volatility and disperses (Mishra & Zurich, 2014).

### **2.2.2.2 Hydroxylation**

Water is a coolant to decrease the grinding temperature (Mishra & Zurich, 2014). Coolant water and moisture absorbed by the raw meal cause hydroxylation. Hydroxylation is a phenomenon in which water molecules stick on the clinker surface due to the polarity of water and clinker particles. This phenomenon paves the way for reduced adhesive forces (Mishra & Zurich, 2014; Prziwara & Kwade, 2020).

### **2.2.2.3 Surface Energy**

Solids and liquids contain countless internal forces resulting from the interaction between atoms, molecules, and ions. These forces cancel out each other except closer ones to the surface. Because the forces near the surface do not neutralize one another, solids have surface energy, and liquids have surface tension (Mishra & Zurich, 2014).

Surface tension affects the droplet shape of a liquid on a solid surface. As the surface tension increases, the molecules cluster together and the droplet shape becomes more rounded. However, the liquid wets the surface if the surface tension and surface energy are close to each other (Blake, 2006). Polar groups of the GA interact with the hydroxylated electrostatic surface. Carbon chains of GA, which are non-polar, lie on the top layer of particles and decrease the surface tension. Moreover, the GA

nullifies the surface energy on the outermost layer of the solid. Thus, the interaction between solid particles decreases, as shown in Figure 2.6 (Jeknavorian et al., 1998; Mishra & Zurich, 2014; Teoreanu & Guslicov, 1999; Toprak et al., 2020).

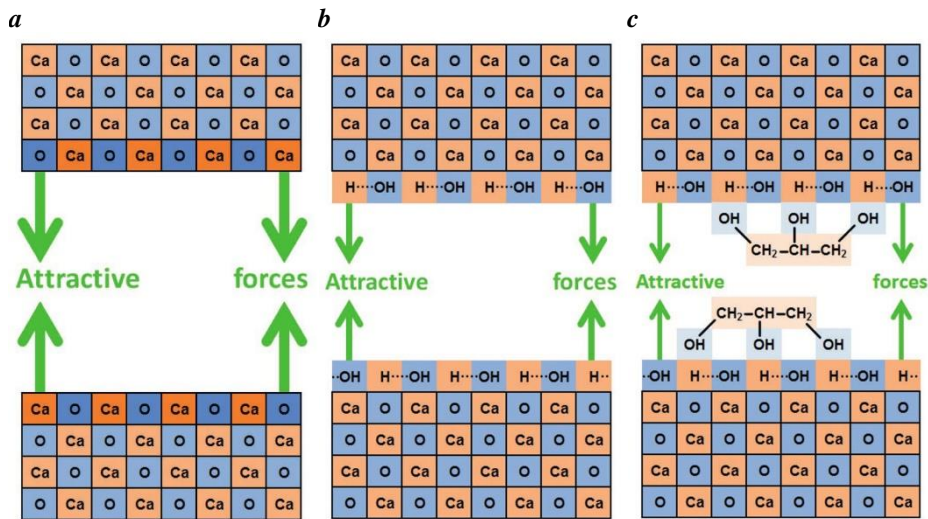


Figure 2.6. Attractive forces between surfaces a) without hydroxylation and GAs, b) with hydroxylation, and c) GA (thickness of attractive force arrows represents the magnitude) (Mishra & Zurich, 2014)

### 2.2.3 Grinding Chemicals

GAs include asserted organic and inorganic chemicals. Organic chemicals are the focus of this study. Thus, organic GCs will be discussed under that heading. As mentioned above, the role of organic GCs is to reduce surface energy. Therefore, the organic substance should have a low surface tension to act as a grinding aid. The performance of GAs consisting of mixtures of these chemicals may differ from the performance of the chemicals they contain. Therefore, optimization of the mixture plays a crucial role (Akalin, Akay, & Sennaroğlu, 2010; Akalin, Akay, Sennaroğlu, et al., 2010; Toprak et al., 2014). Toprak et al. (2014) showed that GAs can outperform GCs with the synergetic effect. On the other hand, Akalin, Akay, and Sennaroğlu (2010) and Akalin, Akay, Sennaroğlu et al. (2010) discussed the

antagonistic effect in addition to the synergetic effect. According to these studies, a mixture containing different chemicals can have higher performance, which means a synergetic effect, or lower performance, which means an antagonistic effect, than its constituent chemicals.

These selected organics will be grouped and discussed: Alkanolamines, which include MEA, TEA, TIPA, DEIPA, and THEED; Polyols, which include MEG, PG, Glycerol, DEG, and PEG 400; Antifoams; and Polycarboxylate Ethers.

### **2.2.3.1 Alkanolamines**

Alkanolamines are organic substances composed of an alkane chain, hydroxy, and amino substituents (Figure 2.7). Alkanolamines find widespread utilization in various industries, such as biochemistry, cosmetics, and pharmacology, in addition to the cement industry. Alkanolamines are employed to take advantage of as foaming agents, pH adjusters, lubricants, and pharmaceutical ingredients due to their ability to remove acidic gases from a solution and wetting properties (Headley et al., 2002; Kavita et al., 2022).

#### **2.2.3.1.1 Monoethanolamine**

Monoethanolamine (MEA) is a simple alkanolamine. The molecular structure can be seen in Figure 2.7.a. MEA increases the grinding performance and is industrially used as a GA (Hao et al., 2017). However, MEA reduces the surface tension of water if it dissolves (Han et al., 2012). A study using MEA as a CA in white Portland cement (Heren & Ölmez, 1996) has shown that it retards the hydration of cement. However, this research cannot evaluate MEA's effect on ferrite because white cement is used.

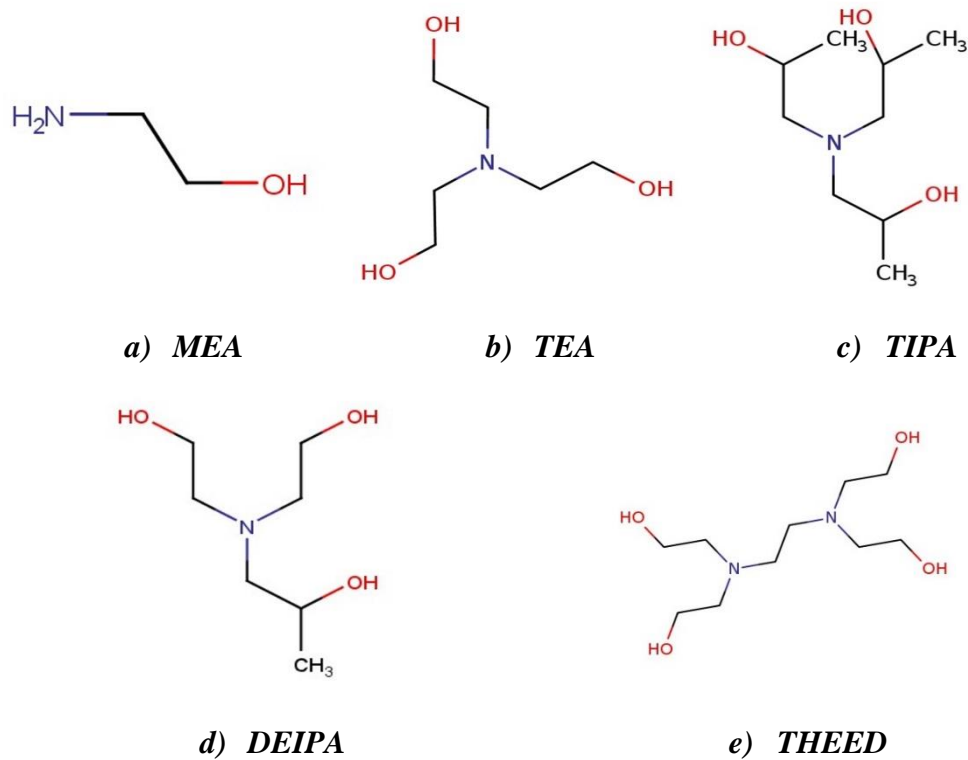


Figure 2.7. Molecular structures of alkanolamines

### 2.2.3.1.2 Triethanolamine

Triethanolamine (TEA) is a tertiary alkanolamine. The molecular structure can be seen in Figure 2.7.b. TEA is among the most common GAs (Jardine, 2003; Sun & Liu, 2016; Sverak et al., 2013). Besides, it is used as an accelerator/retarder. Its dosage changes whether it acts as an accelerator or retarder (Dodson, 1990; Fraser, 2003; Katsioti et al., 2009).

The effect of TEA on hydration was evaluated in earlier studies (Gartner & Myers, 1993; Han et al., 2015; Heren & Ölmez, 1996; W. Li et al., 2015; Roskopf et al., 1975). TEA retards the hydration, according to Roskopf et al. (1975) and Heren and Ölmez (1996), as it accelerates, according to Gartner & Myers (1993), Han et al. (2015), and W. Li et al. (2015).

The mineralogical composition of the cement is vital in terms of the impact of TEA on the hydration of the cement, in addition to the impact of dosage Dodson (1990) revealed. TEA is a retarder for the hydration of alite. On the other hand, TEA interrupts the reaction mechanisms between tricalcium aluminate and gypsum. Therefore, TEA accelerates the hydration of tricalcium aluminate (Hewlett et al., 2019).

### 2.2.3.1.3 Triisopropanolamine

Triisopropanolamine (TIPA) is a tertiary alkanolamine. The molecular structure can be seen in Figure 2.7.c. TIPA, in addition to being a common GA, increases strength in late age, but its effect can be ignored in early age (Huang & Shen, 2014; Katsioti et al., 2009; Kobya et al., 2022; W. Li et al., 2015). Studies were conducted to explain the ultimate strength increase. The chemical aspect of the effect of TIPA is linked to the hydration of ferrite and AFm formation (Gartner & Myers, 1993; Huang et al., 2016; Huang & Shen, 2014).

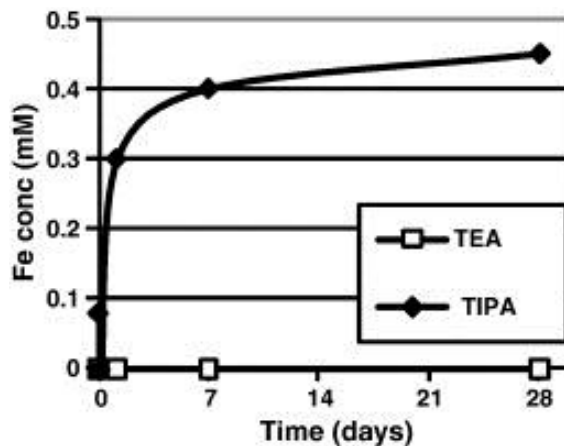


Figure 2.8. Iron concentration of cement paste pore solution with 200 g/t TIPA and TEA (Cheung et al., 2011; Sandberg, 2003)

TIPA increases iron solubility with the iron-amine “complexation.” (Cheung et al., 2011; Sandberg, 2003). This phenomenon is the formation of chemical complexes bonding at least two molecules or ions to constitute a stable unit. Cheung et al. (2011) demonstrated that the iron concentration in the pore solution of cement paste contains 200 g/t TIPA from the data Sandberg (2003) obtained (Figure 2.8). Gartner and Myners (1993) claimed that ferrite contributes to the AFm formation as well as the tricalcium aluminate. This “facilitated transform” leads to more hydration products, which promotes the ultimate strength of the paste.

#### **2.2.3.1.4 Diethanolisopropanolamine**

Diethanolisopropanolamine (DEIPA) is a novel type of alkanolamine (W. Li et al., 2015; Wang et al., 2022). The molecular structure can be seen in Figure 2.7.d. DEIPA is used as an accelerator as well as a GA (Jardine, 2003). It is shown in earlier studies (W. Li et al., 2015; Ma et al., 2015; Riding et al., 2010; Wang et al., 2022) that DEIPA accelerates the hydration of Portland cement. In contrast to these studies, Kobya et al. (2022) have shown that DEIPA reduces hydration at early ages but enhances strength at late ages.

Wang et al. (2022) obtained some proof that DEIPA promotes the consumption of gypsum, so the hydration of tricalcium aluminate and ferrite and AFm formation is accelerated. W. Li et al. (2015) exhibited that DEIPA facilitates the amorphization of gypsum with XRD and FT-IR results. In addition, Riding et al. (2010) and Ma et al. (2015) reveal that DEIPA advances the hydration rate of tricalcium aluminate and ferrite and the phase transformation of AFt to AFm.

Also, Wang et al. (2022) explain the acceleration of alite and belite hydration with the complexation effect. They claimed that the complexation of DEIPA with  $\text{Ca}^+$  ions increases the solubility of the ions. Riding et al. (2010) and Ma et al. (2015) have shown that portlandite formation was reduced. Ma et al. (2015) revealed that AFm and C-S-H gel leads to a pore refinement and porosity decrease.



#### **2.2.3.1.5 Tetrahydroxyethylethylenediamine**

Tetrahydroxyethylethylenediamine (THEED) is an alkanolamine containing four hydroxyl and two amine groups. The molecular structure can be seen in Figure 2.7.e. THEED is used as a GA like other alkanolamines discussed above (Jardine, 2003; W. Li et al., 2015; Liu et al., 2020; Ma et al., 2019).

The effect of THEED on cement hydration was investigated (W. Li et al., 2015; Ma et al., 2019). W. Li et al. (2015) and Ma et al. (2019) have revealed that THEED accelerates cement hydration. Ma et al. (2019) have conducted an XRD analysis of hydrated cement pastes with different dosages of THEED. In these studies, it is observed that the AFt phase decreases and the AFm phase increases when the dosage increases, so it can be inferred that THEED accelerates the phase transfer of AFt to AFm. They have attributed the strength development effect of THEED to this.

#### **2.2.3.2 Polyols**

Polyols are organic compounds, including multiple hydroxy groups. The molecular structure of some polyols can be seen in Figure 2.9. Diols (containing two hydroxyls) and triols (containing three hydroxyls) are primarily used in the cement industry. Diols and their derivatives are utilized in polymer, food, and pharmacology industries (Vivek et al., 2021). As for the triols, glycerol is the most common one. The utilization of glycerol, a by-product commonly found in related industries alongside diols, is frequently encountered. (Mohan & Long, 2021).

##### **2.2.3.2.1 Monoethyleneglycol**

Monoethyleneglycol (MEG) is a diol. Its molecular structure can be seen in Figure 2.9.a. MEG is used in the cement industry as a GA. It is shown that the adsorption of MEG reduces the adhesive forces on the cement particle surface (Prziwara &

Kwade, 2020; von Seebach, 1969) and increases the specific surface area when used as a GA (Çallı & Pehlivan, 2019; Teoreanu & Guslicov, 1999).

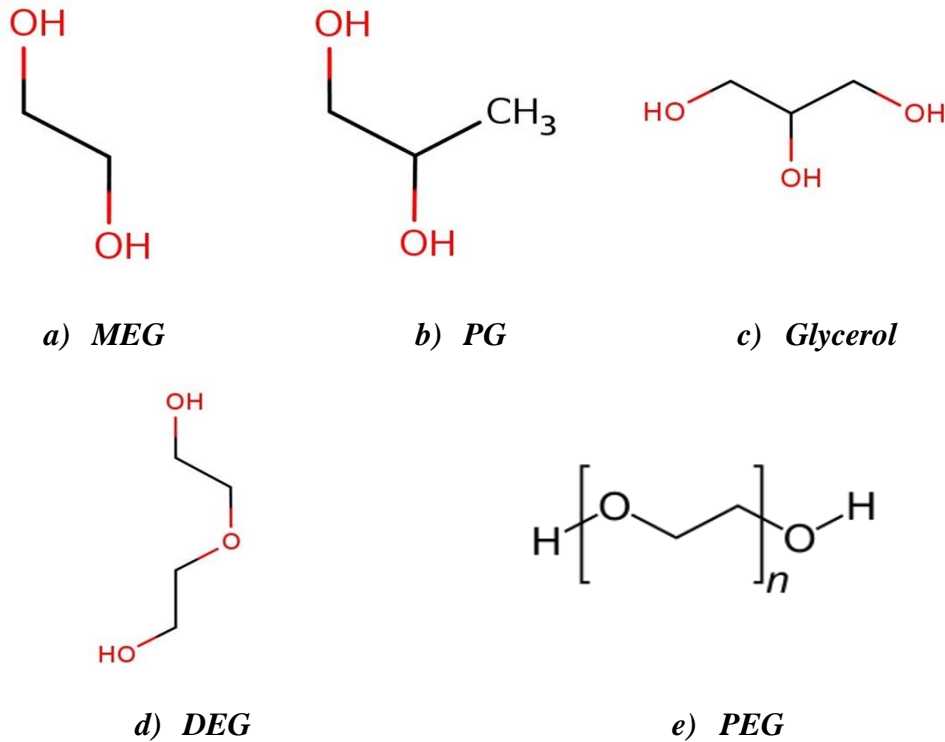


Figure 2.9. Molecular structures of polyols

Çallı et al. (2019) also revealed that MEG increases the compressive strength of mortar samples. Furthermore, other researchers (Kobyta et al., 2022) investigated the mechanical properties of hydrated cement mortar ground with MEG but can demonstrate no significant effects. However, in a further earlier study (Chalasanı et al., 2009), in lower dosages like 200 g/t or 400 g/t, which is similar to the dosages of GAs, XRD results showed that MEG involved in the C-S-H gel and changes the gel phase microstructure. However, a significant literature gap exists in understanding how MEG affects cement hydration.

#### **2.2.3.2.2 Propyleneglycol**

Propyleneglycol (PG) is another diol used as a GA (Teoreanu & Guslicov, 1999). The molecular structure can be seen in Figure 2.9.b. PG is also used in higher dosages in comparison to the dosage used as a GA in mineral trioxide aggregate (MTA), which is a dental root repair material containing Portland cement, to improve the strength and decrease the solubility, setting time and permeability of the material (Marciano et al., 2016; Natu et al., 2015).

PG also has the potential to modify the hydration process of cement in addition to the fineness or specific energy consumption when used as a GA (Sun & Liu, 2016). Sun and Liu (2016) described the effect of PG on strength development with hydration rate retardation. PG bonds with oxides of hydrates and water with its hydroxy groups and forms a membrane layer on cement. Therefore, C-S-H gels form slower initially, leading to a better packing of gels, resulting in a lower porosity.

#### **2.2.3.2.3 Glycerol**

Glycerol is a triol, and its molecular structure can be seen in Figure 2.9.c. It is also a by-product of soap, fatty acid, and biodiesel manufacturing facilities. It is an economic substance due to oversupply (Anitha et al., 2016). Glycerol's ability to surface energy modification of solids allows it to be used as a GA (Parvulescu et al., 2011; Xi et al., 2012).

Glycerol can affect the hydration process like other GAs. A study shows that glycerol slightly increases early and late-age compressive strengths (Zhang et al., 2016). Another research is carried out on the cement treatment of glycerol-contaminated soils (Estabragh et al., 2016). Estabragh et al. (2016) showcased that glycerol contamination in smaller dosages than excessive dosages compared to a GA dosage increased the effect of cement on soil stabilization. However, the effect of glycerol on cement hydration is not well understood at present.

#### **2.2.3.2.4 Diethyleneglycol**

Diethyleneglycol (DEG) is an organic substance of two ethanol bonding with an ester group. The molecular structure can be seen in Figure 2.9.d. It is shown in earlier studies that DEG reduces surface energy and increases the fineness and flowability of cement powder (Prziwara et al., 2019). DEG is also a shrinkage-reducing admixture (Ran et al., 2015).

Çallı et al. (2019) showcased that DEG improves early-age strength but decreases late-age compressive strength. On the contrary, the research results of Kobya et al. (2022) indicate that DEG decreases compressive strength in the early stages. Its effect changes as the curing duration increases. Furthermore, it affects the standard strength positively, 1, 3, and 7-day strength negatively in 250, 500, 750, and 1000 g/t dosages. In addition, Fraser (2003) conducted experiments on the hydration of pure ferrite phase ground with DEG and revealed that it retards hydration. Like MEG, the effect of DEG on the hydration of cement is not well studied yet.

#### **2.2.3.2.5 Polyethyleneglycol 400**

Polyethyleneglycol (PEG) is a polymer derived from ethylene oxide groups, including hydroxy in two ends, as shown in Figure 2.9.e. The number of ethylene oxide groups varies. PEG with approximately 400 g/mol is called PEG-400. The mean number of ethylene glycol groups is between 8.2 and 9.1.

