COMPARISON OF THE STRENGTH DEVELOPMENTS OF INTERGROUND AND SEPARATELY GROUND MARBLE-INCORPORATED CEMENT MORTARS

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ABSTRACT

COMPARISON OF THE STRENGTH DEVELOPMENTS OF INTERGROUND AND SEPARATELY GROUND MARBLE-INCORPORATED CEMENT MORTARS

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Production of Portland cement clinker contributes significantly to global warming and has a large environmental footprint. To reduce the amount of kiln-produced clinker in cement, the use of substitute natural or industrial waste materials has been gaining popularity. The use of $CaCO_3$-containing natural materials such as limestone and waste marble pieces has been increasing around the world, particularly after modifications made to cement production standards.

Two types of marble-containing blended Portland cements were produced; CEM II/A-L and CEM II/B-L according to TS EN 197-1. The marble content was varied from 0 to 30 % by mass of the clinker. Two different grinding methods, intergrinding and separate grinding were employed. Two different Blaine finenesses were targeted. Several properties of mortar specimens made with the blended cements were compared with each other and with the Portland cement control mortars.

Separate grinding of raw materials gave higher compressive strengths than intergrinding, for all cases at all ages. The initial and final setting times of the interground cement mortars were considerably longer. The differences were attributed to differences in the particle size distributions and the median particle diameters of the clinker and additive in the cement.

Keywords: cement, waste marble, particle size distribution, specific surface area, intergrinding, separate grinding.

ÖZ

BERABER VE AYRI ÖĞÜTÜLMÜŞ MERMER İÇEREN ÇİMENTO HARÇLARININ DAYANIM GELİŞİMLERİNİN KARŞILAŞTIRILMASI

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Portland çimento üretiminin küresel ısınmanın artmasında büyük bir payı vardır ve çevreyi de doğrudan etkilemektedir. Çimentodaki döner fırın mamulü klinker miktarını azaltmak için ikame malzeme olarak, doğal ya da endüstriyel atık kullanımı giderek daha yaygın hale gelmektedir. Özellikle çimento üretim standartlarında yapılan değişikliğin ardından kalker ve mermer tozu gibi $CaCO_3$ içeren malzemelerin kullanımı tüm dünyada artmaktadır.

Bu çalışmada, TS EN 197-1'e göre CEM II/A-L ve CEM II/B-L olmak üzere iki tipte mermer katkılı Portland çimento üretilmiştir. Beraber öğütme ve ayrı öğütme yöntemleri kullanılarak, klinker ağırlığı bakımından 0 ile % 30 arasında değişen oranlarda mermer katkısı kullanmıştır. Bu harmanlarda iki farklı Blaine incelik değeri hedeflenmiştir. Neticede elde edilen katkılı çimentolarla hazırlanan harç numunelerinin çeşitli özellikleri birbirleriyle ve Portland çimentosu kontrol harcı ile karşılaştırılmıştır.

Hammaddelerin ayrı öğütülmesi her durum ve zamanda beraber öğütme metodundan daha yüksek basınç dayanımı değerleri vermiştir. Beraber öğütülmüş çimento harçlarının ilk ve son priz zamanları önemli oranda daha uzun olmuştur. Bu farklar, klinker ve katkı maddesinin parçacık boyut dağılımındaki farklılıklar ve medyan parçacık çapı farklılıklarına bağlanmıştır.

Anahtar Kelimeler: Çimento, atık mermer, parçacık boyut dağılımı, özgül yüzey alanı, birlikte öğütme, ayrı öğütme.

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LIST OF ABBREVIATIONS

ASTM	:American Society for Testing and Materials
C2S	:Di calcium Silicate
C3A	:Tri Calcium Aluminate
C3S	:Tri Calcium Silicate
C4AF	:Tetra Calcium Alumina Ferrite
CEN	:European Committee for Standardization
g	:gram
GBFS	:Ground Granulated Blast Furnace Slag
GGBFS	:Granulated Blast Furnace Slag
IG	:Interground
L	:Limestone
LOI	:Loss on Ignition
m	:meter
MAC	:Minor Additional Components
min	:minute
µm	:Nanometer
MPa	:Mega Pascal
PC	:Portland Cement
PLC	:Portland Limestone Cement
PSD	:Particle Size Distribution
SG	:Separately Ground
TCMA	:Turkish Cement Manufacturer Association
TS	:Turkish Standard
EN	:European Norms
XRF	:X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 General

Portland cement is a man-made calcareous and clayey inorganic material, in finely ground form, can react with water to form hydraulic compounds. Cement is made by heating limestone (mainly calcium carbonate), with small quantities of other materials (such as clay and iron ore) to ~1450°C in a rotary kiln, in a process known as calcination. Carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or lime, which is then blended with the other materials that have been included in the mix. The materials undergo partial melting and form new compounds, mainly calcium silicates and calcium aluminates. The resulting material, called clinker, is then ground with a small amount of gypsum rock into a powder to make Ordinary Portland Cement [Kuleli, 2009].

When cement is batched and mixed with aggregates, water, chemical and mineral admixtures if necessary, in specified amounts, concrete is obtained. With an estimated annual consumption of 7.9 billion m^3 [U.S. Geological Survey, 2009], concrete is the most widely used construction material in the world. Cement is one of the main constituents of concrete and 2.8 billion tons of cement were produced worldwide, in 2007 [Kuleli, 2009]. This production amount is now believed to have surpassed 3.0 billion tons. Turkey is the 5th largest cement producer in the world and the largest cement producer in Europe, with a total cement production of 63.4 million tons per annum (see Fig. 1.1.) [Cembureau, 2011].

Country	Cement production° (Million tonnes)							
	2001	2005	2006	2007	2008	2009	2010	2011 P
China	661.0	1 068.8	1 236.8	1 361.2	1 388.4	1 644.0	1 881.9	2 063.2
India	102.9	142.7	159.0	170.5	183.3	186.9	213.9	223.5 e
European Union	225.9	248.0	264.8	271.0	251.8	201.0	190.9	195.3
USA	88.9	99.3	98.2	95.5	86.3	63.9	65.5	67.7
Brazil	39.4	38.7	41.4	45.9	51.6	51.7	59.1	63.9
Turkey	30.0	42.8	47.4	49.3	51.4	54.0	62.7	63.4
Russian Federation	28.7	48.7	54.7	59.9	53.5	44.3	50.4	56.1
Japan	75.9	68.7	69.9	67.8	63.0	54.9	51.7	51.5
Korea, Rep. of	52.0	47.2	49.2	52.2	51.7	50.1	47.4	48.3
Saudi Arabia	20.0	26.1	27.0	30.3	37.4	37.8	42.5 e	47.0 e
Indonesia	31.1	33.9	33.0	35.0	38.5	36.9	39.5	45.2
Mexico	30.8	36.0	38.8	39.5	38.3	37.1	38.9	39.8 e
Germany	32.1	31.0	33.6	33.4	33.6	30.4	29.9	33.5
Italy	39.8	46.4	47.8	47.4	43.0	36.4	34.4	33.1
France	19.1	20.9	22.0	22.1	21.2	18.1	18.0	19.4
Canada	12.1	13.5	14.3	15.1	13.7	11.0	12.4	12.3 e
Argentina	5.5	7.6	8.9	9.6	9.7	9.4	10.4	11.6
South Africa *	8.4	12.1	13.1	13.7	13.4	11.8	10.9	11.2
Australia	6.8	9.1	9.2	9.5	9.7	8.7	9.1	9.6 e
United Kingdom	11.9	11.6	12.1	12.6	10.5	7.8	7.9	8.3