PEG-400 is a self-curing agent, shrinkage-reducing admixture, dispersant, and superplasticizer (Ran et al., 2015; K. Singh, 2021; Yang et al., 2020). In another study (Tao et al., 2014), PEG-400 is copolymerized with maleic anhydride and acroleic acid. As a result of this study, positive effects of these polymers on specific surface area and compressive strength are observed. However, the effect of PEG-400 on cement and mortar properties when used as a GA by itself is a literature gap.

### 2.2.3.3 Antifoams

Foam is bubbles in a liquid occurring with the dispersion of gas inside. As discussed below, the water surface shows a different property because the intermolecular attraction forces differ. Amphipathic substances insoluble in water can dissolve on the water's surface and undergo adsorption, forming monolayers. AFs and defoamers dissolve on the surface of the liquid, reduce the surface tension, and create a barrier on the surface. If the substance is used to prevent foaming, it is called an AF. However, if it is used to reduce foam that has already formed, it is called a defoamer. Therefore, they destabilize foam bubbles and supply collapse of foams and foam formation avoidance (Ross, 1996).

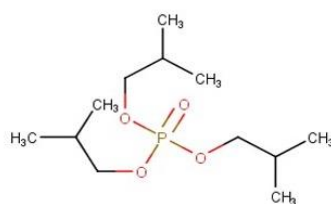


Figure 2.10. Molecular structure of TIBP, an antifoam agent

Triisobutylphosphate (TIBP) is an organophosphate. The molecular structure can be seen in Figure 2.10. TIBP is utilized as an antifoaming agent. Organophosphates are also used as plasticizers (Pantelaki & Voutsas, 2019). On the other hand, they are the strongest retarders (Mansouria et al., 2021). The retardation effect of these compounds is reported, despite the underlying mechanism cannot be fully understood (Al-Yami et al., 2017).

#### 2.2.3.4 Polycarboxylate Ethers

PCEs are polymers that contain polyoxyalkylene, in particular, polypropylene and polyethylene glycol functional groups. PCEs are used as superplasticizers and water reducers (Hewlett et al., 2019; Sun et al., 2016). PCE-based superplasticizers were developed in 1981 (Sha et al., 2020). PCE disperses the cement particles attaching to the charged surface through their carboxylate groups. The hydrophilic side chains elongate towards the surrounding water. Therefore, they generate a repulsive force and supply fluidity to the fresh concrete (Cadix & James, 2022). The molecular structure can be seen in Figure 2.11.

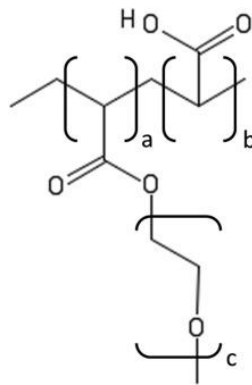


Figure 2.11. Molecular structure of polycarboxylate (Cadix & James, 2022)

Due to their adsorption and dispersive properties, PCEs are used as GAs (Cheung et al., 2015; Pakusch et al., 2012; Prziwara & Kwade, 2021; Sun et al., 2016). The adsorption energy is calculated by a computational model (Mishra et al., 2012). Mishra et al. (2012) compared the GA performance of PCEs with TEA and TIPA. It is found out that their performances are alike. Moreover, experimental studies (He et al., 2021; Sun et al., 2016; Toprak et al., 2014) have revealed that PCEs modify the particle size distribution (PSD) and mechanical properties when used as a GA. He et al. (2021) and Sun et al. (2016) have shown that PCEs increase the fineness

and heat of hydration rate. Toprak et al. (2014) have shown that GAs containing PCEs enhance the diaphragm by-pass and production capacity.





## CHAPTER 3

### EXPERIMENTAL PROGRAM

The study is carried out in three phases. In phase 1, GCs and clinker are used and the effect of each GC on fineness, consistency, and compressive strength is investigated. In Phase 2, ordinary Portland cement and GCs are used to investigate the chemical effect of GCs on the consistency and mechanical properties of fresh cement mortar. In phase 3, GAs are used with clinker, and the synergetic effect of the GCs is evaluated.

In Phases 1 and 3, Blaine fineness, air-jet sieving, flow table, and early and standard compressive strength tests are carried out on the Control group to demonstrate the effect of Blaine fineness on these parameters and the specific energy consumption during grinding.

Regressions are calculated between these parameters except for standard compressive strength. Specific energy consumption, consistency, and early age compressive strength values can be calculated from these regressions for each Blaine value. This allows the effect of GC and GA to be shown independently of cement fineness.

Blaine fineness, air-jet sieving, flow table, and early and standard compressive strength evaluations are carried out for the other cement groups. The results are compared with the Control cement to show the effect of GCs on constant energy consumption. In addition, the effect of GCs on constant fineness can be shown by comparing the results with the data calculated from the regressions.

Finally, in Phase 2, cement mortars are prepared with Portland cement. GCs are used as CAs. The consistency and mechanical properties are compared with the Control sample prepared without GCs to show the effect of GCs on constant fineness. The

following sections describe the materials and methods used in the experimental program. The experimental program is shown in Table 3.1.

Table 3.1. Experimental Program

	<i>Phase 1</i>	<i>Phase 2</i>	<i>Phase 3</i>
Cement	Ground Clinker and Gypsum	Ordinary Portland Cement	Ground Clinker and Gypsum
Additives/Admixtures	GCs are used as Additive During Grinding	GCs are used as Admixture During Mortar Mixture	GAs are used as Additive During Grinding
Air Jet Sieving	X	X	X
PSD	X	X	
Blaine Fineness	X	X	X
Isothermal Calorimetry	X		
Flow Table Test	X	X	X
Compression Test	X	X	X
Statistical Analysis	X	X	X
Estimation at Constant Fineness via Regressions	X		X

### 3.1 Materials

#### 3.1.1 Clinker

A single type of clinker is used as the raw material in Phase 1 and 3 of the study (Figure 3.1). The chemical analysis provided by the cement plant is shown in

Table 3.3. The mineralogical composition is calculated using Bogue's formulae (Table 3.2). XRD analysis is also carried out using an Olympus BTX III Benchtop XRD Analyzer available at the METU Civil Engineering Materials and Construction

Laboratory, as shown in Figure 3.2. The density of the ground pure clinker is 3.19 g/cm<sup>3</sup>. Its density with 5% gypsum addition is 3.13 g/cm<sup>3</sup>. These are measured according to the appropriate standard using the Le Chatelier flask (Figure 3.7) (ASTM C 188, 2023).



Figure 3.1. Clinker

Table 3.2. Mineralogical composition of clinker

Compound	Amount (%)
C <sub>3</sub> S	69.13
C <sub>2</sub> S	11.05
C <sub>3</sub> A	7.67
C <sub>4</sub> AF	12.15

Table 3.3. Chemical composition of clinker

Oxides	Amount (%)
SiO <sub>2</sub>	20.59
Al <sub>2</sub> O <sub>3</sub>	5.10
Fe <sub>2</sub> O <sub>3</sub>	3.74
CaO	66.47
MgO	1.81
SO <sub>3</sub>	0.68
Cl	0.01
Loss on Ignition (LoI)	0.16
Insoluble Residue	0.15
Free CaO	1.71
Cr(VI)	0.001
Na <sub>2</sub> O	0.08
K <sub>2</sub> O	0.65
Na <sub>2</sub> OEq. (Na <sub>2</sub> O+0.658 K <sub>2</sub> O)	0.51

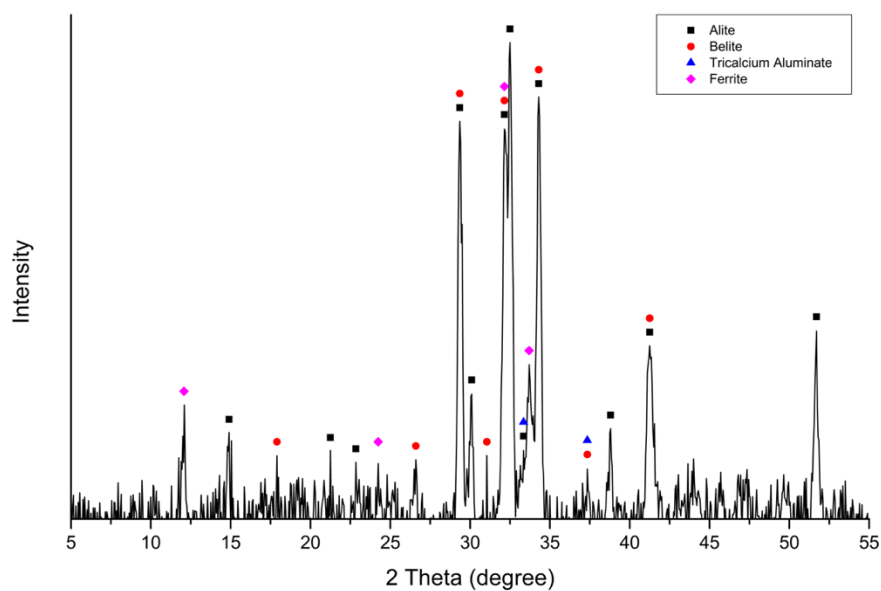


Figure 3.2. XRD pattern of clinker

### 3.1.2 Gypsum

A single type of gypsum provided from the same cement plant with the clinker is used in Phase 1 and 3 of the study (Figure 3.3). Similarly, the chemical analysis is provided by the cement plant, and XRD analysis is performed with Olympus BTX III Benchtop XRD Analyzer at the METU Civil Engineering Materials and Construction Laboratory, as seen in Figure 3.4 and Table 3.4. The density of the ground gypsum is measured to be  $2.31 \text{ g/cm}^3$  using the Le Chatelier flask (Figure 3.7) (ASTM C 188, 2023).

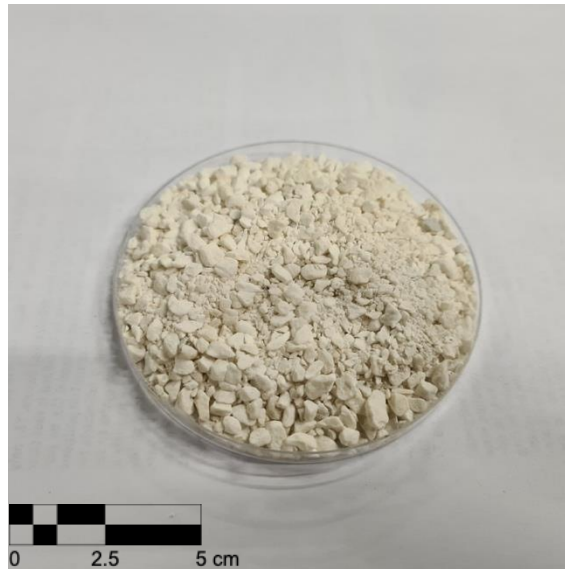


Figure 3.3. Gypsum

Table 3.4. Chemical composition of gypsum

Oxides	Amount (%)
SiO <sub>2</sub>	0.29
Al <sub>2</sub> O <sub>3</sub>	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.06
CaO	33.24
MgO	0.20
SO <sub>3</sub>	45.99
Free CaO	2.31
Cl	0.01
Na <sub>2</sub> O	0.10
K <sub>2</sub> O	0.03
SrO	0.22
TiO <sub>2</sub>	0.04
P <sub>2</sub> O <sub>5</sub>	0.51
Loss on Ignition (LoI)	20.35

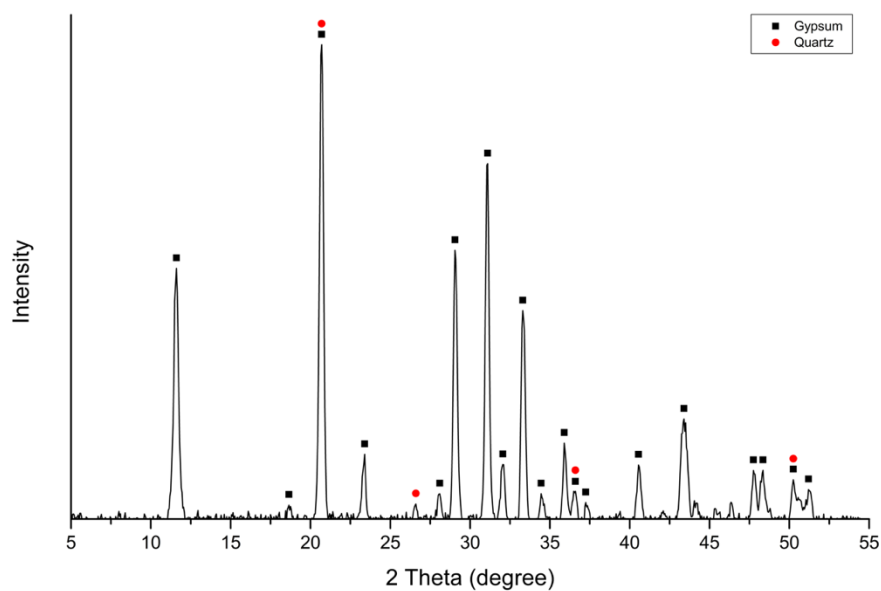


Figure 3.4. XRD pattern of gypsum

### 3.1.3 Cement

A commercially available Portland cement labeled as CEM I 42.5 R according to EN 197-1 is used in Phase 2. The XRD pattern is given in Figure 3.5. XRD analysis is conducted at the METU Civil Engineering Materials and Construction Laboratory. The chemical composition of Portland cement, provided by the cement manufacturer, is given in Table 3.5. The mineralogical composition, calculated from Bogue's formulas, is given in Table 3.6. The Blaine fineness of the Portland cement is measured as 3460 cm<sup>2</sup>/g. The Portland cement contains more alite, tricalcium aluminate, and less belite and ferrite than the clinker.

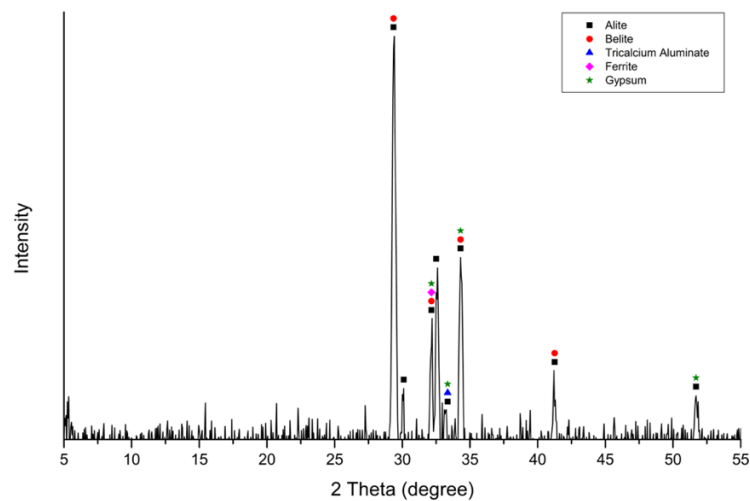


Figure 3.5. XRD pattern of the Portland cement

Table 3.5. Mineralogical composition of Portland cement

Compound	Amount (%)
C <sub>3</sub> S	72.24
C <sub>2</sub> S	8.98
C <sub>3</sub> A	8.52
C <sub>4</sub> AF	10.41

Table 3.6. Chemical composition of Portland cement

Oxides	Amount (%)
SiO <sub>2</sub>	18.32
Al <sub>2</sub> O <sub>3</sub>	4.48
Fe <sub>2</sub> O <sub>3</sub>	2.84
CaO	61.30
MgO	1.59
SO <sub>3</sub>	2.78
Cl	0.04
Loss on Ignition (LoI)	6.82
Na <sub>2</sub> O	0.28
K <sub>2</sub> O	0.81
Na <sub>2</sub> OEq. (Na <sub>2</sub> O+0.658 K <sub>2</sub> O)	0.81

### 3.1.4 Grinding Chemicals

15 GCs are used in this study. GCs are used in a 40% water solution of pure chemicals except antifoams. The chemicals are grouped into four. MEA, TEA, TIPA, DEIPA, and THEED are grouped as amine, MEG, PG, Glycerol, DEG, and MEG as Polyol, TIBP, AF-A and AF-B as Antifoam, PCE-A and PCE-B as PCE. Each GC, its group, dosage, molar mass, purity, pH, and density are listed in Table 3.7. AFs are insoluble in water, so we could not prepare them as 40% water solutions like others. In addition, the dosages are determined by Plustechno based on their previous experience. Molar mass, purity, pH, and density data are provided by Plustechno.



Table 3.7. Chemical properties and dosages of GCs

Group	Grinding Chemical	Dosage (g/t)	Molar Mass (g/mol)	Purity (%)	pH	Density (g/cm <sup>3</sup> )
Amine	MEA	400	61.08	99%	12.1	1.01
	TEA	400	149.19	≥85%	10.5-11.5	1.12
	TIPA	400	191.27	≥85%	10.0-11.0	1.00-1.02
	DEIPA	400	163.21	≥85%	10.0-11.0	1.08-1.09
	THEED	400	236.31	≥85%	-	1.10
Polyol	MEG	400	62.07	99%	6.0-7.5	1.11
	PG	400	76.09	99%	6.0-8.0	1.04
	Glycerol	400	92.09	70%	12.0	1.25
	DEG	400	106.12	99%	5.5-7.0	1.12
	PEG	400	~ 400.00	99%	-	1.13
Antifoam	TIBP	100	266.31	99%	2.0-4.0	0.96
	AF-A	100	-	-	4.0	0.99
	AF-B	100	-	-	4.5-7.5	1.00
PCE	PCE-A	400	-	-	6.5	1.04
	PCE-B	400	-	-	6.5	1.04

### 3.1.5 Grinding Aids

Seven commercially available GAs are used in Phase 3 of the study. GAs are labeled as GA-A to GA-G. The chemical properties and dosage levels of the GAs are listed in Table 3.8. The GAs are optimized and contain various GCs, as shown in Table 3.9. As they are commercially available, the exact formulas cannot be obtained.

Table 3.8. Chemical properties and dosages of GAs

Grinding Chemical	Dosage (g/t)	pH	Density (g/cm <sup>3</sup> )
GA-A	400	10.68	1.063
GA-B	400	11.37	1.041
GA-C	400	10.43	1.072
GA-D	400	11.70	1.050
GA-E	400	10.27	1.073
GA-F	400	7.12	1.040
GA-G	400	11.96	1.021

Table 3.9. Chemical content of grinding aids

Grinding Aid	Grinding Chemical			
	Amines	Polyols	Antifoams	Set Accelerators
GA-A	X	X	X	
GA-B	X			X
GA-C	X	X	X	
GA-D	X	X	X	
GA-E	X	X	X	
GA-F		X		
GA-G	X	X	X	

### 3.1.6 Sand

1350 g weighted and packed EN 196-1 standard sand is used for preparing mortar samples to be used in the flow table and compressive strength tests.

### 3.1.7 Water

Tap water from the Middle East Technical University network is used when preparing mortar samples. All the samples are cured in the lime-saturated water solution in a moist condition and at room temperature.

## 3.2 Methods

### 3.2.1 X-Ray Diffraction

XRD analysis is performed on clinker and gypsum to verify the raw material analysis result provided by the cement plant. Olympus BTX III Benchtop XRD Analyzer device (Figure 3.6) is used to obtain XRD patterns, which is available at the METU Civil Engineering Materials and Construction Laboratory. X'Pert HighScore Plus software and Crystallography Open Database are used for XRD data processing.



Figure 3.6. Desktop XRD device

### 3.2.2 Density and Fineness

The density of clinker, gypsum, and cement is determined using the Le Chatelier flask (Figure 3.7) according to the relevant standard (ASTM C 188, 2023) at the METU Civil Engineering Materials and Construction Laboratory. The flask is filled with kerosene, a liquid that does not react with clinker and cement and is not a solvent for gypsum. The flask is weighed and recorded. The flask is kept at room temperature. The liquid level is recorded every 15 minutes until three repeated readings are the same. The powdered material is then added to the flask and the flask is shaken (about 65 g for clinker and cement, 45 g for gypsum). The flasks are weighed again and recorded. This gives the net amount of material added. After 24 hours, the liquid level in the flask is read. The density is calculated from the net volume and the mass of the material.



Figure 3.7. Le Chatelier flask

The fineness of the cement is measured using the Blaine apparatus (Figure 3.8) in accordance with the relevant standard (ASTM C 204, 2023) at the METU Civil

Engineering Materials and Construction Laboratory. The density of the cement is used to calculate the mass to be placed in the Blaine cell.



Figure 3.8. Blaine apparatus

### 3.2.3 Air Jet Sieving

Rantek air jet sieving is used to obtain the particle size distribution of the cement, as seen in Figure 3.9. Firstly, 10 g of cement is sieved through 25 $\mu$ m apertured sieves. The residual part is weighed and sieved through 45, 50, 63, and 75  $\mu$ m apertured sieves, and residual parts are weighed in order. The percentage of passed cement for each sieve is calculated. The air jet sieving tests are conducted at the METU Civil Engineering Materials and Construction Laboratory.