Notes: ° Cement production including cement produced with imported clinker
P: Preliminary – e: Estimation – *: Estimation including cementitious

Figure 1.1. Yearly cement production in main world producers & Turkey [Cembureau, 2011].

The cement industry is one of the largest energy intensive industries responsible for about 1.5 % of the total world fuel consumption and about 2 % of the global electricity consumption [Norholm, 1995]. Furthermore, the cement industry is one of the world's largest industrial sources of CO_2 emissions (Fig.1.2.) Over the years the cement industry has substantially reduced emissions of CO_2 per ton of cement by improved energy efficiency but still accounted for 1.8 Gt/y CO_2 emissions in 2005 [IEAGHG, 2008].

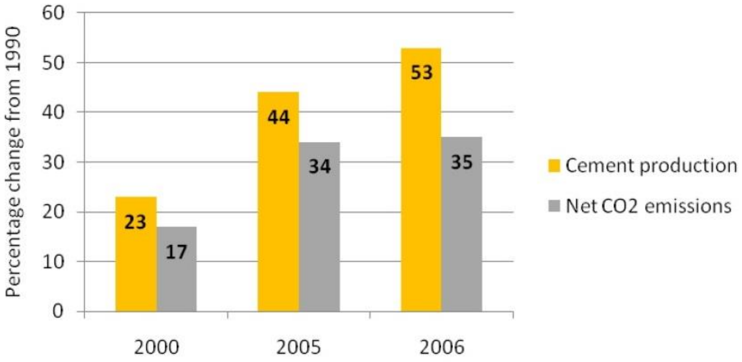


Figure 1.2. Partial decoupling of cement production from net CO_2 emissions over time [WBCSD, 2008].

CO_2 emissions arise from the calcination of the raw materials as well as from the combustion of fossil fuels. CO_2 resulting from calcination can be influenced to a very limited extent only. Emissions of CO_2 resulting from fuel combustion have been progressively reduced due to the strong economic incentive for the cement industry to minimize fuel energy consumption. CO_2 reduction of some 30 % in the last 25 years (arising mainly from the adoption of more fuel efficient kiln processes) leaves little room for further improvement. Further reduction is possible through increased utilization of renewable alternative fuels or other waste derived fuels and mainly the production of blended cements with mineral additions partly substituting clinker [IEAGHG, 2008].

The main steps of cement production are crushing, grinding, burning and final grinding operations. In the final grinding operation, which comes after the burning procedure, in order to produce Portland cement, clinker must be ground in cement mills.

Grinding is the further size reduction step of clinker particles. Some of the important reasons for grinding are [Avşar, 2003];

- separating one or more valuable minerals from the gangue components,
- increasing the specific surface area for specific chemical reaction,
- reducing the size of material to prepare it for the forthcoming process, and,
- providing market need about particle size specifications.

In the cement industry there is no need for separating one or more valuable minerals from the gangue components. However, it is absolutely necessary to increase the specific surface area of raw material for further steps and providing market needs about particle size specifications in cement mills. In the last step of producing Portland cement, clinker is ground with approximately 3-5 % amount of gypsum. In the production of Portland composite cements there are two alternatives for grinding clinker and additives: intergrinding and separate grinding. Both of these methods offer some advantages and disadvantages for cement plants. [Öner, 2000].

Developed countries have strict rules to protect the environment whereas many developing countries have almost no rules to protect the environment against wastes. However, wastes can be used to produce new products or can be used as admixtures so that natural sources are used more efficiently and the environment is protected from waste deposits. In Turkey marble dust is settled by sedimentation and leaved directly in situ which result in ugly appearance of environment and also causes dust in the summer and threat both to agriculture and health [Binici, 2007].

Turkey has even more, 40% of total marble reserves in the world. Seven million tons of marble are produced in Turkey annually. In processing marble such as cutting to size and polishing etc. for decorative purposes, marble dust and aggregate are created as byproducts. High volume of marble production generates a considerable amount of waste materials; almost 70% of this mineral gets wasted in the mining, processing and polishing stages - with obvious impact on the environment. More specifically, during the cutting process 20 – 30% of the marble block turns into dust. Thus, waste materials from marble processing plants represent millions of tons. Such waste is often disposed near residential areas. Stocking of these wastes is impossible, hence marble wastes constitute an environmental pollutant. 1400 tons of waste marble per day are left and stored in depot areas as wastes in Turkey [Gencel et al. 2012].

Blended cements based on the partial replacement of Portland cement clinker by wastes have been the subject of many investigations in recent years. The use of the replacement materials offer cost reduction, energy savings, arguably superior products, and fewer hazards in the environment. These materials participate in the hydraulic reactions, contributing significantly to the composition and microstructure of hydrated product [Kavas and Olgun, 2007].

In Portland composite cements, in accordance with specified standards, in addition to clinker, some materials such as granulated blast furnace slag (GBFS), natural pozzolans, fly ash, or limestone are ground with the clinker. The cement/clinker ratio can be increased by using these additives so plants can produce more cement with less clinker. It is obvious that using less clinker is good not only for economical but also environmental reasons. Therefore, cement additives are commonly used in the cement industry especially in clinker grinding. CEM (II-III-IV-V) types comprise 60 percent of the total cement sales in 2008 according to statistics of Turkish Cement Manufacturers' Association (58 percent in 2007 and 57 percent in 2006) [TCMA, 2009].

Usage of limestone as a mineral additive has recently increased with the advent of new European Cement Standards. Being an easily available material and often having no remarkable transportation cost for cement plants, limestone addition appears likely to increase in the near future. Therefore, it is essential to understand the effects of finely ground limestone on cement hydration and properties. The idea of using limestone as an interground cement addition material seems to have originated from the following two reasons; decreased energy consumption and CO_2 emission in cement production and decreased water requirement in cement with better mortar plasticity and water retention.

Grinding influences the strength that can be achieved by a given amount of clinker. Grinding too coarsely wastes the potential of the clinker. Coarse grinding is detrimental considering bleeding, plasticity and some other properties of concrete. Environmental regulations direct cement factories to produce with less harmful effects to the environment. Accordingly, while increasing their production, cement factories should reduce their harmful emissions by mixing some addition materials with clinker which is finely ground for not wasting the potential and for accepting more addition amounts. In essence mineral additives can replace a certain size fraction of the clinker in cement to yield environmental and performance benefits [Hawkings et al., 2003].

1.2 Objective and Scope of This Study

This study focuses on comparing the influence on mortar properties of separately grinding and blending marble with Portland cement clinker and intergrinding them. This type of mineral addition is quite new in cement production when compared to natural pozzolans, fly ash and blast furnace slag. As such, the knowledge on cements containing marble is considerably inadequate, and there is a need for further research on this topic. With this in mind, for more efficient usage of marble wastes in cement production the current study was designed;

- to determine the effects of marble addition on main properties of cements which are grinding properties, particle size distribution, strength, setting time, and
- to determine potential usability of marble wastes from marble factories as a limestone-like additive in blended cement production.

This thesis consists of five chapters. Chapter 2 presents a literature review and provides a general background on cement production, the use of mineral additives and particularly the use of waste marble for clinker replacement. Chapter 3 introduces the materials used in the experimental program, and the standard laboratory tests performed. Chapter 4 presents the results of the test program focusing on the particle size distribution and compressive strength development of the control and marble blended cement mortars. Chapter 5 gives a summary of the work done, highlights key findings, and recommends areas for further research to complement and reinforce the findings of this study.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

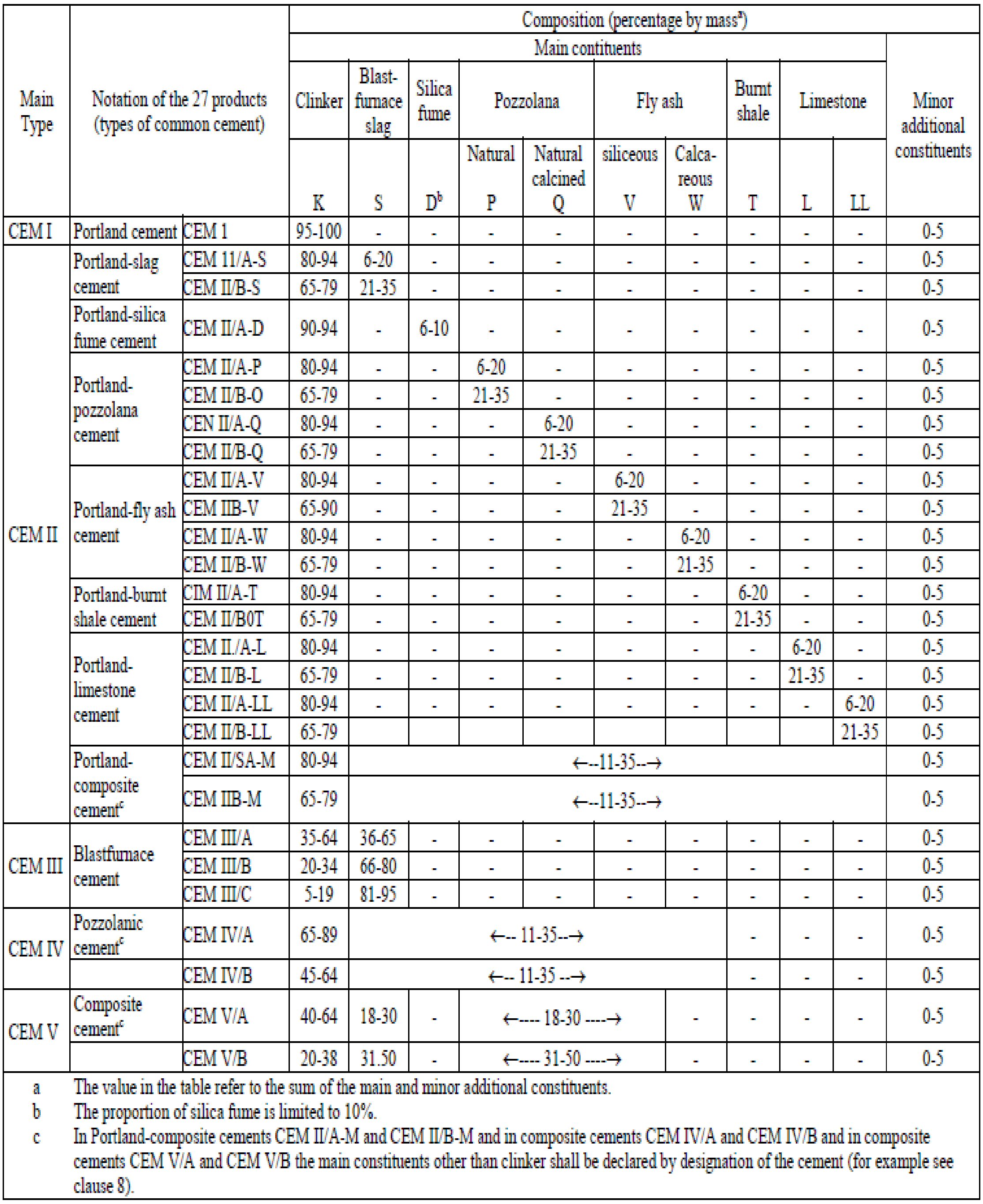
2.1 General: Portland cement, Marble Dust

Portland cement is a binder which mainly consists of compounds of calcium, silicon, aluminum, iron and small amounts of other materials. Hydraulic cements are those used in the production of concrete which set, harden and gain strength when combined with water [Hewlett, 2004].

In the early the 19th century, Joseph Aspdin, a bricklayer, first made and patented Portland cement whose name was given since the hardened cement resembled the color and quality of limestone quarried on the tied island of Portland [Erdoğan and Erdoğan, 2007]. Since then, Portland cement has been produced by mixing together calcareous and argillaceous, or other silica-, alumina-, and iron oxide-bearing materials, burning them in a kiln at a temperature of about 1450°C, and grinding the resulting clinker with a small amount (3 - 5 %) of gypsum [Neville, 2003].

There are many types of cements defined in different standards. In the harmonized Turkish standard TS EN 197-1, there are 27 different main types of cement and which can be grouped into 5 general categories and 3 strength classes: ordinary, high and very high the nomenclature can be seen in Table 2.1. This European standard covers both Portland and blended cements while there are three different standards at the American Society for Testing and Materials (ASTM); one for various types of Portland cement (ASTM C 150), the second for blended cements (ASTM C 595) and third for a broad performance based specs (ASTM C 1157).