Figure 3.9. Air jet sieving device

### 3.2.4 Isothermal Calorimetry

The heat of hydration of selected cements is measured for 72 hours in the Plustechno R&D laboratory. Cement paste is prepared from 50 g of cement and 25 g of water. Calmetrix I-CAL 400 HPC device is utilized for isothermal calorimetry tests, as shown in Figure 3.10.

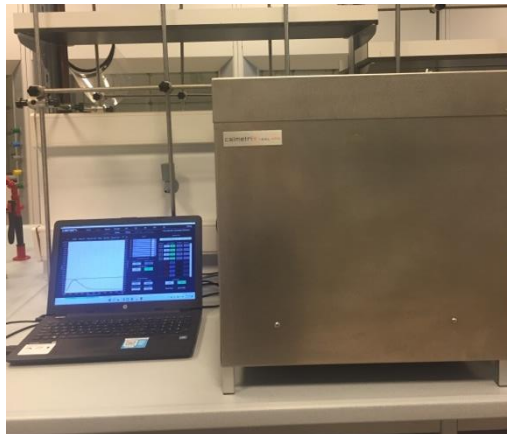


Figure 3.10. Isothermal calorimetry device

### **3.2.5 Particle Size Distribution**

In order to evaluate the fineness and the effect of grinding duration GCs on the particle size distribution, PSD analysis is conducted by the Turkish Cement Manufacturers Association (TCMA). Hopper apparatus and Mastersizer 2000 are used. Dry powder measurements are carried out using about 20 g of cement.

### **3.2.6 Scanning Electron Microscope**

The surface morphology of Control, THEED, MEG, PEG, and AF-A is investigated via scanning electron microscope (SEM) Quanta 400F Field Emission SEM device in the METU Central Laboratory. Energy dispersive X-ray (EDX) analysis is also conducted.

### **3.2.7 Flow Table**

The water-to-cement ratio of cement mortars is kept constant in the study. Therefore, the flow table test is applied to exhibit the effect of GCs and fineness on the consistency of fresh mortar at the METU Civil Engineering Materials and Construction Laboratory (ASTM C 230, 2021). The flow table is manually dropped 25 times in 15 seconds (Figure 3.11). The spread of the fresh cement mortar is recorded as a percentage increase in diameter. Flow table spread results are measured to an accuracy of 1 mm.



Figure 3.11. Cement mortar before (below) and after (above) spreading during the flow table test

### 3.2.8 Compressive Strength

Cement mortar samples are prepared to obtain the mechanical performance of all cement groups. 1350 g of sand, 450 g of cement, and 225 g of water are used in the mortar mixture. The mixing procedure conforms to the related standard (EN 196-1, 2016). An automatic mixer is used shown in Figure 3.12. After the flow table test, the mortar is added to the mixing bowl and mixed for 10 seconds.

The mortar is filled into the 50x50x50mm cube molds and compacted (ASTM C 109, 2021). The cube samples are demolded after 24 hours when the mortar is set. The samples are cured in lime-saturated water in room temperature condition till the compression test.





Figure 3.12. Automatic mixer

The UTEST UTCM-3742.FPR Automatic Cement Flexure/Compression Testing Machine is used to perform the compressive strength test, following the guidelines of ASTM C 109. Early age compressive strength is assessed using samples cured for two days, while standard compressive strength is evaluated using samples cured for 28 days. The coefficient of variation (CoV) is computed to maintain the reliability of the test outcomes. All samples with a CoV greater than 10% are discarded.

### 3.2.9 Statistical Analysis

In this study, Duncan's one-way analysis of variation (ANOVA) test is applied to the data obtained by Blaine and compression tests. SPSS software is used for statistical analysis. In Duncan's ANOVA test, all the data are sorted from the smallest to the largest according to the mean. Then the software compares two data sets starting from the smallest and calculates a significance. The software expands the subset until the significance of the subset is below the significance level, which in this study is set at 0.05. Then the software cuts off the subset and generates another one starting with the data set below.

### 3.3 Grinding Process

The raw materials are stored in a dry environment to save their chemical and physical properties during the experimental period. The clinker is crushed with a jaw crusher at the METU Civil Engineering Transportation Laboratory (Figure 3.13). Retsch PM 100 planetary ball mill is used as a grinding mill at the METU Civil Engineering Materials and Construction Laboratory (Figure 3.14).



Figure 3.13. Jaw crusher



Figure 3.14. Planetary ball mill



Figure 3.15. Clinker sieved and packed

After the clinker is crushed, the clinker particles are sieved using 0.25, 0.5, 1, 2, and 4 mm sieves to reduce the batch-to-batch variations in the grinding process. Residues are packed separately in plastic bags to prevent moisture (Figure 3.15). Raw materials residues over the 4 mm apertured sieve and passed through the 0.25 mm apertured sieve are discarded. Raw materials are used in the amounts shown in Table 3.10 to keep the initial particle size distribution similar. 294 g of raw material is used, with 100% clinker and 5% gypsum ratio in each grinding.

Table 3.10. Particle size distribution of raw material before grinding

Particle Size Range (mm)	<i>Clinker (g)</i>	<i>Gypsum (g)</i>
2.00-4.00	137.0	7.0
1.00-2.00	75.0	4.0
0.50-1.00	36.0	2.0
0.50-0.25	32.0	1.0

15 steel balls with a diameter of 15 mm and 99 steel balls with a diameter of 10 mm are used in this study, as shown in Figure 3.16. The raw material is prepared and put with the amounts as remarked in Table 3.10 into the jar with 0.5 l volume after the balls are placed inside. GC or GA is dropped with the automatic pipette shown in Figure 3.17 inside the jar, in 400g/t dosage for all GAs and GC groups except for the Antifoam group. GC is dropped 100 g/t dosage for the Antifoam group. The jar cap is closed and placed inside the planetary grinding mill, and the machine is turned on.



Figure 3.16. Steel balls in the jar of the planetary ball mill

The rotation speed of the jar is set at 400 RPM throughout the study. To reveal the effect of the fineness in and of itself on specific energy consumption, physical and mechanical properties of cement mortar in fresh and hardened conditions, and the relationship between them, a Control group of cement is ground without any GCs or GAs for different durations. Their specific surface area (SSA) values can be seen in Table 3.11. For other groups, 15 minutes of grinding is selected because it has provided the aimed fineness (about 3500 cm<sup>2</sup>/g Blaine fineness). Other cement groups are ground for 15 minutes at 400 RPM with GCs and GAs. All cements have

labeled the same as the GC or GA that they have ground with. Ground cements are packed in plastic bags and kept inside a plastic container.



Figure 3.17. Automatic pipette

Table 3.11. Cement labels of Control group

Cement Label	<i>Grinding Duration</i> (minutes)	<i>Grinding Speed</i> (RPM)	<i>SSA</i> ( $cm^2/g$ )
Control	15	400	3490
Control-16m	16	400	4110
Control-17m	17	400	4240
Control-18m	18	400	4530
Control-19m	19	400	4660
Control-20m	20	400	4860



## CHAPTER 4

### RESULTS AND DISCUSSIONS

This chapter presents the experimental results and their interpretation. As mentioned above, the effect of GCs and GAs on cement properties is analyzed in three phases. In the first phase, the effect of GCs on cement fineness, mortar consistency, early age, and standard compressive strength is evaluated at a fixed grinding time, i.e., constant energy consumption, and later at a constant fineness, using clinker ground in the laboratory. In the second phase, GCs are used as CA with Portland cement. The chemical effect of GCs on consistency and hydration is evaluated. Finally, in Phase 3, a similar experimental program to Phase 1 will be followed using GAs instead of GCs to evaluate the combined effect of GCs.

#### **4.1 Phase 1: The Effect of Grinding Chemicals on the Properties of Cement**

Fifteen different GCs are used in Phase 1. In this phase, the performance of pure chemicals is investigated at constant energy consumption and later estimated at constant fineness.

##### **4.1.1 Constant Energy Consumption**

During grinding, 280 g of clinker and 14 g of gypsum are ground together with GCs at 400 and 100 g/t to obtain 294 g of ground cement. Grinding was performed at least twice to obtain 550 g of cement in excess for mortar preparation. The Control cement without any of the GCs was also prepared. Using each of the ground cements, Blaine fineness or specific surface area (SSA), air jet sieving, particle size distribution (PSD), flow table, isothermal calorimetry, 2-day (early) and 28-day (standard) compressive strength results are obtained and the cements with GCs are compared

to the Control group. Scanning Electron Microscopy (SEM) analysis is also performed to observe the particle morphologies and validate the PSD analysis results. Later, the SSA, early and standard strength test results are grouped using Duncan's new multiple range test, a one-way ANOVA test, via SPSS software.

#### **4.1.1.1 Fineness**

Blaine fineness of cement samples is measured according to ASTM C 204 with an accuracy of  $\pm 10 \text{ cm}^2/\text{g}$ . The difference between batches for each cement does not exceed  $100 \text{ g}/\text{cm}^2$ . SSA and CoV values are given in Table 4.1. Blaine test results, Duncan subsets, and subset significances are given in Table 4.2. The significance level, which is the limit that the software cutoffs the subset and generate another subset, is appointed as 0.05. PSD and air jet sieve analysis using 25, 45, 50, 63, and  $75 \mu\text{m}$  sieves for each group is carried out to showcase the fineness difference.

According to Duncan's test presented in Table 4.2, if all cements are ranked from smallest to largest according to their SSA values, subset 1 contains only Control, subset 2 contains cements from DEIPA to PEG, subset 3 contains cements from PCE-A to TEA, subset 4 contains cements from TIPA to THEED, subset 5 contains cements from TIBP to MEG, and finally subset 6 contains cements from PCE-B to PG. Control is not grouped with any other cement. Thus, the analysis shows that all the GCs used are effective on the fineness. It is also clear from the PSD and air jet sieving curves that the GCs have shifted the curve upwards. This means that the smaller particles are more abundant compared to the Control. This explains the increase in fineness.

All the GCs have significantly increased the fineness of the cement, as observed in Figure 4.1. Overall, while TIPA and DEIPA cements and the Antifoam and PCE groups show a slight increase in fineness, the Polyol and Amine group seems to be more effective in terms of Blaine fineness increase.



Table 4.1. Blaine fineness of cements ground with GCs

Group	Cement Label	SSA ( $cm^2/g$ )	
		Mean	CoV (%)
Control	Control	3490	3.8
Amine	MEA	3940	1.8
	TEA	4010	1.8
	TIPA	3780	1.5
	DEIPA	3750	2.6
	THEED	4020	1.9
Polyol	MEG	4050	1.5
	PG	4100	0.3
	Glycerol	3960	1.5
	DEG	4020	1.4
	PEG	3960	4.4
Antifoam	TIBP	3830	3.7
	AF-A	3840	2.3
	AF-B	3910	3.6
Polyol	PCE-A	3770	4.7
	PCE-B	3910	1.8

Figure 4.2 and Figure 4.3 present the air jet sieve analysis and the PSD analysis results of all cements, while the dashed line shows the Control cement that does not incorporate any GCs. The detailed air jet sieving and PSD diagrams of each cement group are given in Appendix A. Both of these figures show that the incorporation of a GC during grinding increased the number of fine particles. Moreover, the increased number of fine particles can also be seen in SEM images of Control and MEG (Figure 4.4). Detailed SEM images of Control, THEED, MEG, PEG, and AF-A are given in Appendix B. Therefore, these results verify the Blaine fineness results.

Table 4.2. Blaine fineness and Duncan's ANOVA subsets of cements ground with GCs

Group	Cement Label	SSA ( $cm^2/g$ )	Subset						
			1	2	3	4	5	6	
<b>Control</b>	<b>Control</b>	<b>3490</b>	<b>X</b>						
Amine	DEIPA	3750		X					
PCE	PCE-A	3770		X	X				
Amine	TIPA	3780		X	X	X			
Antifoam	TIBP	3830		X	X	X	X		
Antifoam	AF-A	3840		X	X	X	X		
PCE	PCE-B	3910		X	X	X	X	X	
Antifoam	AF-B	3910		X	X	X	X	X	
Amine	MEA	3940		X	X	X	X	X	
Polyol	Glycerol	3960		X	X	X	X	X	
Polyol	PEG	3960		X	X	X	X	X	
Amine	TEA	4010			X	X	X	X	
Amine	THEED	4020				X	X	X	
Polyol	DEG	4020					X	X	
Polyol	MEG	4050					X	X	
Polyol	PG	4100							X

*significance*

1.000  
0.090  
0.050  
0.050  
0.068  
0.112

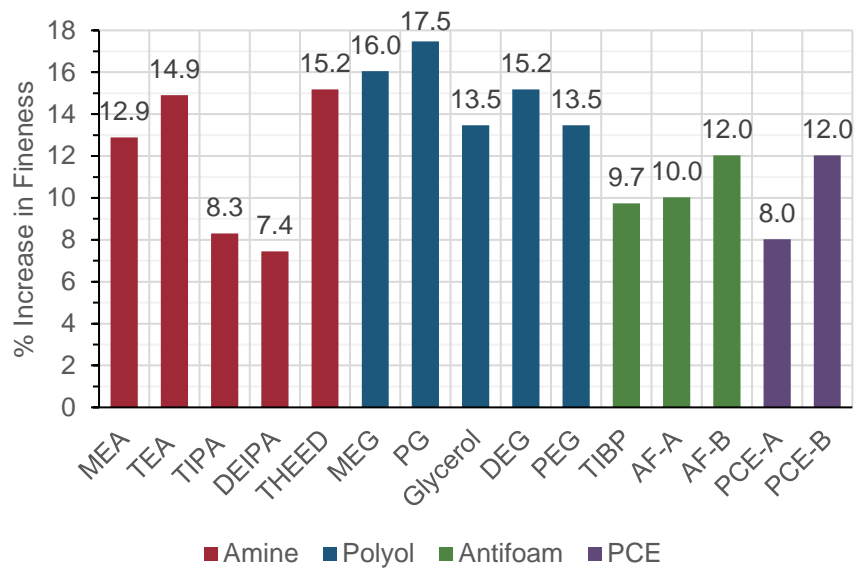


Figure 4.1. Blaine fineness increase provided by GCs

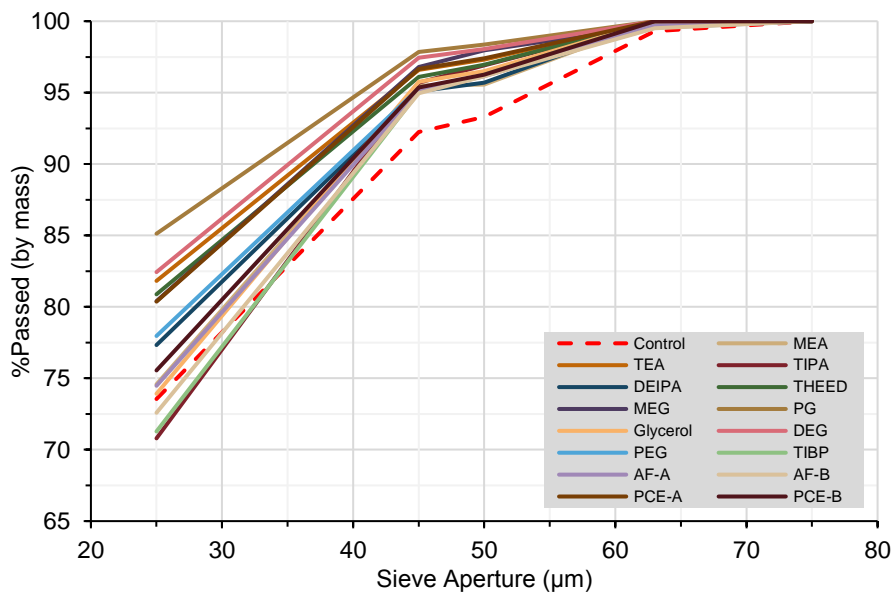


Figure 4.2. Air jet sieving analysis of Phase 1

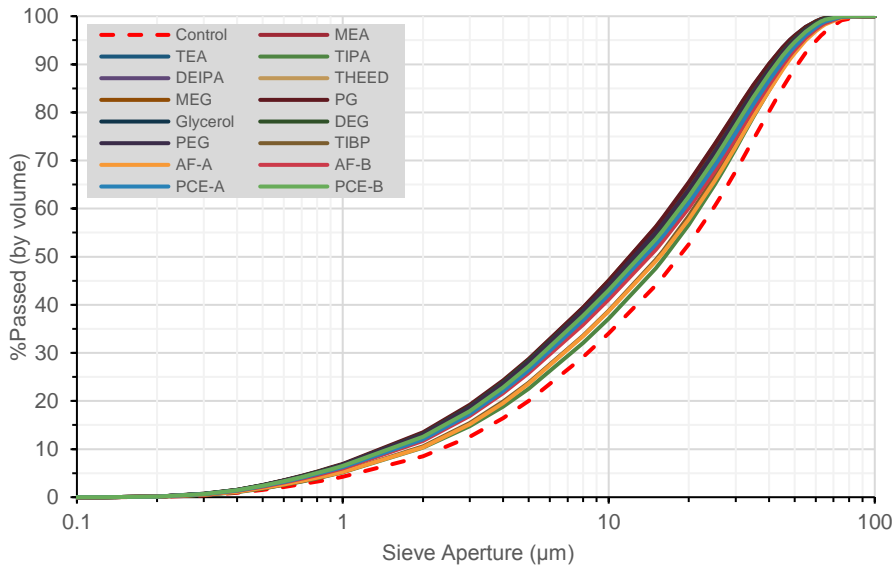


Figure 4.3. PSD analysis of Phase 1

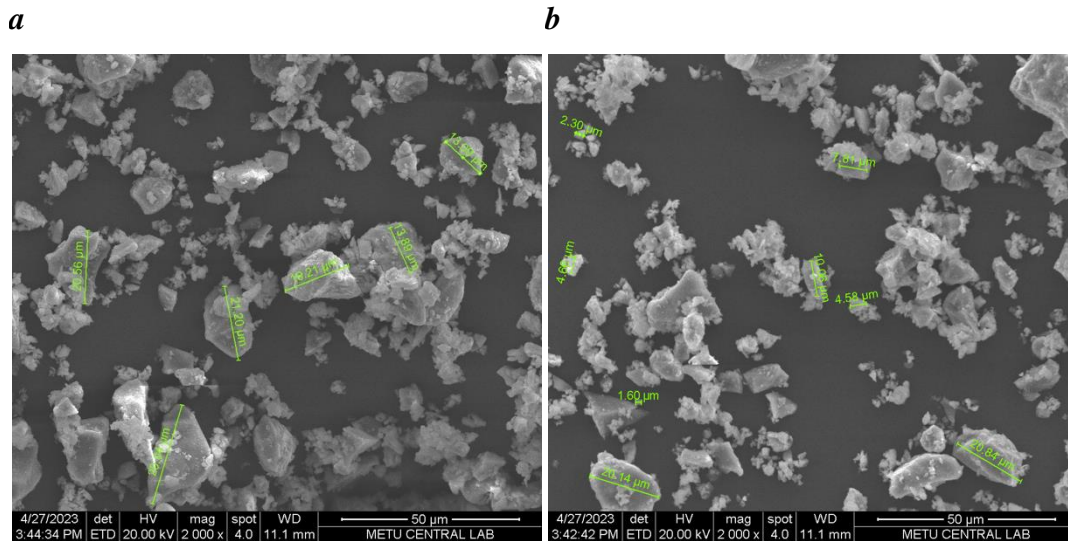


Figure 4.4. SEM images of a) Control and b) MEG cements

#### 4.1.1.2 Consistency

Cement mortar mixes are prepared from ground cements in accordance with EN 196-1. The consistency of each fresh cement mortar is also determined according to ASTM C 230. Flow, shown in Table 4.3, is defined as the percentage increase in the spread diameter of each mortar compared to the initial diameter (100 mm).