Table 2.1. Percentage of Cement Composition According to TS EN 197-1



Main Type	Notation of the 27 products (types of common cement)		Composition (percentage by mass[a])										
			Main contituents										Minor additional constituents
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						Natural	Natural calcined	siliceous	Calca-reous				
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM 1	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM 11/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-O	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEN II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM IIB-V	65-90	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CIM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B0T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II./A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79									21-35	0-5
	Portland-composite cement[c]	CEM II/SA-M	80-94	←--11-35--→									0-5
		CEM IIB-M	65-79	←--11-35--→									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement[c]	CEM IV/A	65-89	←-- 11-35--→						-	-	-	0-5
		CEM IV/B	45-64	←-- 11-35 --→						-	-	-	0-5
CEM V	Composite cement[c]	CEM V/A	40-64	18-30	-	←---- 18-30 ----→			-	-	-	-	0-5
		CEM V/B	20-38	31.50	-	←---- 31-50 ----→			-	-	-	-	0-5

a The value in the table refer to the sum of the main and minor additional constituents.
b The proportion of silica fume is limited to 10%.
c In Portland-composite cements CEM II/A-M and CEM II/B-M and in composite cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

Limestone is a sedimentary rock which is essentially composed of the minerals calcite and aragonite, each a different crystal form of calcium carbonate ($CaCO_3$) and a fundamental raw material of the cement. It is widely available in nature. It constitutes ~10 % of the total volume of the sedimentary rocks on the Earth. The most common forms of calcium carbonate in nature are limestone and chalk. The hardness of limestone is generally less than 4.0 according to the Mohs' scale of hardness and its solid forms' specific gravity differs within the range of 2.6 to 2.8. Only the purest varieties of limestone are white. Limestone usually contains admixtures of clay substance or of iron compounds which influence its color. The most common impurity in limestone is $MgCO_3$ [Kranjc, 2006].

One of the many main usage areas of limestone is the cement industry. In cement raw materials the lime component is generally represented up to 76 - 80 %. Limestone decarbonates starting at ~600 ˚C. After the formation stage of clinker in the kiln the presence MgO causes volume instability and its content is limited to 5% [TS EN 197-1, 2002]. The typical amount of MgO in Portland cement is about 1% [Hewlett, 2004].

Marble is a metamorphic rock resulting from the recrystallization of carbonate minerals, most commonly calcite or dolomite. The purity of the marble is responsible for its color and appearance: it is white only if the limestone is composed solely of calcite (100 % $CaCO_3$). Marble is always in great demand, used for construction and decoration as it is durable, and has a pleasant appearance. A large quantity of powder is generated during the marble cutting process. This waste product is used to replace limestone in cement production; it does not significantly alter concrete characteristics and also reduces the landfill impact of the waste material [Messaoudene and Jauberthie, 2011].

Large quantities of marble dust are produced in Turkey. The marble dust is generated as a by-product during the cutting of marble. During the cutting process, about 25 % marble is resulted in dust. The marble cutting industries are dumping the marble dust in any nearby pit or vacant spaces. This imposes threats to eco-system, and physical, chemical and biological components of the environment. Therefore, utilization of marble dust in the production of new materials will help to protect environment [Kavas and Olgun, 2007].

2.2 Portland Limestone Cements

Blended cements are made out of clinker and mineral additions such as ground, granulated blast furnace slag (GGBFS), fly ash, natural pozzolans, limestone, burnt clay, etc. Replacing part of the clinker causes not only a reduction in the consumption of natural resources, fossil fuels and in gas emissions, but can also contribute to better concrete properties in both the fresh and hardened states [De Weerdt, 2007].

Today, utilization of blended cements is usually preferred due to their economic and technical benefits and indirect advantages such as their ability of decreasing CO_2 emissions by reducing clinker production in plants. Recently, materials possessing pozzolanic property are usually employed for the same purpose, and utilization of limestone is limited to 5 % by weight usually as minor component in normal Portland cement production [Tosun, 2009].

In Europe, a number of countries allowed different percentages of limestone prior to adoption of EN 197-1. For example, Schmidt (1992) states that large quantities of 20% limestone cements were produced by Heidelberg Cement as early as 1965 for specialty applications. Its use in France dates back to at least the 1970s. In the 1987 draft of EN 197, a cement designated as PKZ was composed of 85+/-5% clinker and 15+/-5% limestone [Schmidt, 1992]. By 1990, 15 +/- 5 % limestone blended cements were reported to be commonly used in Germany. In the UK, BS 7583 allowed up to 20% limestone cement in 1992 [Hooton et al., 2007].

While limestone/cement blends have been employed for many years in Europe, it was only in 2004 that the ASTM C150 standard specification for portland cement was modified to allow the incorporation of up to a 5% mass fraction of limestone in ordinary portland cements, and this was done only after an extensive survey of the available literature led to the conclusion that in general, “the use of up to 5% limestone does not affect the performance of portland cement.” Higher addition rates of 10 to 15% are currently being discussed in the U.S. and in 2009, the Canadian Standards Association in fact approved Portland Limestone Cements with an upper limit of 15 %. In the U.S. some ready mixed concrete producers already add limestone powder above a 5% level directly to their concrete mixtures. In the Netherlands and elsewhere, limestone powder is commonly employed as a filler in self-consolidating concretes, once again at values well above the 5% level [Bentz D. et al., 2009].

Nowadays, the production of blended cements incorporating limestone as major additive is increasing by the validation of EN 197-1 standard. Limestone blended cement types such as CEM II/A-L, CEM II/B-L conforming to TS EN 197-1 standard are available in the market. Limestone is also employed as an additional component in the production of CEM II type Portland composite cement. The codes of materials used in the production of blended cement are required to be used in cement nomenclature.

The current EN 197-1 (2000) allows all of the 27 common types of cement to contain 5% minor additional components (MAC), which most typically are either limestone or cement raw meal. 4 types of cement allow higher amounts of limestone in two replacement level ranges, CEM II/A-L and CEM II/A-LL (6- 20% limestone), as well as CEM II/B-L and CEM II/B-LL (21-35% limestone) in addition to the 5% minor additional components (Table 2.2.). The difference between the –L and the –LL designations are based on different qualities of the limestone used. For both L and LL, $CaCO_3 \geq$ 75% and clay content ≤ 1.20 g / 100 g. The difference is in the allowable total organic carbon (TOC) content: Type LL restricts TOC ≤ 0.20 % by mass while Type L restricts TOC ≤ 0.50 % by mass.