Table 4.3. Compression and flow table test results of cements ground with GCs

Group	Cement Label	Flow (%)	Compressive Strength (MPa)			
			2-day		28-day	
			Mean	CoV (%)	Mean	CoV (%)
Control	Control	85	26.9	5.3	48.8	6.9
	MEA	88	28.5	1.6	47.0	4.9
	TEA	78	28.4	4.4	50.8	7.1
Amine	TIPA	88	27.6	2.7	48.9	0.4
	DEIPA	85	29.6	2.9	45.3	8.7
	THEED	88	32.6	2.8	47.1	5.1
	MEG	86	31.7	3.0	52.0	7.6
Polyol	PG	90	28.5	6.3	49.0	6.6
	Glycerol	90	31.6	2.8	49.1	4.6
	DEG	89	27.9	2.3	47.8	3.6
	PEG	94	27.8	4.0	46.3	4.6
	TIBP	83	28.4	8.3	47.4	5.2
Antifoam	AF-A	97	26.1	4.3	48.8	7.6
	AF-B	87	28.5	4.2	47.7	5.0
Polyol	PCE-A	91	27.7	4.7	48.0	3.6
	PCE-B	93	29.3	7.5	48.4	6.8

The increase in flow over the Control is shown in Figure 4.5. As can be seen in the figure, although all cements ground with a GC have a higher SSA compared to the Control, their increase in consistency does not show a similarity with the increase in SSA, and the consistency of the mortars slightly decreased, remained constant and

even increased compared to the Control. This result indicates that GCs, even when added in rather small amounts, can manipulate the consistency of cement mortars.

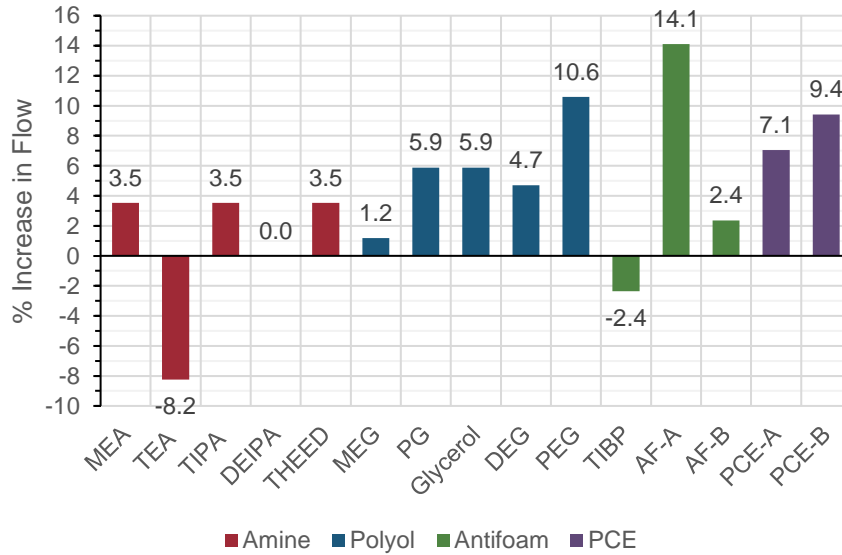


Figure 4.5. Flow increase provided by GCs

#### 4.1.1.3 Compressive Strength

Cement mortars are molded and cured for 2 and 28 days in lime-saturated water to determine the early age and standard compressive strength, according to the ASTM C 109 standard. The results are presented in Table 4.3. For 2-day compressive strength test results, Duncan's ANOVA test was conducted. Duncan subsets and 2-day compressive strength are given in Table 4.4.

Table 4.4. 2-day compressive strength and Duncan's ANOVA subsets of cements ground with GCs

Group	Cement Label	2-day Comp. Strength (MPa)	Subset			
			1	2	3	4
Antifoam	AF-A	26.1	X			
<b>Control</b>	<b>Control</b>	<b>26.9</b>	<b>X</b>	<b>X</b>		
Amine	TIPA	27.6	X	X	X	
PCE	PCE-A	27.7	X	X	X	
Polyol	PEG	27.8	X	X	X	
Polyol	DEG	27.9	X	X	X	
Antifoam	TIBP	28.4		X	X	
Amine	TEA	28.4		X	X	
Polyol	PG	28.5		X	X	
Antifoam	AF-B	28.5		X	X	
Amine	MEA	28.5		X	X	
PCE	PCE-B	29.3			X	
Amine	DEIPA	29.6			X	
Polyol	Glycerol	31.6				X
Polyol	MEG	31.7				X
Amine	THEED	32.6				X

<i>significance</i>	0.095	0.157	0.076	0.309
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MEA, TEA, TIPA, PG, DEG, PEG, all the Antifoam group, and PCE-A all belong to the same subset (1 and 2) with Control. Other GCs considerably affect early strength. Figure 4.6 shows the 2-day compressive strength difference according to Control.

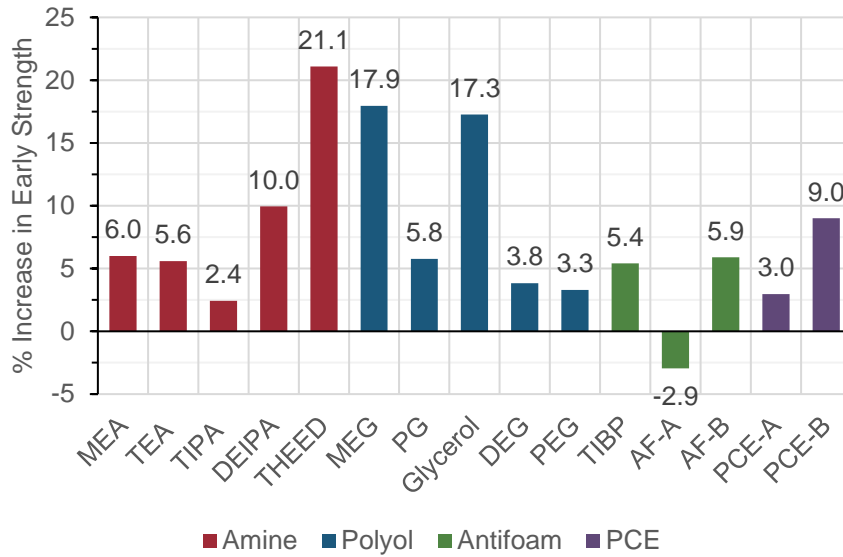


Figure 4.6. 2-day compressive strength increase provided by GCs

Although the fineness of cement increases with MEA, TEA, TIPA, PG, DEG, PEG, TIBP, AF-A, AF-B, and PCE-A, early strength is little or not affected. In addition, comparing the SSA and early strength, fineness is not the only factor that affects early strength. Earlier studies (Al-Yami et al., 2017; Heren & Ölmez, 1996; Kobya et al., 2022; Mansouria et al., 2021; Roskopf et al., 1975; Sun & Liu, 2016) indicate that GCs can retard hydration reactions.

Isothermal calorimetry test is performed for 72 hours for Control, THEED, MEG, PEG, and AF-A. THEED and MEG are selected because of their great performance on early strength. PEG and AF-A are selected because they improve the consistency of the mortar, while they do not have a significant effect on the early strength. The results show that hydration accelerates in THEED, MEG, and PEG, as shown in Figure 4.7. The heat of hydration curve of AF-A is close to Control. That validates the early strength results.



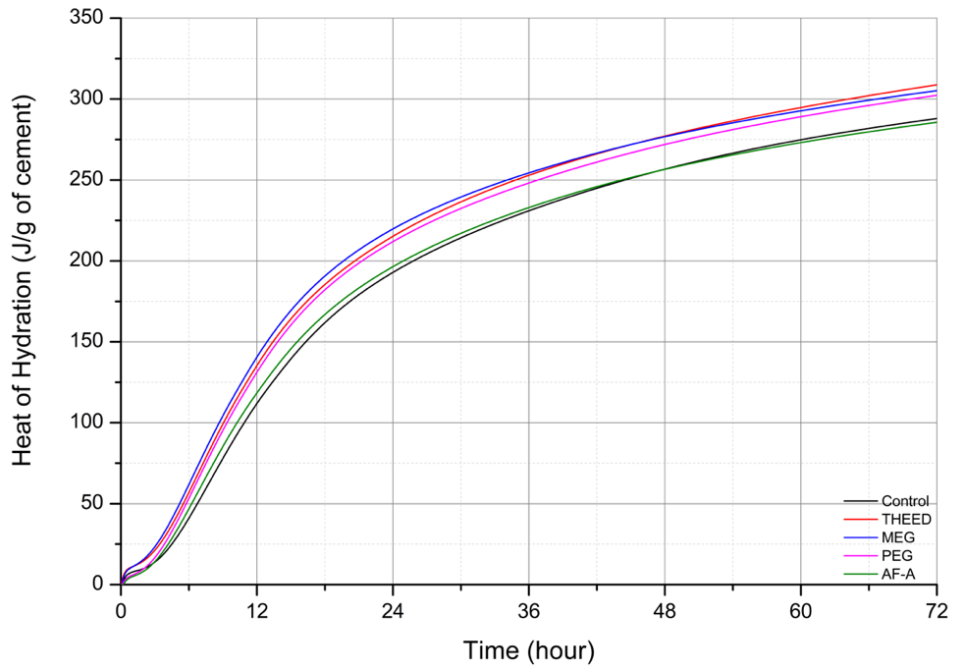


Figure 4.7. Heat of hydration of selected cements

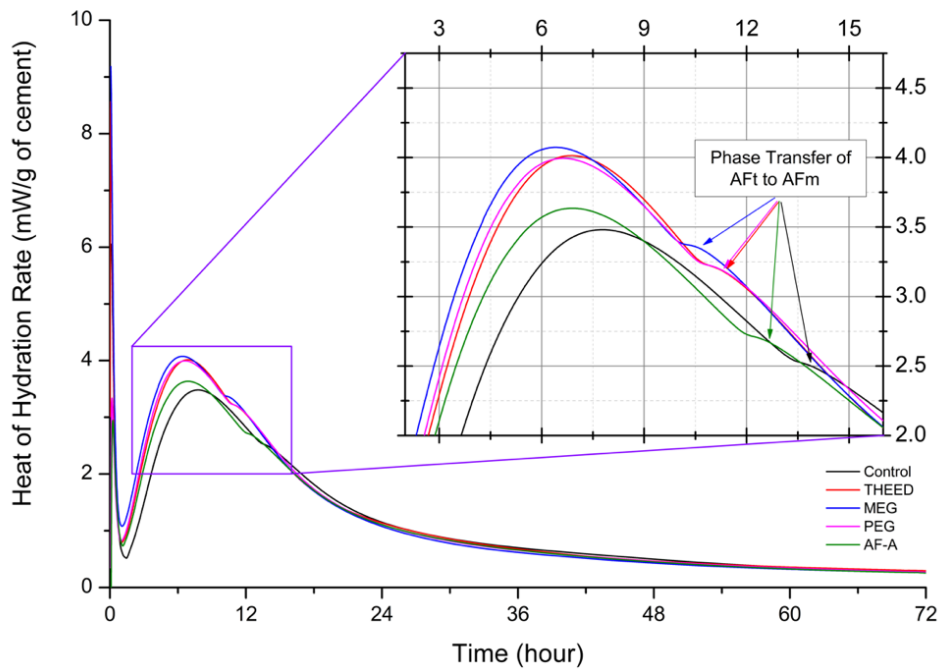


Figure 4.8. Heat of hydration rate of selected cement

Isothermal calorimetry results also show that the GCs increase the heat of hydration rate (Figure 4.8), as there is a slight shift in the time at which peaks are observed. AF-A has no effect and PEG has little effect on the hydration rate. THEED and MEG significantly increase the hydration rate. These results are consistent with the early strength results. On the other hand, the phase change from AFt to AFm occurs at earlier stages. This may be due to the increase in SSA and acceleration of tricalcium aluminate hydration and the chemical effect of GCs. Ma et al. (2019) and W. Li et al. (2015) mentioned that THEED enhances this phase transfer.

As with the early age compressive strength, the data obtained are classified using Duncan's ANOVA test for the standard compressive strength results. The difference in standard compressive strength by Control is shown in Figure 4.9. Duncan's subsets and 28-day compressive strengths are shown in Table 4.5.

All GCs are grouped in the same subset (1 and 2) with Control. It can be inferred that GCs do not significantly impact the standard strength, as also can be seen in Figure 4.9.

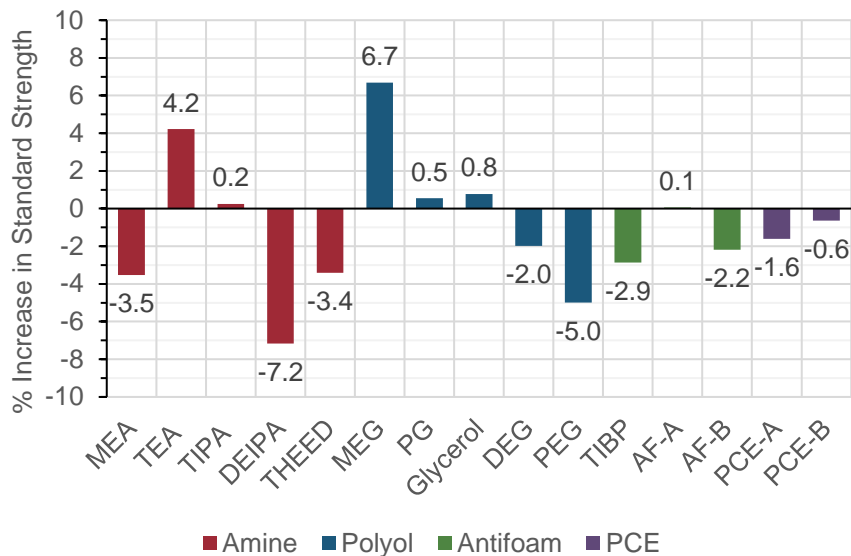


Figure 4.9. 28-day compressive strength increase provided by GCs

Table 4.5. 28-day compressive strength and Duncan's ANOVA subsets of cements ground with GCs

Group	Cement Label	28-day Comp. Strength (MPa)	Subset	
			1	2
Amine	DEIPA	45.3	X	
Polyol	PEG	46.3	X	X
Amine	MEA	47.0	X	X
Amine	THEED	47.1	X	X
Polyol	Glycerol	47.2	X	X
Antifoam	TIBP	47.4	X	X
Antifoam	AF-B	47.7	X	X
Polyol	DEG	47.8	X	X
PCE	PCE-A	48.0	X	X
Polyol	MEG	48.7	X	X
<b>Control</b>	<b>Control</b>	<b>48.8</b>	<b>X</b>	<b>X</b>
Antifoam	AF-A	48.8	X	X
Amine	TIPA	48.9	X	X
PCE	PCE-B	48.9	X	X
Polyol	PG	49.0	X	X
Amine	TEA	50.8		X

*significance*

0.116      0.062

#### 4.1.2 Constant Fineness

As it is well known, the fineness of cement affects its rheological and mechanical properties (Sultan et al., 2023). In the earlier part of this study, it was shown that the incorporation of GCs increased the fineness of the cements and that this increase in fineness did not result in a significant reduction in consistency. Therefore, it was verified that the GCs affect the rheological properties of the cement mortars. Earlier studies (W. Li et al., 2015; Ma et al., 2019) claim that GCs can change hydration products.

As a second part of Phase 1, the clinkers could be ground together with the GCs at different times to achieve a specified cement fineness, which will then eliminate the interdependence of fineness and consistency and also quantify the energy savings. However, this can only be done through a trial-and-error approach that significantly increases the number of grindings for each GC. Therefore, this approach was not pursued. Instead, a different approach is taken, where the Control group - in the absence of GCs - is prepared by varying the grinding time to obtain cement batches with different finenesses. The specific energy consumption (SEC), which can be described as the energy required to grind one ton of cement under laboratory conditions, can then be calculated for each cement using these grinding times. Table 4.6 shows the properties of the Control group ground at six different times ranging from the original 15 minutes to 20 minutes. As can be seen from this table, SSA and consistency are inversely proportional, and SEC and early compressive strength are proportional to SSA.

The third column of the table includes the specific energy consumption, which is calculated with the current power usage readings from the grinding mill device. The calculations were made as follows:

- The power of the mill is 750 W (0.75 kW).
- At 400 RPM, the mill consumes 45% of its power (0.3375 kW).
- In one hour, it consumes 0.3375 kWh of energy and it consumes  $5.625 \times 10^{-3}$  kWh of energy in one minute.
- This energy is consumed by 294 g of cement, so for one ton of cement, 19.13 kWh of energy would be spent in one minute. Therefore, in one minute of grinding, the specific energy consumption (SEC) is 19.13 kWh/t of cement.

It should be noted that these values are representative of the laboratory scale grinding and depending on the equipment used and its capacity, actual field grinding would yield totally different results. As expected, the SEC increases with increased grinding times.

Coefficients of correlation between the SSA and each parameter listed in that table are calculated as presented in

Table 4.7. As mentioned earlier, all the parameters other than standard strength have a strong correlation with SSA. Thus, it can be said that standard strength is independent of fineness. The following sections elaborate on the correlations between the SSA and other related parameters listed in that table.

Table 4.6. Test results of the Control group

Cement Label	Grinding time (min)	SEC (kWh/t)	SSA (cm <sup>2</sup> /g)	Flow (%)	Compressive Strength (MPa)			
					2-days	CoV (%)	28-days	CoV (%)
Control	15	287.0	3490	85	26.9	5.3	48.8	6.9
Control-16	16	306.1	4110	84	29.3	5.3	55.7	8.4
Control-17	17	325.3	4240	83	30.1	5.2	51.1	3.8
Control-18	18	344.4	4530	78	34.1	4.6	50.7	2.5
Control-19	19	363.5	4660	73	33.3	4.9	53	2.9
Control-20	20	382.7	4860	70	35.1	3.1	50.1	1.4

Table 4.7. Coefficients of correlation between SSA and other parameters

Parameter	Coefficient of Correlation between SSA
SEC	0.963
Flow	-0.884
Early Strength	0.963
Standard Strength	0.169

The SEC, flow, and early age compressive strength values can be calculated using these regressions for any SSA value. These data represent the scenario if the cement is ground without any chemicals. Comparing the values calculated by regressions and experimental data will give clues about the chemical effect of GCs on SEC, flow, and early strength. The data calculated via regressions (SEC, 2-day, and 28-day

compressive strength values assumed if the cement is ground without any GC at constant fineness) and the experimental data (values obtained from grinding mill and compression tests) are compared.

#### 4.1.2.1 Specific Energy Consumption

SEC can be defined as the energy consumed to grind one ton of cement. That energy is directly related to the time. Thus, as the SEC increases, the fineness would also increase. Therefore, the regression function of SSA and SEC should be an increasing function. In addition, during grinding, with the decrease in particle diameter, the transition from brittle to plastic behavior takes place (Jones, 2002; Schonert, 1972). Thus, the energy absorption capacity of the cement particles would increase. Therefore, the energy requirement for grinding would exponentially increase with the fineness increase, as earlier studies suggested (Carpio et al., 2008; Tokyay, 1999). Figure 4.10 presents the SSA and SEC relationship as obtained from the grinding of the Control group at different times. This figure also includes the SSA and SEC values of all the groups. An exponential regression between SEC and fineness is calculated, similar to previous studies (Equation 1).

$$SEC = 132.27 \times e^{(0.2141 \times 10^{-3} \times SSA)} \text{ kWh/ton of cement} \quad [1]$$

GCs have three main functions: 1) increasing SSA at constant SEC, 2) increasing the production capacity, and 3) saving energy at constant SSA. As earlier studies (Assaad & Issa, 2015; Katsioti et al., 2009; Sverak et al., 2013) propounded, all the GCs are beneficial in energy efficiency to produce cement at constant fineness. Consistent with previous studies, as shown in Figure 4.10, all cement groups ground with GCs are below the regression trend.

The energy savings from GCs are calculated as follows:

- The SEC difference between cement ground with and without GCs at the same fineness is calculated.
- This value is divided by the SEC value that would be consumed if no GCs were used and expressed as a percentage.

The energy savings of all GCs are shown in Figure 4.11. GC-related energy savings and SSA increases are directly related.