Table 2.2. Portland Limestone Cement Classification according to EN 197-1

Cement Code	Cement types incorporating limestone		Ingredients (% by mass)				
			Clinker	Blast furnace slag, silica fume, natural pozzolan, fly ash, burnt schist	Limestone		Minor addition
					L	LL	
CEM II	Portland limestone cement	CEM II/A-L	80-94	-	6-20	-	0-5
		CEM II/B-L	65-79	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	21-35	0-5
	Portland blended cement	CEM II/A-M	80-94	← 6-20 →			0-5
		CEM II/B-M	65-79	← 21-35 →			0-5

During the last decades, Portland limestone cement (PLC) has shown a rapid increase of production in the cement industry in order to achieve the goals of lowering consumption of natural raw materials, saving fuel energy for clinker production, and reducing CO_2 emissions [Bonavetti et al., 2011]. According to the CEMBUREAU statistics, two-thirds of the market shares of cement in European countries correspond to CEM II cements, with PLC being the most frequently used [Cembureau, 2008]. According to the European Committee for Standardization (CEN), the use of CEM II limestone cements has grown from 15 % in 1999 to 31.4 % in 2004 and is now the single largest type of cement produced (see Figure 2.1.) [Hooton et al., 2007].

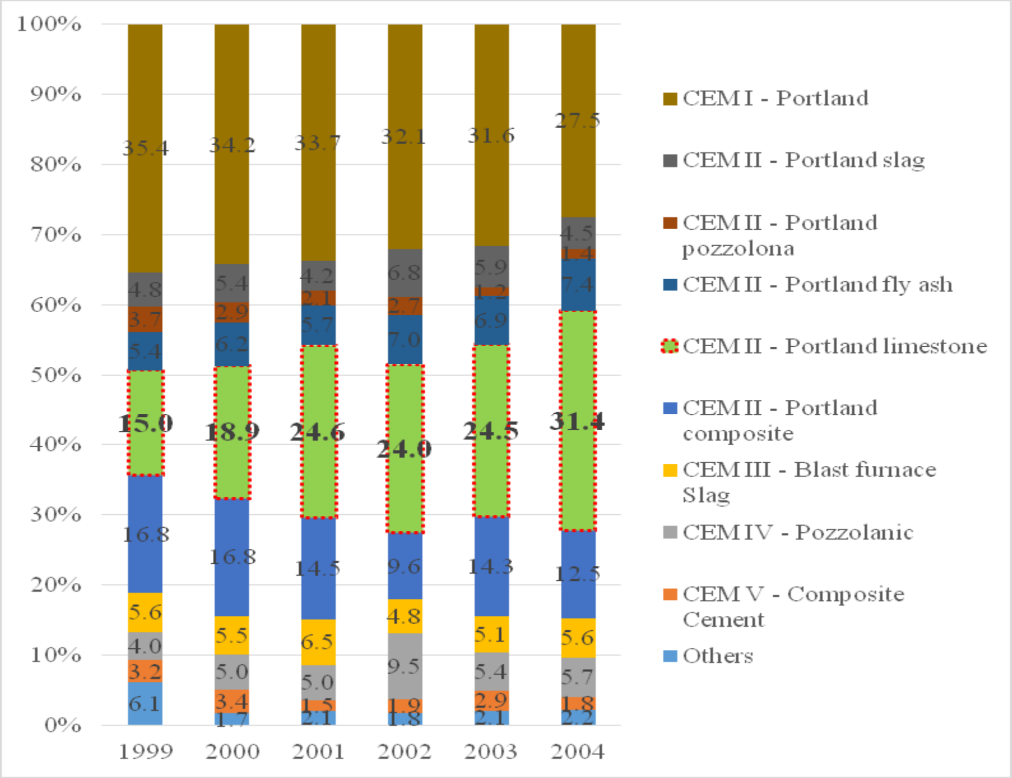


Figure 2.1. CEN Data on Types of Cement Produced in Europe

If the minor component is limestone, the standard allows incorporation of 40% of limestone with a minimum 32.5 MPa 28-day strength (CEM II/B-L 32.5 N). According to TS EN 197-1, the $CaCO_3$ content of limestone employed in the production of blended cement should be at least 75 %. Clay content of limestone should not exceed 1.2 %. Limestone may contain organic carbon, depending on the impurities of the raw materials. The total organic carbon content of limestone should be determined according to the TS EN 13639 standard. High organic carbon contents may cause incompatibilities and problems when air entraining admixtures are employed in concrete production [Tosun, 2009].

2.3 Influence of Limestone as Partial Replacement of Cement

PLC can be produced in two ways, either by intergrinding of Portland cement clinker, limestone and gypsum, or by blending the separately ground Portland cement (clinker + gypsum) and limestone [Opoczky and Tamas, 2002]. Indeed, both processes present advantages and disadvantages. Inter-grinding is easier and the mill acts as a grinding device and a homogenizer at the same time. This technique has good results when it is included in a closed milling system equipped with high efficiency separators. Clinker, gypsum and limestone have different grindabilities, and the individual particle size distribution (PSD) of each component influences the early hydration of interground blended cement [Sprung and Siebel, 1991]. Then, the milling operation requires that parameters can be set according to the proportions of the components in PLC to obtain an optimal efficiency at a given output fineness [Tsivilis et al., 1999]. Separate grinding and mixing technology is more appropriate to design the PSD in a multicomponent cement and to produce a low quantity oriented to the market of tailor-made cement [Bonavetti et al., 2011].

The properties and performance of blended cements are affected by the proportions and the reactivity of the mineral additions but also to a large extent by the particle size distribution (PSD). The different components of the blended cement each need to obtain certain fineness in order to be hydraulically, latent hydraulically or pozzolanically effective. By adapting the PSD of the mineral additions and clinker to each other, the packing can be optimized and the void space between the cement particles can be minimized. The water, formerly filling the voids between the cement particles, can act as lubricant and coat the particles with a film of water so that the constituent particles can move freely. Consequently the workability is improved [Erdoğdu, 2002].

Tsivilis et al. (1999) and von Schiller and Ellerbrock (1992) studied the intergrinding of clinker and limestone. They found that when limestone was interground with clinker, it widened the PSD of the cement (see Fig. 2.2.). The component which was the hardest to grind, clinker, was found in the coarser fraction whilst the easier to grind one, limestone, was concentrated in the finer fraction (Fig. 2.3. & Fig. 2.4.). In Fig. 4 the required energy to reach certain fineness is taken as a measure of grindability is done by Zeisel method [De Weerdt, 2007]. The addition of limestone with a wide PSD led to a decreasing water demand per volume dry material and improved the workability.

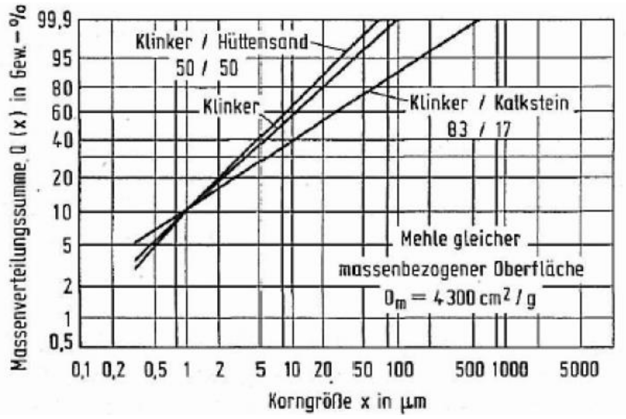


Figure 2.2. Particle size distribution of interground clinker/slag and clinker/limestone with equal Blaine specific surface [von Schiller and Ellerbrock, 1992].

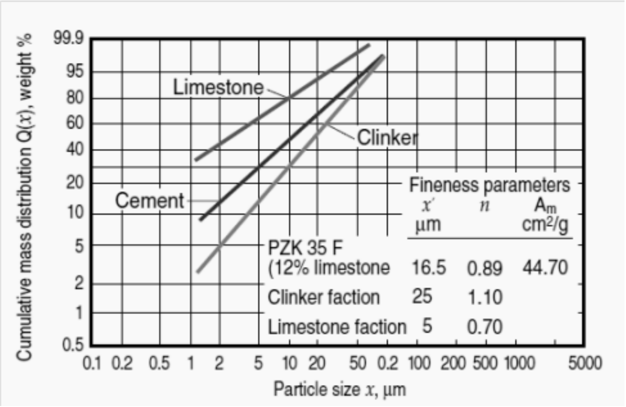


Figure 2.3. Cumulative mass distribution of a limestone cement with limestone content of 12% by weight and of its clinker and limestone components after grinding [von Schiller and Ellerbrock, 1992].

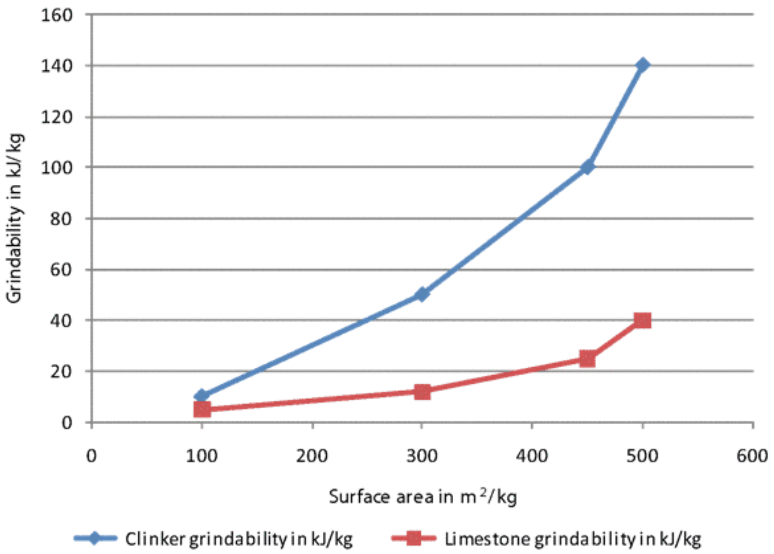


Figure 2.4. Comparison of the grindabilities of limestone and clinker as measured by energy to reach certain fineness [Opoczky, 1993].

Tsivilis et al. (1999) observed a remarkable trend. As the limestone content surpassed 30%, the grinding of both clinker and limestone was inhibited. Samples containing 40% limestone show in spite of a higher Blaine specific surface (due to the higher limestone content) a lower clinker and limestone fineness compared to those containing 30%. Von Schiller and Ellerbrock (1992) experienced a similar phenomenon when increasing the limestone content from 12 to 20 wt. %. The fineness of the limestone cement namely decreased and its PSD became narrower.

Usage of limestone increases rate of the formation of ettringite which results in a retardation in setting. As a result, the effectiveness of gypsum is increased and lower amounts of gypsum can be used in the presence of limestone to enable the same set retardation effect. This brings about the conclusion that limestones can be used as a gypsum replacement material as a set retarder. The amount of the replacement in cement is determined by cement composition, and therefore, it should be done by careful tests [Bernsted, 1983]. Tsivilis et.al. (1999) (A study on the parameters affecting the properties of Portland limestone cements, 1999) studied portland limestone cements produced by using 2 clinkers and 3 limestones and by intergrinding ingredients for specified periods. According to their results initial and final setting times of Portland limestone cements increase with increasing limestone amount in cement.

Von Schiller and Ellerbrock (1992) found that to obtain a 50 MPa 28-day compressive strength the limestone cement has to be ground increasingly finer as the limestone content augmented. The cement had to have a characteristic diameter of 30 µm when no clinker was replaced by limestone, 26 µm for 10 wt. % replacement level, 14 µm for 20 mass % and it is impossible to obtain that strength for a limestone cement containing 30 wt.% limestone. This led to the conclusion that for a strength level of 50 MPa not more than 15-20 wt. % limestone should be applied in limestone cement.

Sprung and Siebel (1999) found that the use of inert material as a very fine filler can lead to an increase in strength due to improved packing of the particles i.e. filling of voids between the cement grains. This effect is seen at early ages, but unlike the case with fly ash or other pozzolanic materials, does not produce additional increases in strength with continued curing. When limestone is included in large quantities (15% to 25%) it acts as a diluent, so that strengths are lower than for comparable Portland cements. To an extent, the loss of strength due to dilution can be offset by finer grinding. Schmidt (1992) observed that cement and concrete strengths normally are not reduced by using 5% to 10% limestone. The dilution effect is seen at higher dosages unless the cement is ground finer to compensate. Reductions in the water cement ratio are often possible because of the improved particle packing; these will further compensate for the dilution effect.

Livesey (1991) reports an investigation of concretes of constant workability made from cements containing up to 25% limestone. He found that the use of 5% limestone had little effect on performance, although at higher levels the properties of the limestone can be significant. Cement containing 5% limestone showed a somewhat accelerated strength gain at early ages, particularly when the cement was more finely ground. The same author reported in another study that the presence of 5% limestone has no significant effect on strength, as some strengths are slightly higher and some slightly lower.