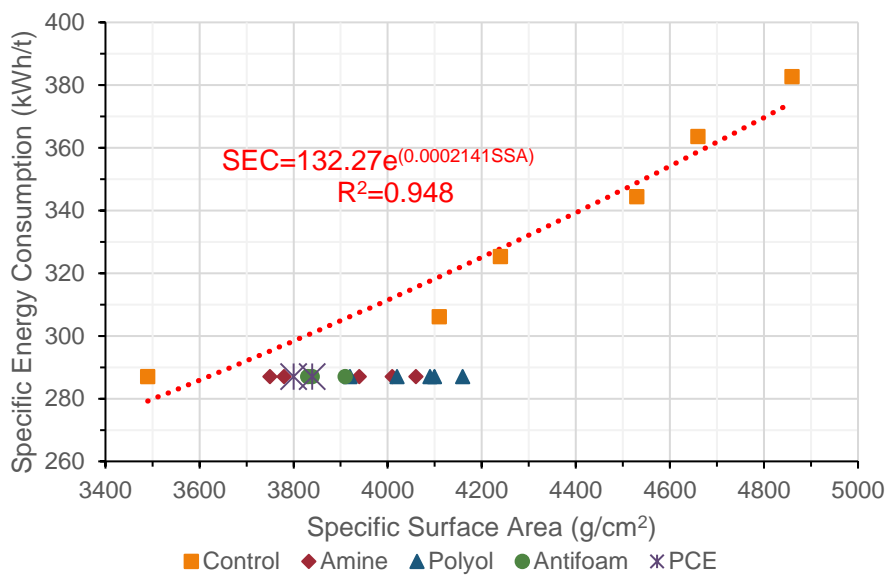


Figure 4.10. SEC-SSA association

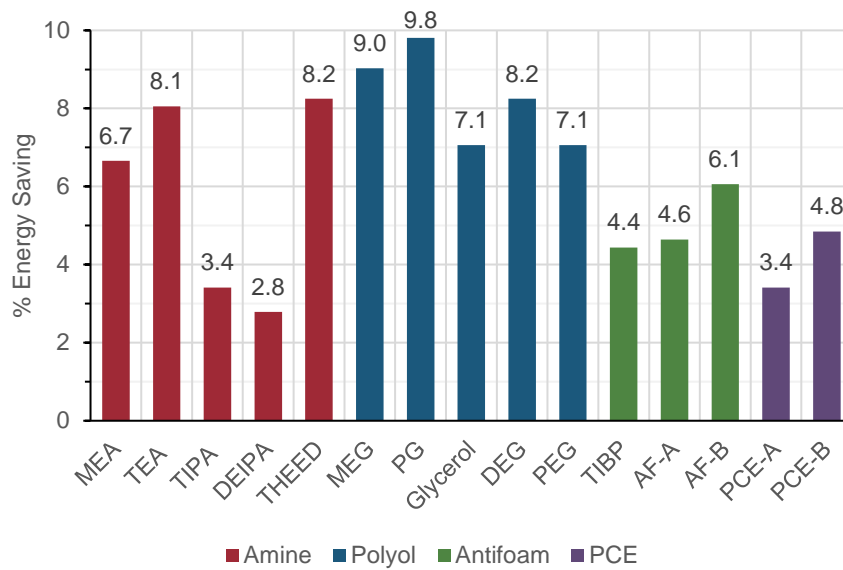


Figure 4.11. Energy savings provided by GCs

#### 4.1.2.2 Consistency

The fineness of cement directly affects the consistency of the mortar. The surface absorbs more water when the SSA increases, and the mortar gets harsher (Sultan et al., 2023). Because the rheology of cement mortar and concrete is not well studied, the relationship between fineness and flow of the mortar could not be defined properly yet. However, for this case, a negative exponential regression function is determined (Equation 2) because the regression equation has the highest coefficient of determination.

$$Flow = 87.4 - 6.2663 \times 10^{-3} \times e^{(1.6245 \times 10^{-3} \times SSA)} \% \quad [2]$$

It can be seen in Figure 4.12 that cement groups other than Control do not fit the trendline, meaning GCs manipulate the rheological properties of the mortar. The flow difference between the regression and experimental data is given in Figure 4.13. In an overall look, it can be observed that PG, PEG, AF-A, and PCE-B have



increased the flow. That increase can result from reducing cement agglomeration in mortar, as Assaad and Issa (2015) have explained. The impact of other GCs can be ignored.

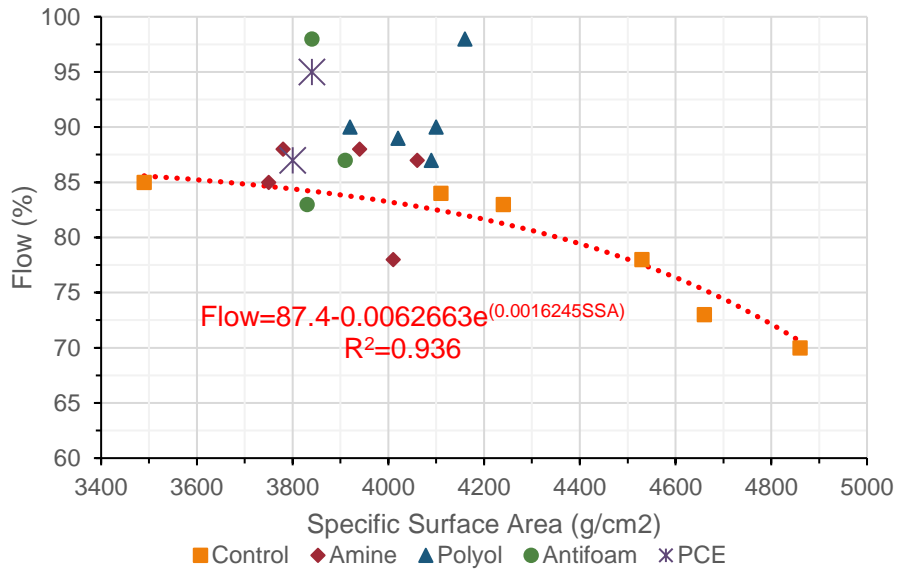


Figure 4.12. Flow-SSA association

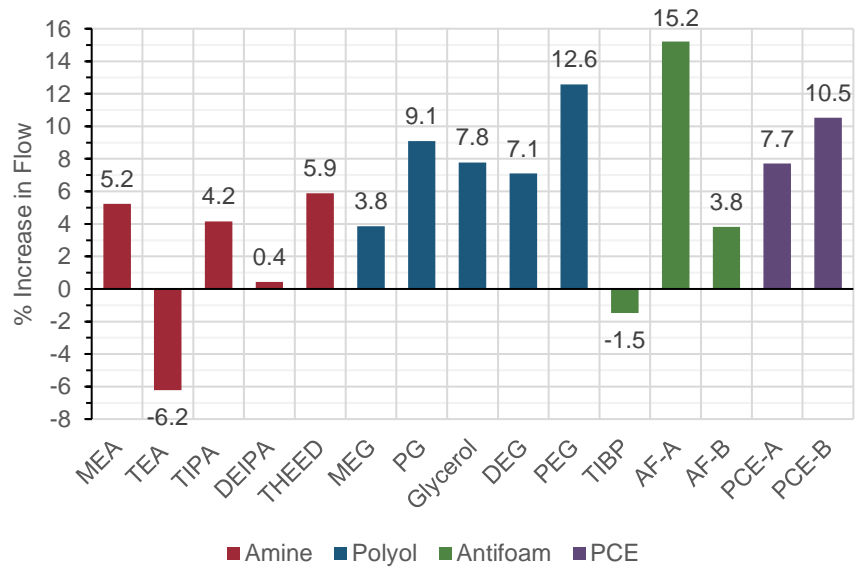


Figure 4.13. Flow increase provided by GCs regardless of fineness

### 4.1.2.3 Compressive Strength

The hydration reactions occur when the cement particles interact with water. The cement surface area is critical to the initial hydration rate. As the SSA of the cement increases, more water can initially react with more cement. Therefore, the initial strength increases as the SSA increases (Adu-amankwah et al., 2019). However, the standard strength of the mortar is relatively less dependent on the fineness of the cement. Therefore, since the early strength cannot exceed the standard strength, the function would approach the ultimate strength, which is a constant value, as the fineness increases. Therefore, a logarithmic function, which also has the highest coefficient of determination, is chosen as the regression function, as shown in Figure 4.14 (Equation 3).

$$\text{Early Strength} = 25.742 \times \ln(\text{SSA}) - 183,83 \text{ MPa} \quad [3]$$

During cement hydration, GCs adsorbed on the surface can modify the hydration process by the phase transition from AFt to AFm and hydration of alite, belite, and ferrite (Gartner & Myers, 1993; Hewlett et al., 2019; Huang et al., 2016; Huang & Shen, 2014; W. Li et al., 2015; Ma et al., 2015, 2019; Riding et al., 2010; Wang et al., 2022). As can be seen in Figure 4.14, while most points are close to the trend line, some GCs are above and below the regression line. Therefore, it can be inferred that GCs act as accelerators or retarders independent of their effect on fineness.

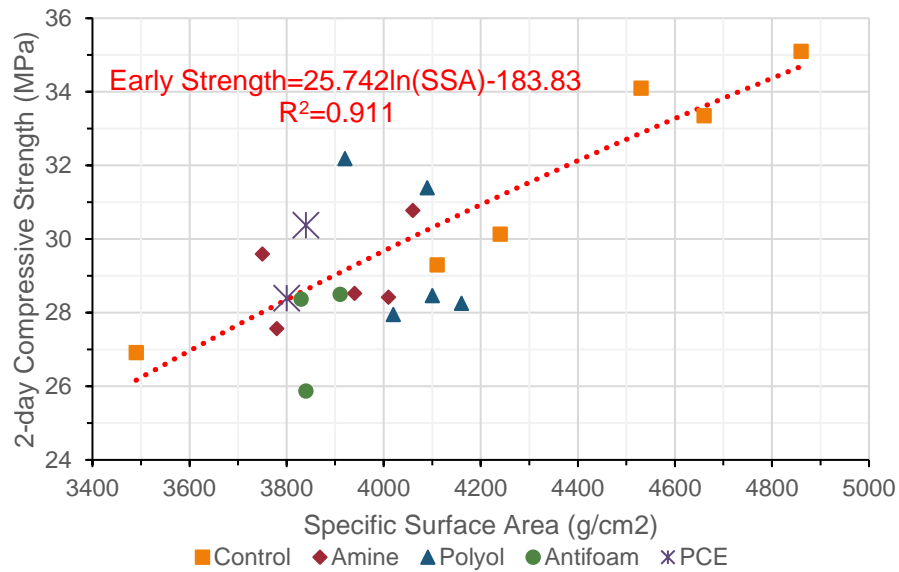


Figure 4.14. Ealy Strength-SSA association

The early strength change at constant cement fineness is shown in Figure 4.15. THEED and Glycerol have a positive and AF-A a negative effect on early strength. Other GCs have little or no effect on hydration. Previous studies (W. Li et al., 2015; Ma et al., 2019) explain the acceleration of cement hydration by THEED with the phase transition from AFt to AFm. The phase transition is also shown in Figure 4.8. The effect of glycerol on hydration has been shown in previous studies (Estabragh et al., 2016; Zhang et al., 2016). Regarding the strength reduction of AF-A, Mansouria et al. (2021) express that antifoaming agents are strong retarders.

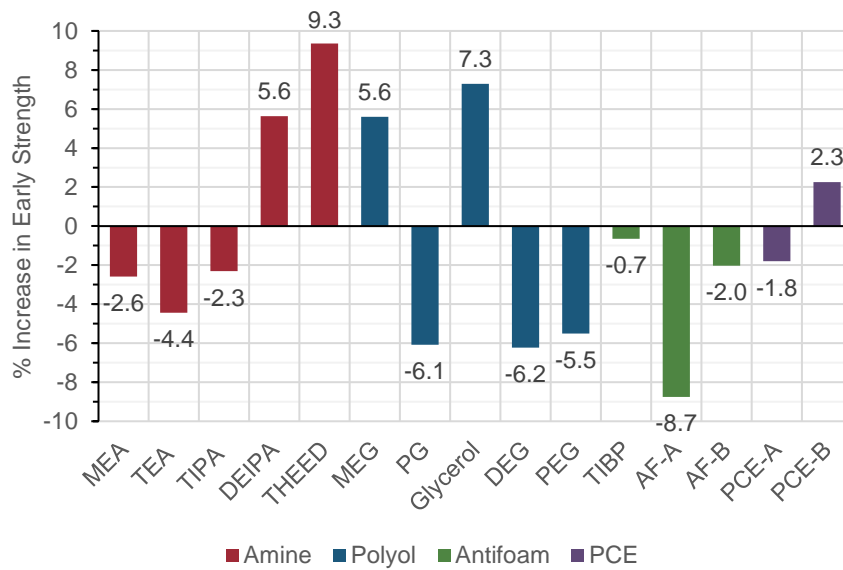


Figure 4.15. 2-day compressive strength increase provided by GCs regardless of fineness

Cement fineness increases the SSA and the rate of hydration reaction because water interacts with more cement surfaces (Adu-amankwah et al., 2019). However, it can change the standard strength relatively less because it is closer to the ultimate compressive strength that a cement mortar can potentially achieve. When comparing the 28-day compression test results of the Control group, it was observed that the standard strength of the mortar was independent of its SSA. The CoV of the results is 10.3, which is slightly above the limit set in the study. On the other hand, the correlation coefficient between SSA and 28-day compressive strength is 0.1693. Figure 4.16 shows that the standard strength and SSA have a very weak relationship. Therefore, it can be concluded that the GCs are responsible for the difference in standard strength from the Control.

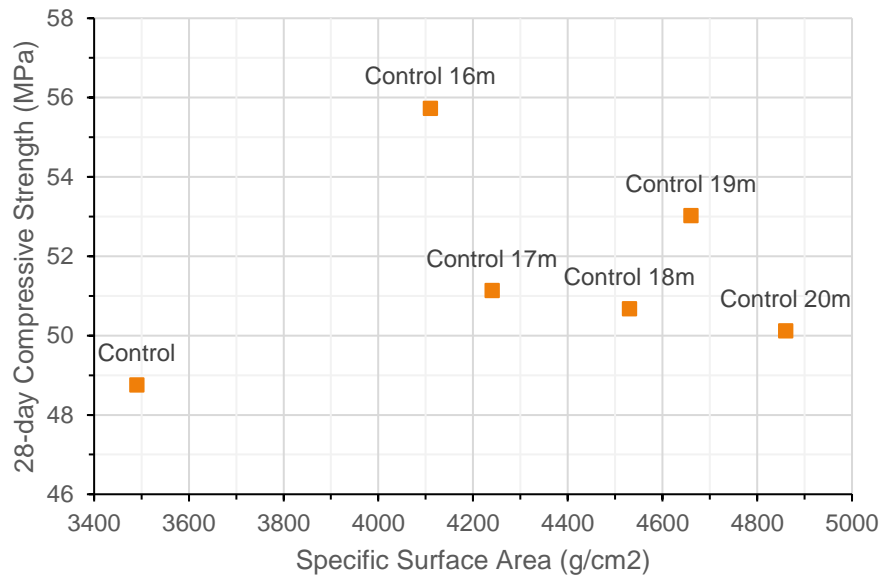


Figure 4.16. Standard Strength-SSA association

## 4.2 Phase 2: Grinding Chemicals as Admixtures

As already explained in Phase 1, GCs not only improve the grindability of the cement, but also affect the consistency of the cement mortar. Therefore, in this phase of the study, GCs are used as CAs and their influence on the chemical, physical, and mechanical properties of mortar samples is determined.

For this purpose, cement mortars are prepared according to EN 196-1 using a commercially available cement CEM I 42.5R, and the flow table test is performed to determine the consistency of fresh mortars according to ASTM C 230. GCs are added to the mortar mixture in the same specified dosages during grinding. The mortar samples are then molded, cured for 2 and 28 days, and the compressive strength is determined according to ASTM C 109.

The flow table and compression test results are shown in Table 4.8. Figure 4.17 also shows the difference in the flow of the mortar samples compared to the Control. The results of the flow table tests show that GCs, with the exception of the PCE group,

which are typically used as superplasticizing admixtures, do not have a significant effect on flow.

Therefore, unlike grinding, the rheological change in mortars of cement ground with GCs is not seen when GCs are used as an admixture. This confirms that the adsorption of GCs on the surface of the cement causes this difference, as shown by Assaad and Issa (2015).

Table 4.8. Compression and flow table test results of cements mortars with GCs as CAs

Group	Cement Label	Flow (%)	Compressive Strength (MPa)			
			2-day		28-day	
			Mean	CoV (%)	Mean	CoV (%)
Control	Control	100	10.8	2.2	43.5	3.7
	MEA	102	10.0	3.0	43.7	8.6
Amine	TEA	103	12.3	1.0	41.9	4.4
	TIPA	105	10.3	2.7	48.5	1.0
	DEIPA	95	16.4	3.9	44.4	6.7
	THEED	97	11.2	4.5	45.4	3.2
	MEG	104	9.9	2.0	40.8	1.1
Polyol	PG	98	9.2	4.6	44.6	1.9
	Glycerol	103	9.2	3.4	38.3	4.8
	DEG	105	8.9	4.3	39.9	6.4
	PEG	101	9.4	4.3	44.7	4.4
	TIBP	96	10.9	3.3	52.5	0.6
Antifoam	AF-A	100	9.5	3.0	45.8	4.0
	AF-B	96	9.8	1.9	46.2	0.9
Polyol	PCE-A	109	8.5	2.5	39.2	4.2
	PCE-B	111	10.0	2.2	38.7	3.9

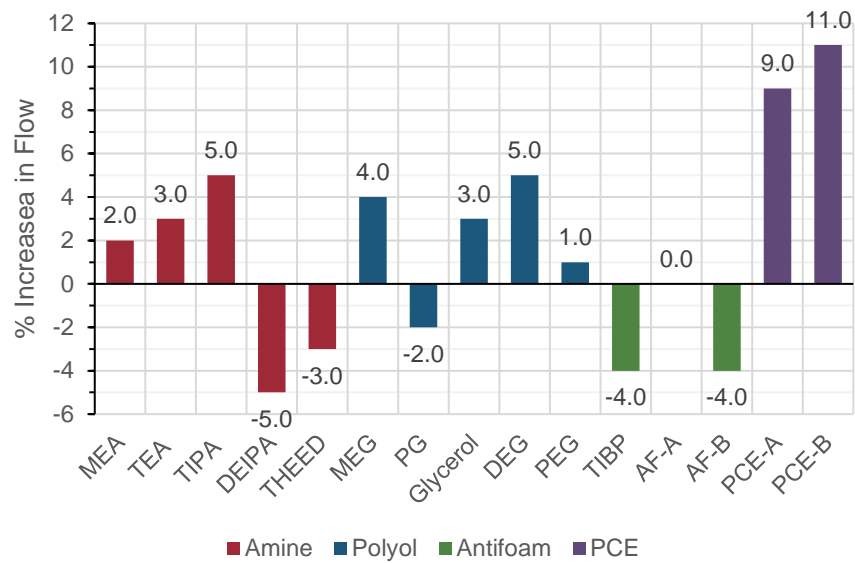


Figure 4.17. Flow increase provided by GCs as CAs

The mechanical properties of the mortars were determined by compression test of mortar specimens cured for 2 and 28 days. The results of the 2-day compression test are shown in Figure 4.18. In addition, Duncan's ANOVA test is performed on the results shown in Table 4.9. TIPA, THEED, and TIBP are grouped in the same subset (7 and 8) as the Control. TEA and especially DEIPA significantly increase early strength. The others have a negative effect on early strength.

DEIPA and TEA have increased early strength when used as GC and CA. However, this increase is more pronounced when used as a CA. On the other hand, some of the GCs retard hydration when used as CA. This difference could be due to three reasons:

- When used as GC, the dissolution of the chemical in water would be slower than that of the CA due to adsorption.
- The mineralogical composition, especially alite, tricalcium aluminate, and ferrite, of clinker and Portland cement are different.

- The Control mortar of the Portland cement gains 24.7% of the standard strength, which is its potential in 2 days, while in the Control of the clinker, this value is 55.2%. Considering that the GCs have a much smaller effect on the standard strength, the effect of the GCs on the mechanical properties decreases with increasing strength compared to the Control. Thus, the effect of GCs is more pronounced in the Portland cement.

Table 4.9. 2-day compressive strength and Duncan's ANOVA subsets of cement mortars with GCs as CAs

Cement Label	2-day Comp. Strength (MPa)	Subset										
		1	2	3	4	5	6	7	8	9	10	
PCE-A	8.5	X										
DEG	8.9	X	X									
Glycerol	9.2		X	X								
PG	9.2		X	X								
PEG	9.4		X	X	X							
AF-A	9.5		X	X	X	X						
AF-B	9.8			X	X	X	X					
MEG	9.9				X	X	X					
PCE-B	10.0				X	X	X					
MEA	10.0					X	X					
TIPA	10.3						X	X				
<b>Control</b>	<b>10.8</b>							<b>X</b>	<b>X</b>			
TIBP	10.9								X			
THEED	11.2								X			
TEA	12.3									X		
DEIPA	16.4										X	
	<i>significance</i>	0.212	0.052	0.079	0.060	0.094	0.112	0.085	0.132	1.000	1.000	



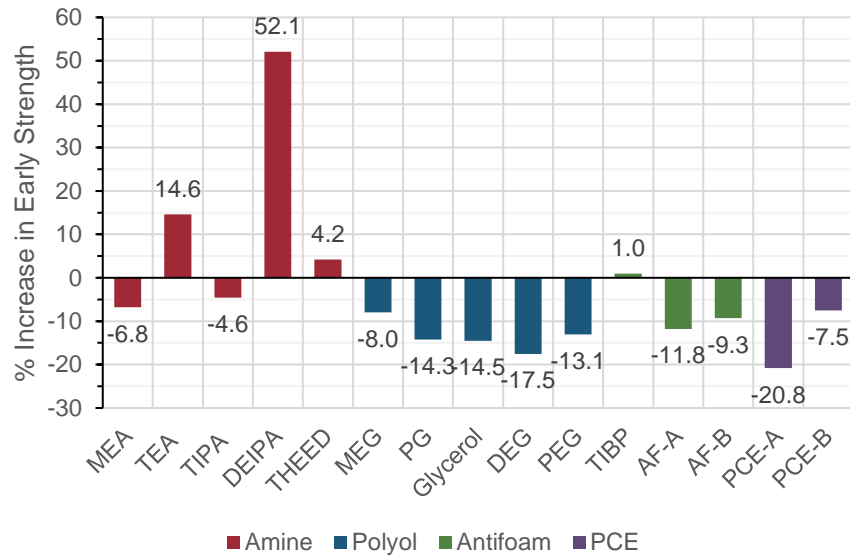


Figure 4.18. 2-day compressive strength increase provided by GCs as CAs

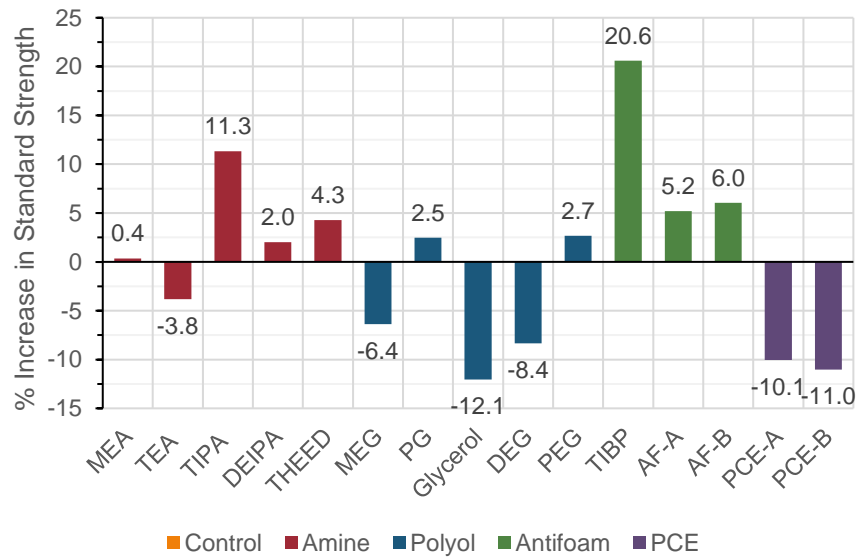


Figure 4.19. 28-day compressive strength increase provided by GCs as CAs

Table 4.10. 28-day compressive strength and Duncan's ANOVA subsets of cement mortars with GCs as CAs

Cement Label	28-day Comp. Strength (MPa)	Subset						
		1	2	3	4	5	6	7
Glycerol	38.3	X						
PCE-B	38.7	X	X					
PCE-A	39.2	X	X					
DEG	39.9	X	X					
MEG	40.8	X	X	X				
TEA	41.9		X	X	X			
<b>Control</b>	<b>43.5</b>			<b>X</b>	<b>X</b>	<b>X</b>		
MEA	43.7			X	X	X		
DEIPA	44.4				X	X		
PG	44.6				X	X		
PEG	44.7				X	X		
THEED	45.4					X	X	
AF-A	45.8					X	X	
AF-B	46.2					X	X	
TIPA	48.5						X	
TIBP	52.5							X

<i>significance</i>	0.212	0.052	0.079	0.060	0.094	0.112	0.085
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The standard strength changes in comparison to the Control are given in Figure 4.19. Duncan's ANOVA test is also performed on the results, as shown in Table 4.10. MEA, TEA, DEIPA, THEED, MEG, PG, PEG, AF-A, and AF-B are grouped in the same subset (3, 4, and 5) with Control. TIPA and TIBP significantly increase the standard strength. Other GCs decrease the standard strength. Previous studies (Huang & Shen, 2014; Katsioti et al., 2009; Kobya et al., 2022; W. Li et al., 2015) have shown that TIPA can improve 28-days compressive strength. However, there are no studies on TIBP.

### 4.3 Phase 3: The Effect of Grinding Aids

Seven different GAs, which are mixtures of GCs, are used in this phase. The performance of the GAs is studied at constant grinding energy and fineness, as in Phase 1.

#### 4.3.1 Constant Energy Consumption

Blaine fineness test and air jet sieve analysis using 25, 45, 50, 63, and 75  $\mu\text{m}$  sieves are conducted to evaluate the fineness of cements. Duncan's ANOVA analysis is carried out to the fineness results (Table 4.12). The Blaine test results are shown in Table 4.11 and the increases in fineness are shown in Figure 4.20.

Table 4.11. Blaine fineness of cements ground with GAs

Cement Label	SSA ( $\text{cm}^2/\text{g}$ )	
	Mean	CoV (%)
Control	3490	3.8
GA-A	4220	2.2
GA-B	4110	2.4
GA-C	3850	3.3
GA-D	4050	0.9
GA-E	4220	2.2
GA-F	3810	2.2
GA-G	4060	1.9

According to Duncan's test and air jet sieving analysis, all the GAs have increased the fineness as in Phase 1. The Blaine test results are given in Table 4.11. It can be seen in Table 4.12 that none of the cements ground with GAs are grouped with the Control. On the other hand, the air jet sieving curve shows that GAs lead to an

increase in fineness (Figure 4.21). Therefore, all the GAs significantly increase the fineness at constant energy consumption.

Table 4.12. Blaine fineness and Duncan's ANOVA subsets of cements ground with GAs

Cement Label	SSA ( $cm^2/g$ )	Subset			
		1	2	3	4
<b>Control</b>	<b>3490</b>	<b>X</b>			
GA-F	3810		X		
GA-C	3850		X	X	
GA-D	4050			X	X
GA-G	4060			X	X
GA-B	4110				X
GA-A	4220				X
GA-E	4220				X

*significance*    1.000    0.691    0.077    0.142

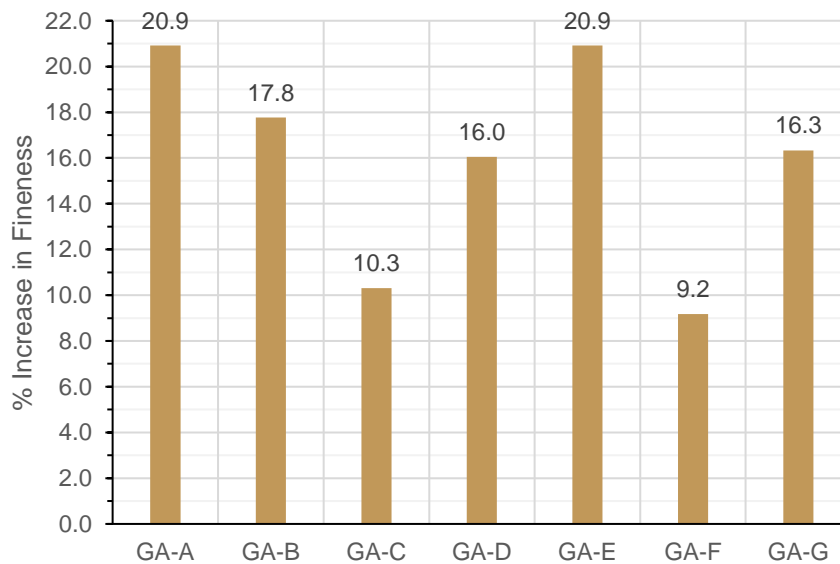


Figure 4.20. Blaine fineness increase provided by GAs

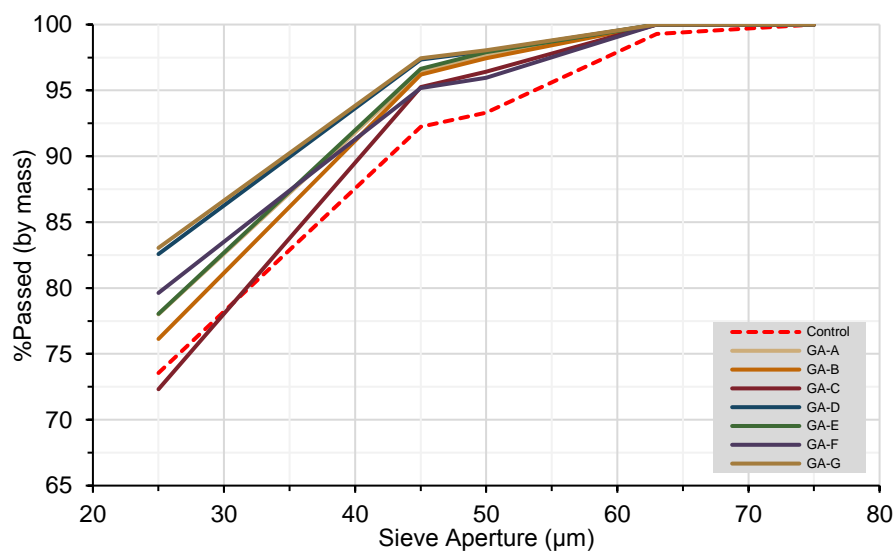


Figure 4.21. Air jet sieving analysis of Phase 3

Table 4.13. Compression and flow table test results of cements ground with GAs

Cement Label	Flow (%)	Compressive Strength (MPa)			
		2-day		28-day	
		Mean	CoV (%)	Mean	CoV (%)
Control	85	26.9	5.3	48.8	6.9
GA-A	96	33.2	5.6	57.3	5.8
GA-B	85	35.4	5.6	50.4	8.9
GA-C	76	35.3	2.8	49.7	2.7
GA-D	85	31.8	2.3	49.2	7.8
GA-E	86	33.3	4.7	46.8	6.0
GA-F	80	31.8	3.2	52.1	5.3
GA-G	82	32.5	8.1	53.6	0.7

Cement mortar mixtures are prepared and the flow table test is performed after all cements are ground with GAs according to the relevant standards (ASTM C 230, 2021; EN 196-1, 2016). The results of the flow table test are shown in Table 4.13 and increases in flow are presented in Figure 4.22. It can be seen that the consistency of the mortars changes independently of the fineness of the cement. This means that GAs, like GCs, affect the consistency of fresh mortar by adsorption.

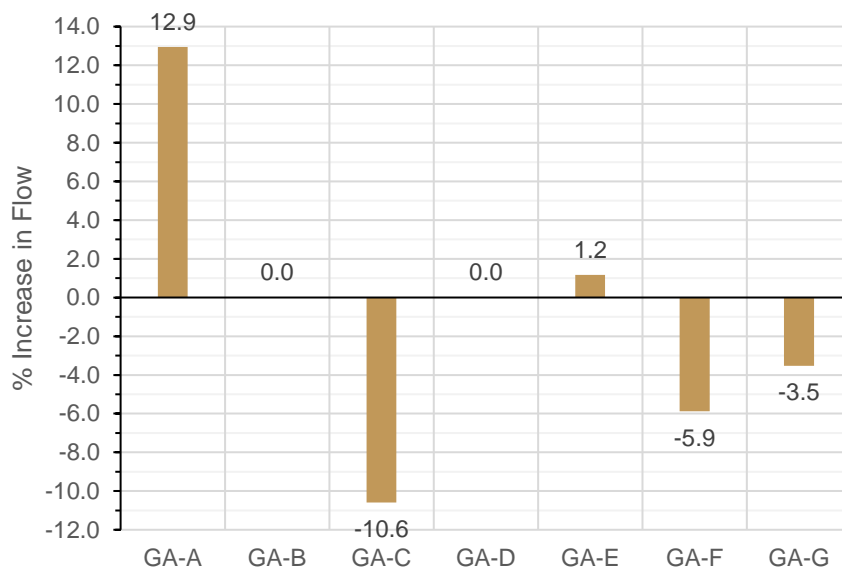


Figure 4.22. Flow increase provided by GAs

The 2-day and 28-day compressive strengths of cement mortars are evaluated in accordance with ASTM C 109 standard. The test results are given in Table 4.13. The data obtained were subjected to Duncan’s test. Table 4.14 shows the subsets generated in the Duncan ANOVA test. According to this analysis, all the GAs are grouped into different subsets from the Control. It can be concluded that all GAs have a significant effect on early strength. Figure 4.23 displays the 2-day compressive strength change due to the use of GAs.

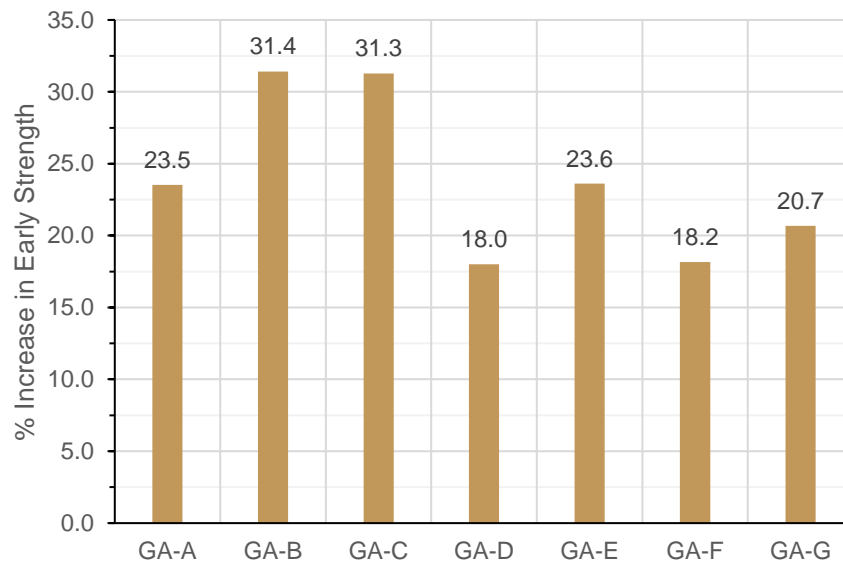


Figure 4.23. 2-day compressive strength increase provided by GAs

Table 4.14. 2-day compressive strength and Duncan's ANOVA subsets of cements ground with GAs

Cement Label	2-day Compressive Strength (MPa)	Subset		
		1	2	3
<b>Control</b>	<b>26.9</b>	<b>X</b>		
GA-D	31.8		X	
GA-F	31.8		X	
GA-G	32.5		X	X
GA-A	33.3		X	X
GA-E	33.3		X	X
GA-C	35.3			X
GA-B	35.4			X

*significance*      1.000      0.322      0.067

Duncan's ANOVA test is also conducted for 28-day compressive strength data. The resulting subsets and 28-day compressive strength values are presented in Table 4.15. The standard strength differences are given in Figure 4.24.

All the GAs except for GA-A are grouped together with the Control in subsets 1 and 2. From this grouping, it can be inferred that the GAs, except for GA-A, do not have a significant impact on the standard strength of the cement. GA-A shows the highest performance in terms of standard strength throughout the study. The increase in standard compressive strength provided by GA-A surpassed all the GCs. On the other hand, it shows a higher performance than GA-C, GA-D, GA-E, and GA-G, although they all contain amines, polyols, and antifoams. This can be explained by the synergetic effect, as mentioned in previous studies (Akalin, Akay, & Sennaroğlu, 2010; Akalin, Akay, Sennaroğlu, et al., 2010; Toprak et al., 2014).

Table 4.15. 28-day compressive strength and Duncan's ANOVA subsets of cements ground with GAs

Cement Label	28-day Compressive Strength (MPa)	Subset		
		1	2	3
GA-E	46.8	X		
<b>Control</b>	<b>48.8</b>	<b>X</b>	<b>X</b>	
GA-D	49.2	X	X	
GA-C	49.7	X	X	
GA-B	50.4	X	X	
GA-F	52.1	X	X	X
GA-G	53.6		X	X
GA-A	57.3			X

	<i>significance</i>	0.073	0.103	0.067
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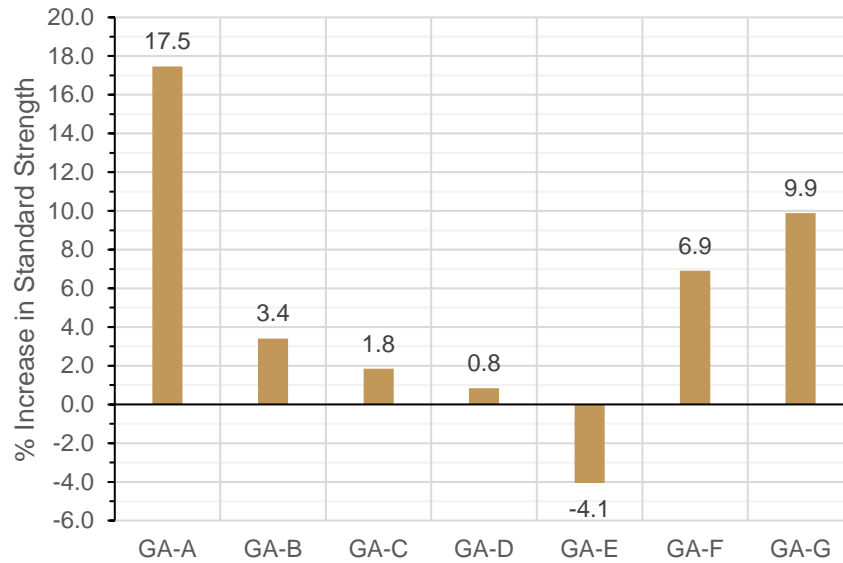


Figure 4.24. 28-day compressive strength increase provided by GAs

#### 4.3.2 Constant Fineness

Regressions calculated are used for the estimation of GAs' effect on energy saving, flow, and early strength. All the calculations in Phase 1 are used similarly in Phase 3.

The SEC is directly related to cement fineness, as discussed below. When GA is used in the grinding process, the fineness of the cement can be improved at constant SEC. Therefore, less SEC is required for the same fineness. The energy savings GAs are given in Figure 4.25. All GAs supply a significant energy saving, as in Phase 1. While GAs containing multiple chemicals can save up to 12.1% energy, GCs can save a maximum of 9.8% energy. This is because GAs are optimized considering the synergetic effect mentioned by Akalın, Akay, and Sennaroğlu (2010), Akalın, Akay, Sennaroğlu, et al. (2010), and Toprak et al. (2014).

In 2019, the average SEC for ball mills in the Turkish cement industry was calculated at 39.02 kWh/t (Department of Energy Efficiency and Environment, 2019). Currently, the unit price of electricity in industrial consumption in Türkiye is about

0.13 US\$/kWh (Solar AVM, 2023). A cement plant needs about  $39.02 \times 10^6$  kWh of energy to grind 1 million tons of cement. For this, it should spend about US\$5.07 million. Taking the average price of grinding aids as about 1 US\$/kg (H. Li et al., 2016) and the dosage as 400 g/t, as in this study, 400,000 kg of GA should be used for 1 million tons of cement, and the cost of this is US\$400,000. Considering the average energy savings (8.7%) provided by the GAs in this study, approximately US\$441,316 in savings were achieved at a cost of US\$400,000. Therefore, the use of GA provided a gain of approximately US\$41,316 in 1 million tons of cement production. Note that this is an estimate of the benefits of GAs on an industrial scale through a pilot application.

As mentioned above, GAs affect the consistency and hydration reactions of cement. The cement particles adsorb the GAs. Since the agglomeration energy of the cement particles is reduced, the cement particles move more easily in the mortar. This increases the consistency of the mortar. In the hydration of cement particles, adsorbed GAs can accelerate or retard hydration or modify the hydration products.