Strength of Portland limestone cements are found to be similar to those of Portland cements at early ages for low addition amounts. However, limestone is reported to have no beneficial effect on strength at later ages, unlike pozzolanic materials. All results from the literature presents compressive strengths at relatively early ages of concrete when compared with the life of concrete which can be measured by decades. A study by Dhir (1994) looked at the 5-year strength of Portland Limestone Cements. The samples containing 5 % limestone, stored in water for five years, had compressive strengths slightly lower than their corresponding Portland cement controls, whilst cements with 25% addition had substantially lower strengths. Also this study exhibited that strength gain behavior of cements with 0, 5 and 25% limestone between 28 days and 5 years are all modest and similar to each other.

CHAPTER 3

EXPERIMENTAL STUDY

The objective of this study is to examine the effects separate grinding and intergrinding of marble blended cements on the mechanical property development of mortars. The selected raw materials were first ground to the chosen finenesses, then they were blended to prepare the cements to be used, and then mortar mixtures made with these cements were tested.

3.1 Materials Used

The materials used are Portland cement clinker, marble dust, and gypsum. The clinker used in this study was obtained from Set Afyon Cement Plant. Marble pieces are the same byproduct marble dust the plant currently uses to produce CEM II/A-LL and which is gathered from several marble plants in the Afyonkarahisar region and piled mixed. The gypsum rock used, from Afyonkarahisar, is also the same as that used in the plant for production of cement. All grinding operations, all chemical, physical and mechanical tests were performed in the Quality Control Laboratory of Set Afyon Cement Plant and low-angle light-scattering (laser diffraction) particle size distribution analyses were performed in the Turkish Cement Manufacturers' Association laboratory, in Ankara. The chemical compositions of the materials used in this study are shown in Table 3.1.

Table 3.1. Chemical Compositions of the materials used

	Clinker	**Marble**	**Gypsum**
(%) SiO_2	20.69	1.33	2.13
(%) Al_2O_3	5.78	0.40	0.62
(%) Fe_2O_3	3.45	0.21	0.34
(%) CaO	66.42	53.49	31.67
(%) MgO	2.21	0.56	0.88
(%) SO_3	0.69	0.07	40.41
(%) K_2O	0.76	0.08	0.12
(%) Na_2O	0.36	0.17	0.34
(%) Na_2O eq. Alkali	0.86	0.22	0.42
(%) Cl^-	0.0081	-	-
(%) LOI	0.25	43.76	18.20
(%) free CaO	0.98		
Lime Saturation Factor	99.14		
Silica Modulus	2.24		
Alumina Modulus	1.68		
C_3S	65.32		
C_3A	9.49		
C_2S	10.06		

Standard Rilem-Cembureau type sand, conforming to TS EN 196-1, was used in the preparation of all the mortars and pastes. The water used in the study was the tap water of Afyon Cement Plant. The main compounds of the Portland cement clinker, shown in Table 3.1, were calculated using Bogue's equation.

3.2 Experimental Procedures

3.2.1. Preparation of the Cements

All the chemical analyses were done by X-Ray Fluorescence (XRF) Analyzer according to TS-EN 196-2, after preparing them for the analysis using a bead fusion machine. Figures 3.1. and 3.2. shows the equipment used for this process.

Figure 3.1. Bead Fusion Machine

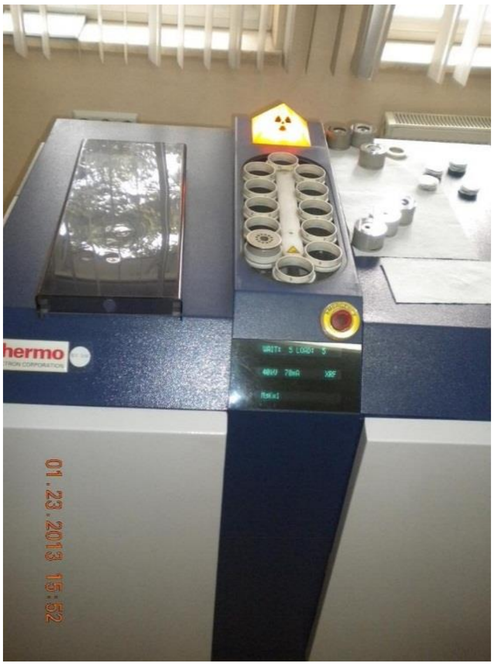


Figure 3.2. X-Ray Fluorescence Analyzer

After the transportation of the materials to the laboratory, all of the materials were dried and crushed (Figures 3.3. and 3.4.). The cement mixes were prepared for examining the properties of the blended cements in various compositions and in various fineness.

Figure 3.3. Oven used to dry the materials

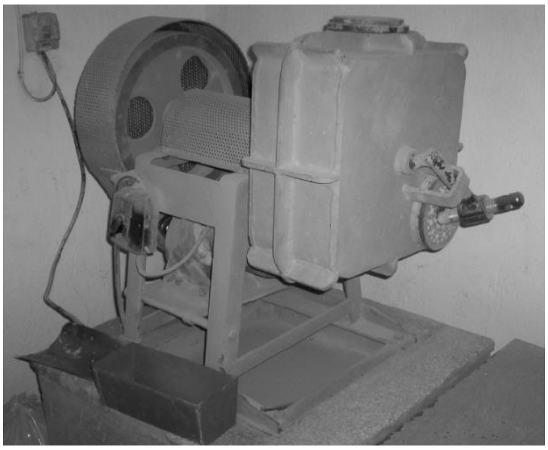


Figure 3.4. Crusher

The cements were prepared in a laboratory type ball mill (see Fig. 3.5.). The capacity of the mill is limited with 3000 grams of material. Size and weight information of the ball/cylpeps are shown in Table 3.2.

Table 3.2. Laboratory mill charge composition

Ball Diameter/cylpeps length (mm)	Count	Ball/cylpeps weight (g)
ϕ50	7	3740
ϕ30	32	3370
ϕ20	158	4990
22x22	246	17540
16x16	423	11850

Figure 3.5. Laboratory mill and charge

The specific surface areas of the samples were aimed as 3000±100 cm^2/g and 5000±100 cm^2/g (Blaine), and the duration of the grinding was adjusted to reach this target. First the samples were ground for specified times like several half-hour periods and a grinding time required to reach certain Blaine values curve was obtained for each material. The duration of the grinding necessary to obtain the targeted finenesses was determined using this curve. A Blaine fineness test was performed according to TS-EN 196-6 to make sure the target was achieved. The densities of the samples for the Blaine test were determined using a gas pycnometer (Fig. 3.6.). The average densities of the samples can be seen in Table 3.3 for both grinding methods with respect to mixture percentages.

Figure 3.6. Gas Pycnometer and Blaine fineness Apparatus

Table 3.3. Average Densities of the samples according to marble percentages (g/cm^3)

	Blank	6%	15%	30%
Separately Ground	3.13	3.12	3.08	3.05
Interground		3.12	3.09	3.05

For both the interground and separately-ground samples laser granulometry analyses were finally conducted in the Turkish Cement Manufacturers' Association laboratory using about 25 g of material.