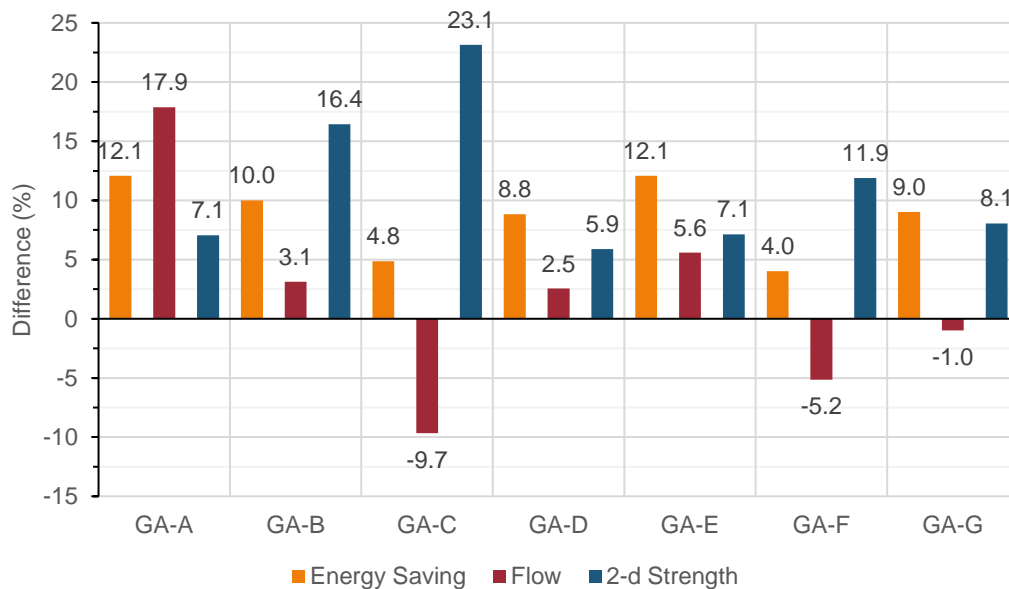


Figure 4.25. Energy saving, flow, and early compressive strength increases provided by GAs regardless of fineness

The change in consistency at constant fineness is shown in Figure 4.25. GA-A has significantly increased the flow of the cement mortar. On the other hand, GA-C has significantly decreased the flow. The decrease in flow can be explained by the antagonistic effect described by Akalın, Akay, & Sennaroğlu (2010) and Akalın, Akay, Sennaroğlu, et al. (2010).

At constant fineness, the difference in 2-day compressive strength is shown in Figure 4.25. It can be concluded that all GA-B, GA-C, and GA-F have significantly accelerated the hydration of the cement, while others have slightly increased it. GA-C has shown the greatest increase in early strength at constant fineness, even more than GA-B containing set accelerators. It contains amines, polyols, and antifoams, so this increase can be explained by the synergetic effect discussed by Akalın, Akay, & Sennaroğlu (2010), Akalın, Akay, Sennaroğlu, et al. (2010), and Toprak et al. (2014).



## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Summary and Conclusion

This study evaluates the performance of 15 grinding chemicals (GC) and 7 grinding aids (GA). The GCs are pure chemicals and the GAs are mixtures of GCs. The evaluation is performed at constant energy consumption and fineness using these GCs as CAs.

First, all GCs are added to the raw material prior to grinding and ground at 400 rpm for 15 minutes. Then Blaine fineness, air jet sieving, particle size distribution (PSD), flow table, and 2-day and 28-day compression tests are performed. The results of each cement with GCs are compared to the results of the Control cement. Duncan's test is performed for specific surface area (SSA) and compressive strength. In addition, isothermal calorimetry and SEM imaging are performed on the Control, tetrahydroxyethylethylenediamine (THEED), monoethyleneglycol (MEG), polyethyleneglycol (PEG), and AF-A cements.

Second, the Control group cement is ground. The grinding time is varied to obtain different finenesses without GCs. Blaine fineness, flow table, and 2-day and 28-day compression tests are performed on this group. Specific energy consumption (SEC) values are calculated from the grinding time. Correlations are sought for SEC, flow, 2-day and 28-day compressive strength with SSA. Regression equations are calculated. SEC, flow, and 2-day compressive strength values are then calculated for each cement according to its SSA. This data set represents the performance of the cement of the same fineness without the use of GC. In this way, the chemical effect of the GCs is revealed.

Third, mortars of the Portland cement GCs are prepared using the GCs as CAs. Blaine fineness, flow table, 2-day and 28-day compression test results are compared using Duncan's analysis of variance (ANOVA).

Finally, GAs are used during grinding. Blaine fineness, air jet sieving, PSD, flow table, and 2-day and 28-day compression tests are performed. The results are compared in terms of constant energy consumption and fineness.

The conclusions of the study can be listed as follows:

- All GCs used significantly increase the SSA at constant energy consumption from 7.4% to 17.5%, indicating that they will lead to energy savings. At constant fineness, laboratory scale grinding results in energy savings ranging from 2.8 to 9.8%, depending on the GCs used. Thus, it can be concluded that GCs improve fineness and provide energy efficiency. The groups providing the most energy efficiency can be classified as Polyol, Amine, Antifoam, and PCE with 8.2%, 5.8%, 5.0%, and 4.1% of energy savings.
- At constant fineness, THEED significantly increases the 2-day compressive strength. On the other hand, diethanolisopropanolamine (DEIPA), MEG, and Glycerol slightly accelerate the hydration reactions. The acceleration of hydration by DEIPA and THEED may be due to phase transfer from AFt to AFm. The 28-day compressive strengths are grouped in the same subset as the Control, meaning that GCs have no significant effect on the standard strength.
- At constant fineness, the consistency of cement mortars is not negatively affected by GCs. Propyleneglycol (PG), PEG, AF-A, and PCE-B significantly increased the flow. This indicates that the use of GCs not only results in energy savings but can also improve the consistency of the fresh mortar. Others have little or no effect.
- On the other hand, GCs have no effect on consistency when used as CAs, except for the PCE group, which are commercially used as superplasticizers, because the adsorption of GCs on the surface is comparatively less. GCs

lubricate the cement particles by adsorption during grinding, thus reducing agglomeration forces in fresh mortar. This results in a more workable mortar at a constant water-to-cement ratio.

- The overall behavior of the GC groups as CA in Portland cement is similar in early strength. The Amine group accelerates hydration and the others retard it. However, the increase and decrease in 2-day strength are more pronounced in the Portland cement mixes. This can be explained by the fact that the Portland Control cement gains 24.7% of the standard strength and the cement with GCs gains 55.2%. This means that the hydration of the Portland cement is in a relatively earlier stage on the second day. In addition, the mineralogical composition of the Portland cement is different from that of the clinker ground with GCs.
- Triisopropanolamine (TIPA) and triisobutylphosphate (TIBP) increase the standard strength of the Portland cement when used as a CA. TIPA is reported to increase the solubility of  $\text{Fe}^{3+}$  ions, resulting in more hydration products. However, TIPA is not effective when used as a GC. This may be because the molecules are dissolved in water when used as a CA but adsorbed on particles when used as a GC.
- The GAs provided an average energy saving of 8.7% and a gain of approximately US\$41,316 in 1 million tons of cement production. At constant fineness, GA-A increases, GA-C decreases, and the others have little or no effect on flow. The 28-day compressive strengths are grouped in the same subset as the Control except for GA-A. GA-A may alter the hydration products. There is no correlation between fineness and 28-day compressive strength. Thus, the strength improvement provided by GA-A is a chemical effect. The GAs may exceed the performance of the GCs due to the synergetic effect. The decrease in flow of GA-C can be explained by the antagonistic effect.

- As a result, chemical interactions in the cement grinding process have a synergetic or antagonistic effect on cement performance. Optimization of chemical mixtures is a critical issue in the cement manufacturing process.

## **5.2 Recommendations for Future Studies**

The following recommendations will also be helpful for future studies:

- The conclusions drawn are based on a single clinker. Clinkers with different chemical compositions can be used to show the effectiveness of GCs on different clinkers.
- Cement will remain a primary construction material for decades to come. The production process would require tailor-made methods to achieve the optimal amount of mix, energy, and cost by using industrial waste. The next research could be to improve cement with the least amount of clinker and to understand the microstructure after chemical interaction.
- Grinding at a constant fineness could be done to show the effect of GCs on energy efficiency and other properties. Using the cement with the same fineness as the Control cement could help to elucidate the chemical effect of the GC.
- The performance of the mixtures could be evaluated in more detail for a more complete understanding of the synergistic and antagonistic effects. For example, cement pastes could be subjected to XRD analysis to see the transformation of the hydration product. While the chemical effect of alkanolamines is well studied, there is a large gap in the literature on other types of GC. Moreover, the interaction between the chemicals deserves further investigation.



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<https://doi.org/10.1016/J.CONBUILDMAT.2016.07.034>





## APPENDICES

### A. Air Jet Sieving and PSD Results

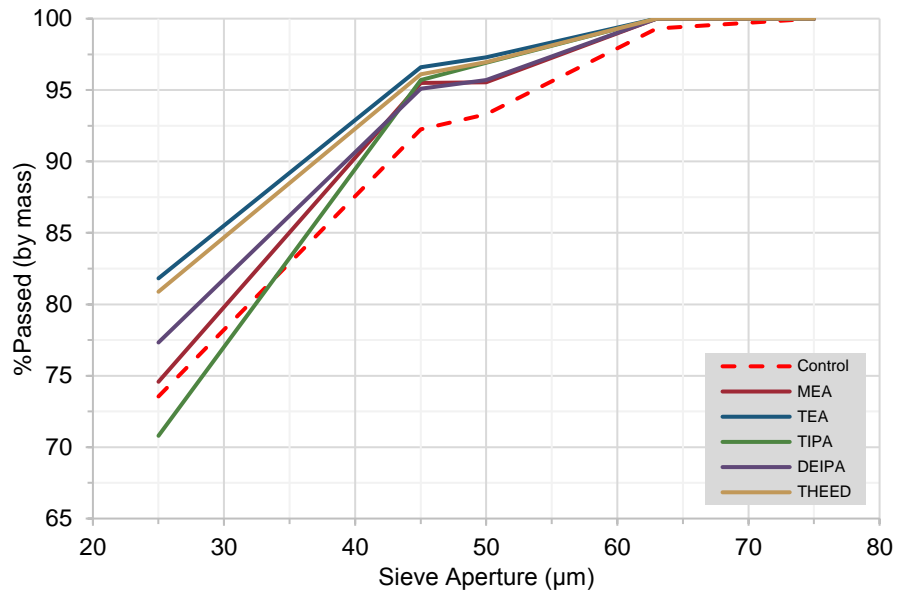


Figure A.1. Air jet sieving analysis of the Amine group

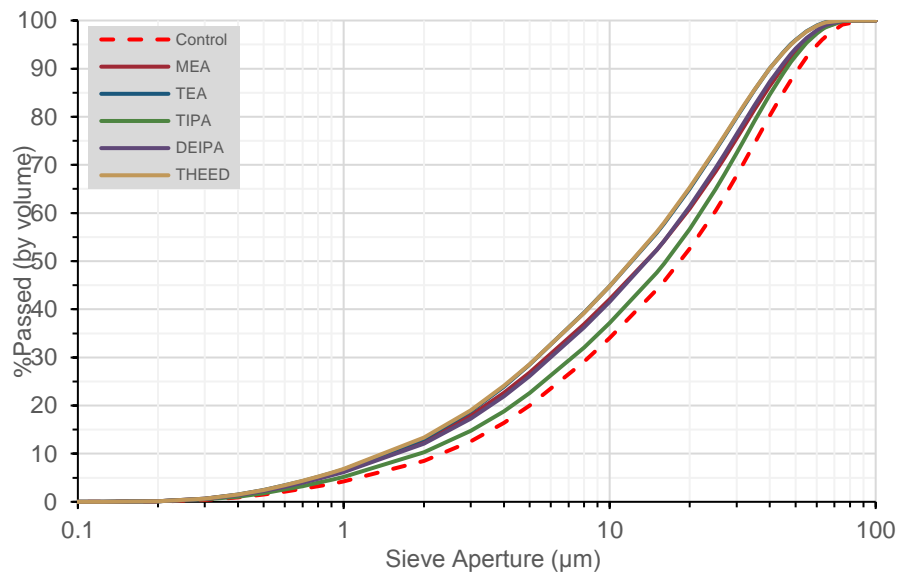


Figure A.2. PSD analysis of the Amine group

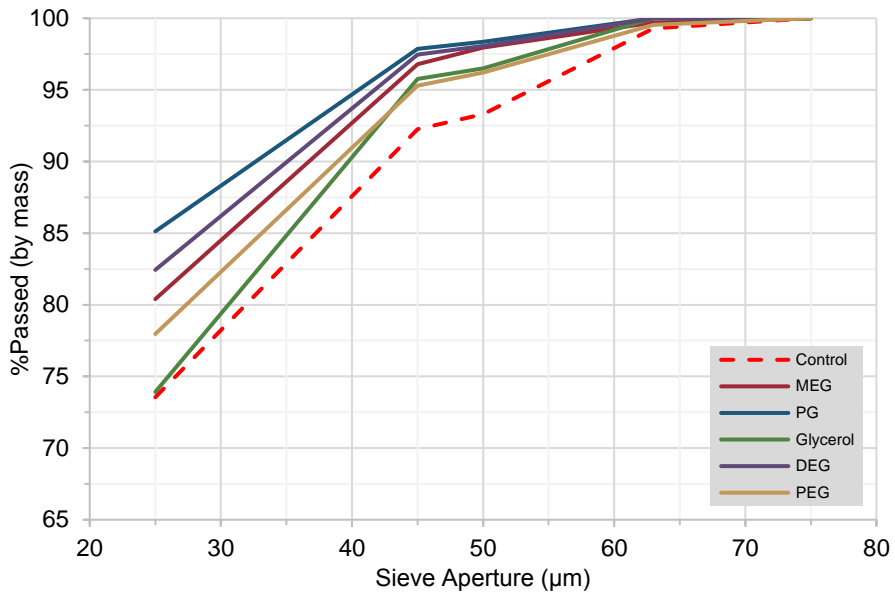


Figure A.3. Air jet sieving analysis of the Polyol group

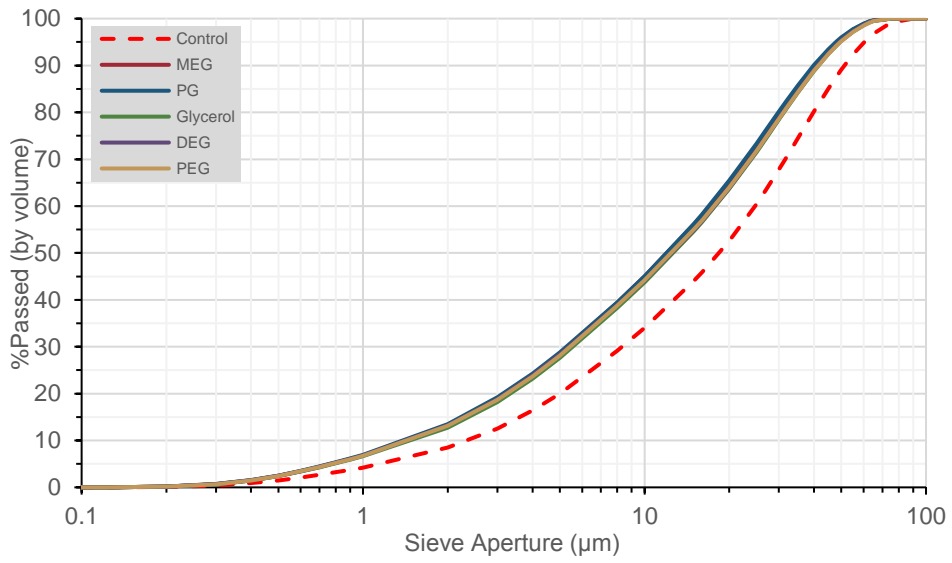


Figure A.4. PSD analysis of the Polyol group

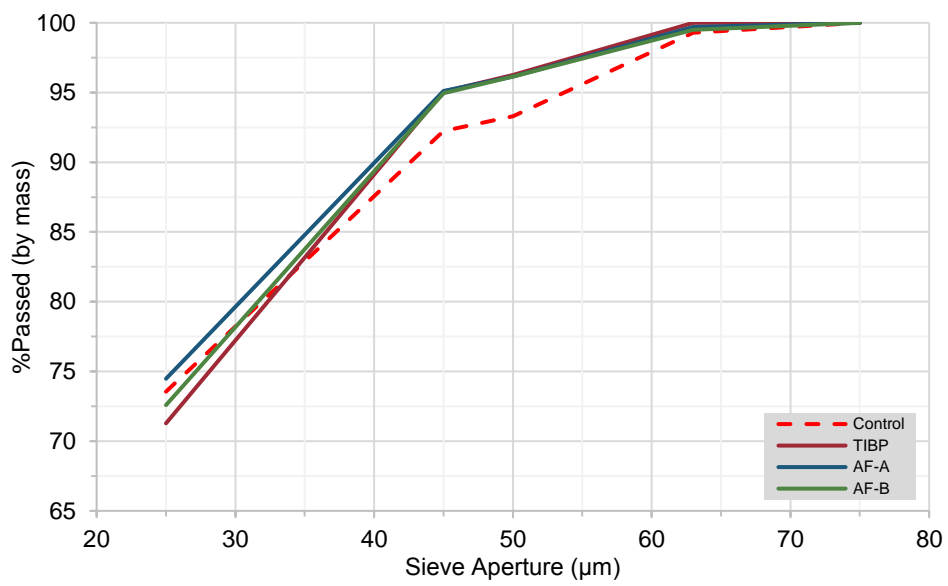


Figure A.5. Air jet sieving analysis of the Antifoam group

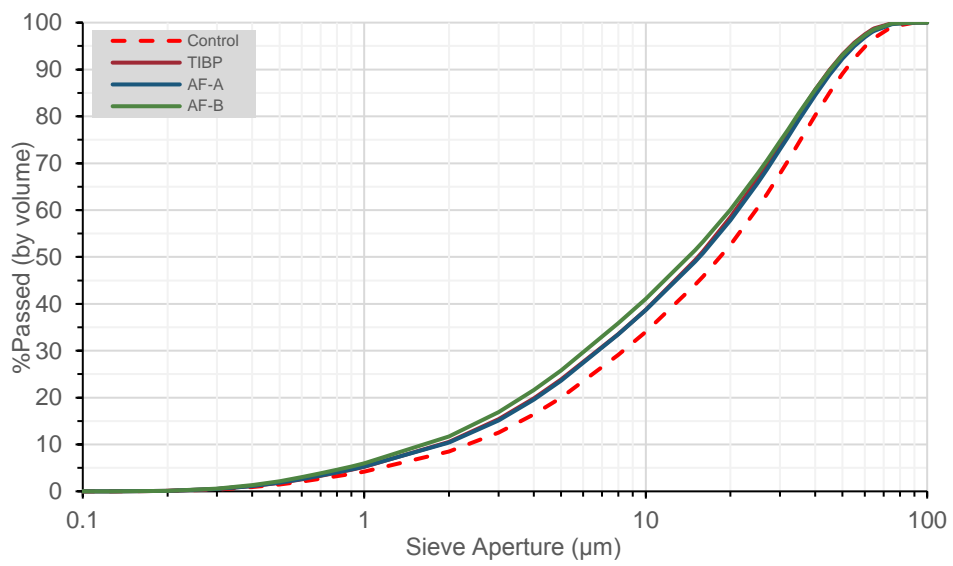


Figure A.6. PSD analysis of the Antifoam group

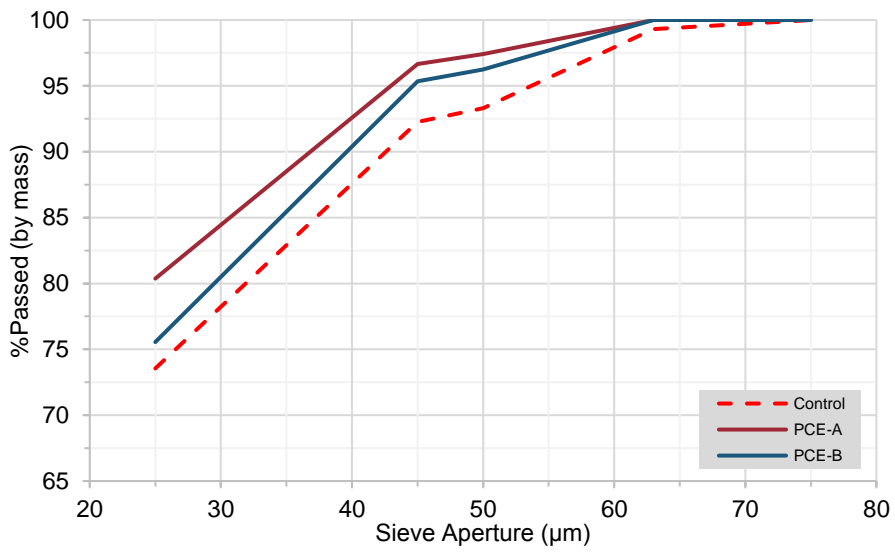


Figure A.7. Air jet sieving analysis of the PCE group

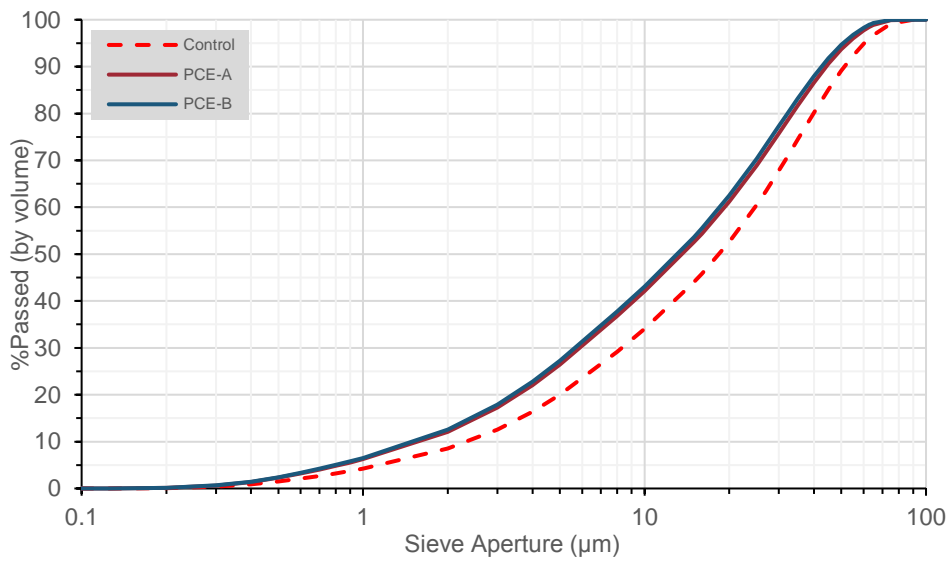


Figure A.8. PSD analysis of the PCE group

## B. Scanning Electron Microscope Images

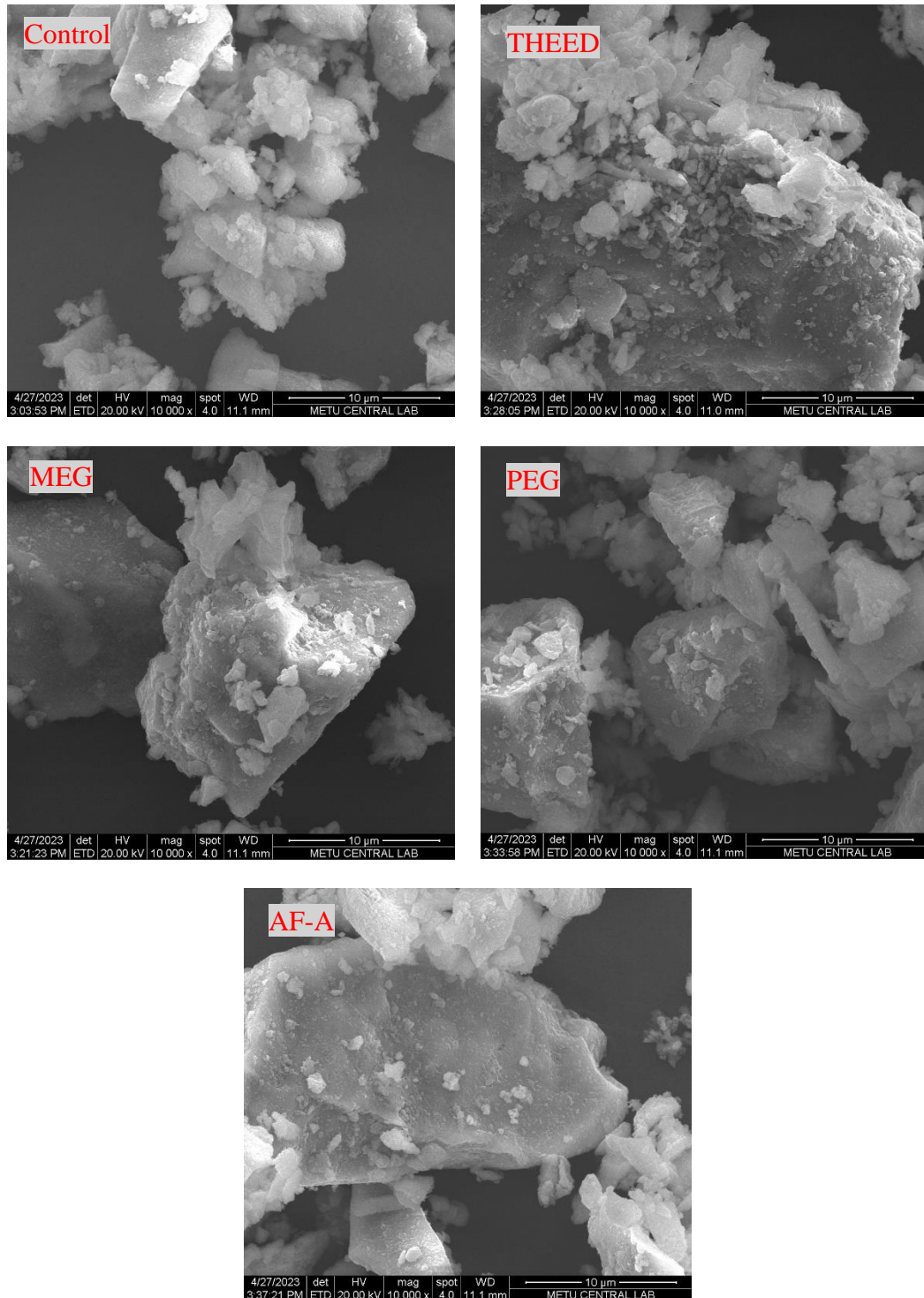


Figure B.1. SEM images of selected cements magnified 10000 times

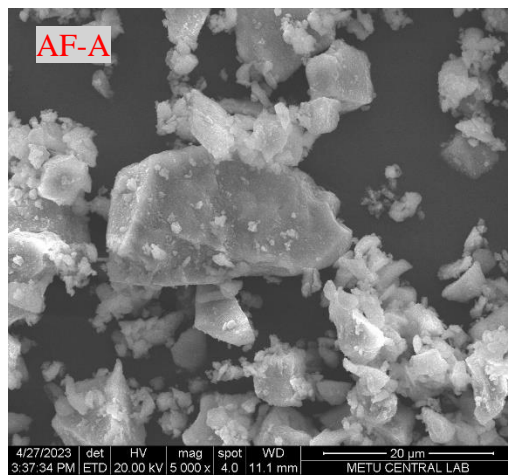
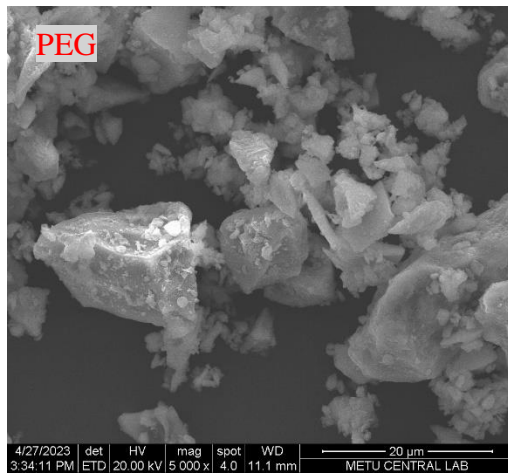
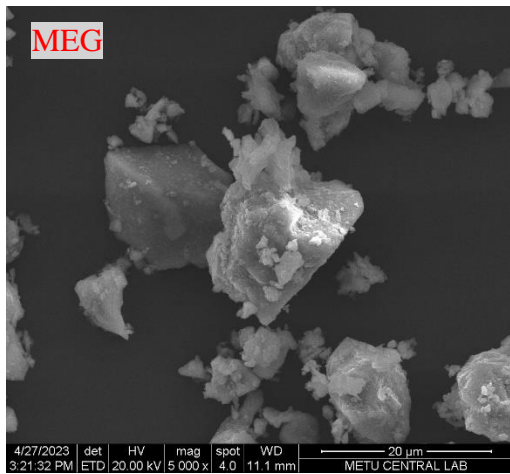
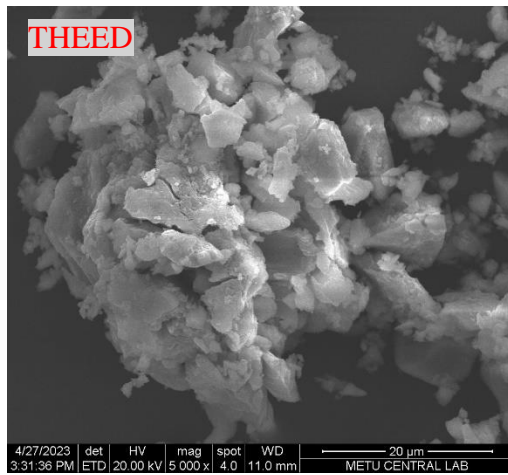
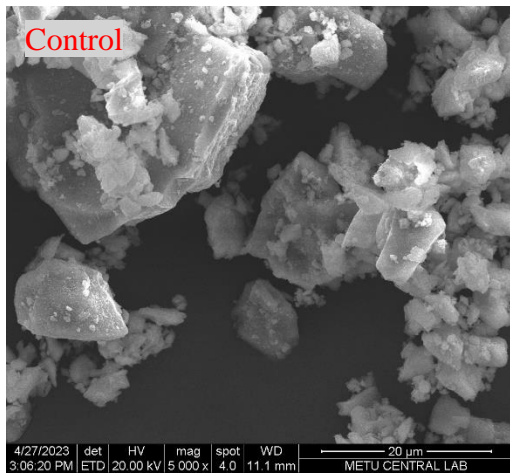


Figure B.2. SEM images of selected cements magnified 5000 times

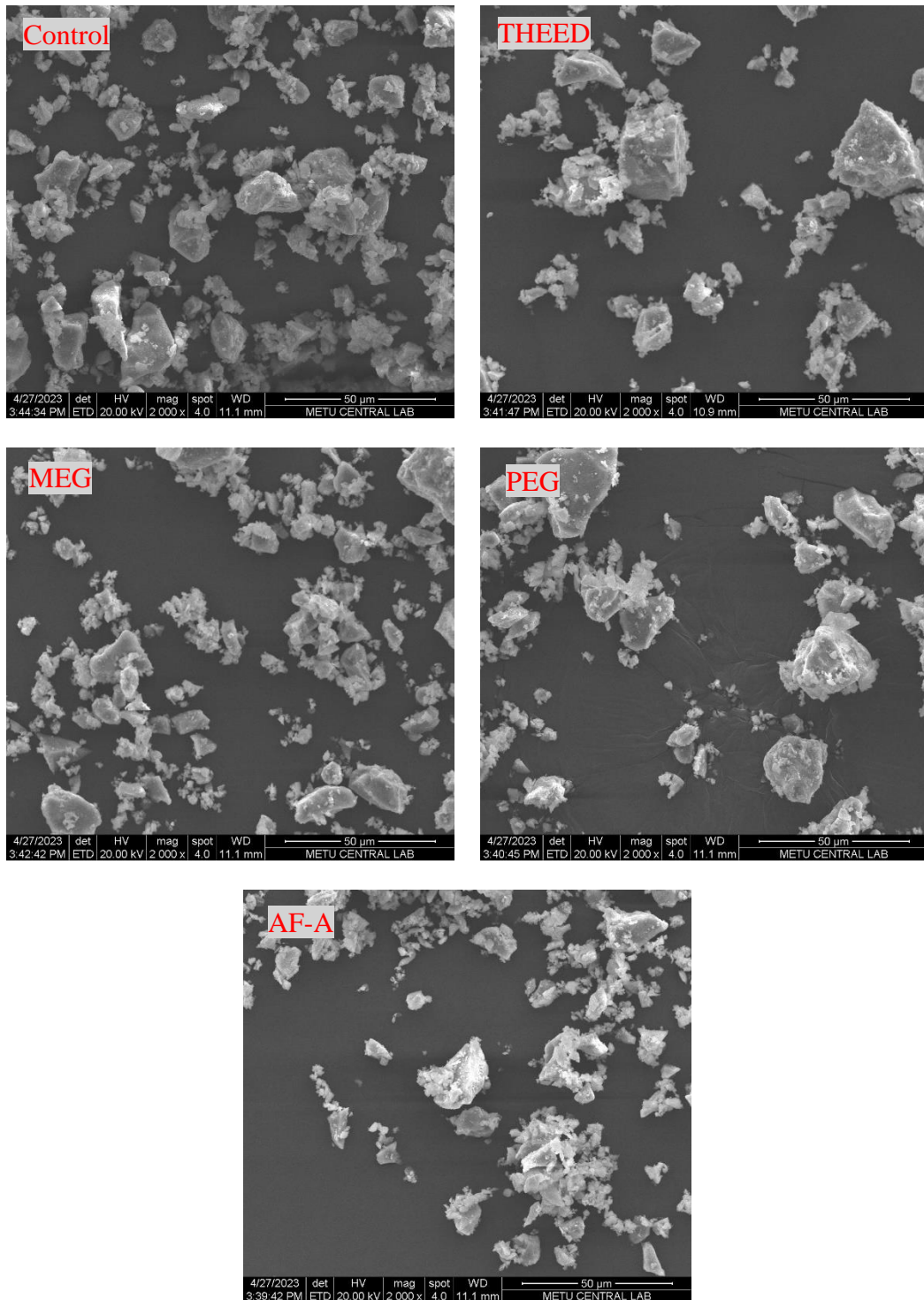


Figure B.3. SEM images of selected cements magnified 2000 times



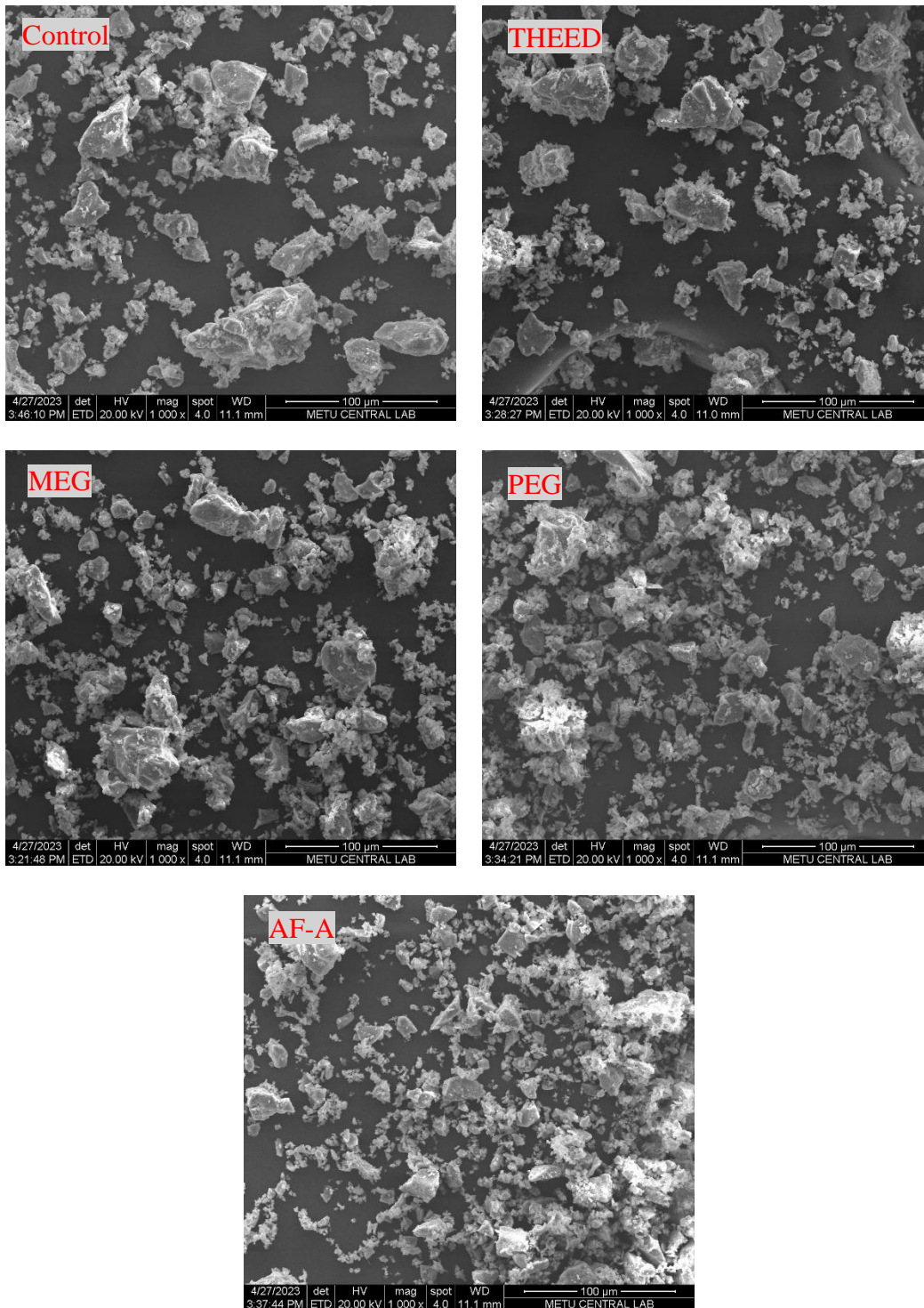


Figure B.4. SEM images of selected cements magnified 1000 times



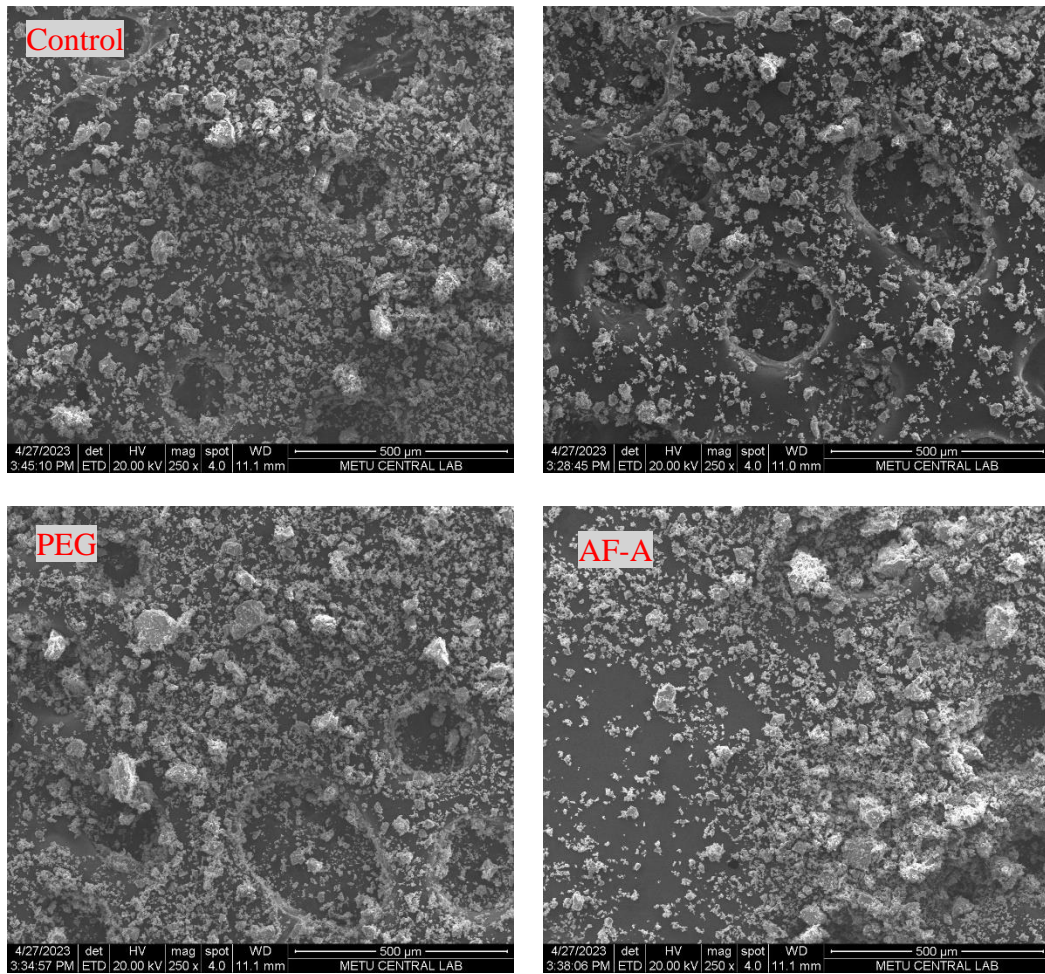


Figure B.5. SEM images of selected cements magnified 250 times