3.2.2. Cements Produced

In this study, a total of 22 different cement samples were prepared. Two of them are the control samples without any admixtures. Control samples were prepared with 96 % clinker and 4% gypsum by weight. The blended cements were prepared by replacing 6 %, 15 % and 30 % by mass of the clinker amount in the mix and keeping the gypsum to clinker amount same as in the control samples. All samples were prepared based on the weight of 3000 grams and its multiples. The calculation of the proportions of ingredients in the control mixtures is as follows: Clinker = 3000*96/100 = 2880 g; Gypsum = 3000*4/100 = 120 g. By keeping gypsum to clinker ratio constant at 120/2880= 0.0417, the clinker, additive and gypsum proportions shown in Table 3.4 were calculated.

Table 3.4. Proportions of raw materials in the different blended cements.

	6%	**15%**	**30%**
Clinker (g) **Marble (g)** **Gypsum (g)**	2723.1 163.4 113.5	2517.5 377.6 104.9	2236.0 670.8 93.2
Total (g)	3000.0	3000.0	3000.0
Marble / Clinker	6.0 %	15.0 %	30.0 %
Gypsum / Clinker	4.17 %	4.17%	4.17%

In this study, 12 mixes were prepared with marble dust, in the amounts of 6 %, 15 % and 30 % by weight both by intergrinding and separate grinding. Table 3.5 shows the labeling of the prepared mixes.

Table 3.5. Labeling format of the different mixtures

	Marble	**Amount (%)**	**Grinding**	**Blaine Fineness (cm^2/g)**	**Code**
1	M	6	Intergrinding	3000	M-6-I-3000
2	M	15	Intergrinding	3000	M-15-I-3000
3	M	30	Intergrinding	3000	M-30-I-3000
4	M	6	Intergrinding	5000	M-6-I-5000
5	M	15	Intergrinding	5000	M-15-I-5000
6	M	30	Intergrinding	5000	M-30-I-5000
7	M	6	Separate grinding	3000	M-6-S-3000
8	M	15	Separate grinding	3000	M-15-S-3000
9	M	30	Separate grinding	3000	M-30-S-3000
10	M	6	Separate grinding	5000	M-6-S-5000
11	M	15	Separate grinding	5000	M-15-S-5000
12	M	30	Separate grinding	5000	M-30-S-5000

These blended cements were prepared by both intergrinding and separate grinding at two fineness levels. In intergrinding, all the constituents (clinker, mineral admixtures and gypsum) were ground until the specified Blaine fineness value was reached. In separate grinding, the clinker and gypsum mixture and the mineral additives were ground separately to approximately the same fineness then blended according to the specified proportions.

3.2.3. Mortar Tests Performed on the Cement Samples

Compressive strength measurements of the mortars were made at 2, 7 and 28 days as per the TS EN 196-1 standard. A water/cement ratio of 0.5 was used for all mixtures. The cement content of the mortar is specified as 450 g in the test method. The ratio of sand-to-cementitious powder was 3 for all mixtures. 40 x 40 x 160 mm rectangular prism specimens were prepared. Specimens were demolded after 24 h, and cured in water at 20±1 ˚C for 2, 7 and 28 days. The prisms were broken in bending and the average compressive strength was determined using four half-specimens on each test day. Figures 3.7 through 3.9 show the equipment used to vibrate the prism specimens, the water curing chamber, and the apparatus used to measure compressive strength.

Figure 3.7. Prism sample mold and vibration shock table

Figure 3.8. Curing chamber

Figure 3.9. Apparatus used for Strength Testing

The normal consistency and setting time analyses were performed according to TS EN 196-3. For normal consistency, cement paste was prepared with 500 g cement and adequate amount of water according to the limits in the standards. After the determination of the water requirement (in percentage) for normal consistency; initial and final setting time were determined using the Vicat needle penetration test for all the cements used (Fig. 3.10.). Expansion tests were also applied to the cement pastes with the help of the Le Chatelier apparatus following TS EN 196-3 (Fig. 3.11.).

Figure 3.10. Automatic Vicat Device

Figure 3.11. Le Chatelier Apparatus

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Grinding times of the Clinker and Marble to reach certain Blaine values

The change in the Blaine fineness values of the clinker, and marble used in the study with continued grinding in the ball mill, are shown in Fig. 4.1.

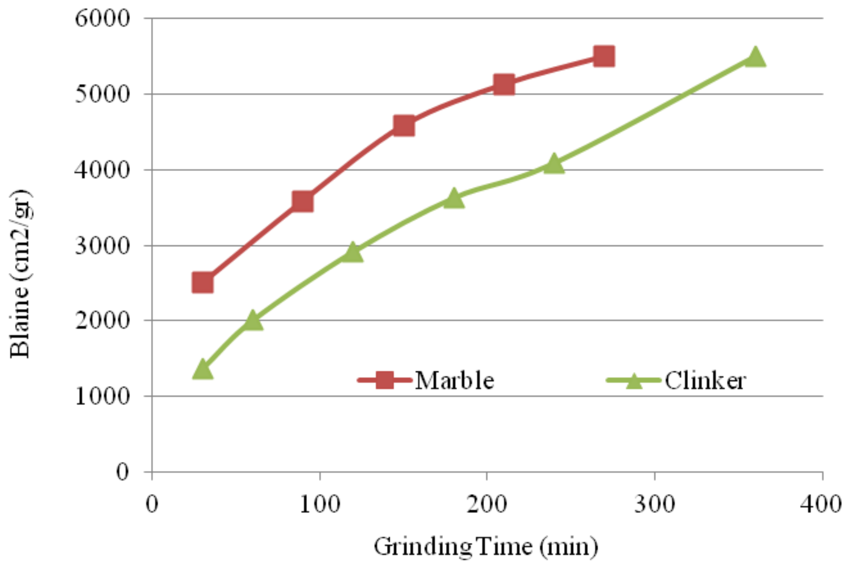


Figure 4.1. The grinding times vs. Blaine values of the marble and clinker used in the study

As expected, the clinker is harder and more difficult to grind than the marble. About two hours in the mill are required to achieve a Blaine fineness value of 3000 cm^2/g with the clinker, as opposed to about only one hour for the marble. For a Blaine of 5000 cm^2/g, three and five hours are required, respectively, for the marble and clinker.

Mixtures of marble and clinker offer intermediate resistance to grinding, as they are softer than the clinker but not as soft as the pure marble case. This is shown in Fig. 4.2. for mixtures containing 6 %, 15 %, and 30 % marble by mass of the clinker. The gypsum content of the mixtures in Fig. 4.2. is 4.15 % by clinker mass.

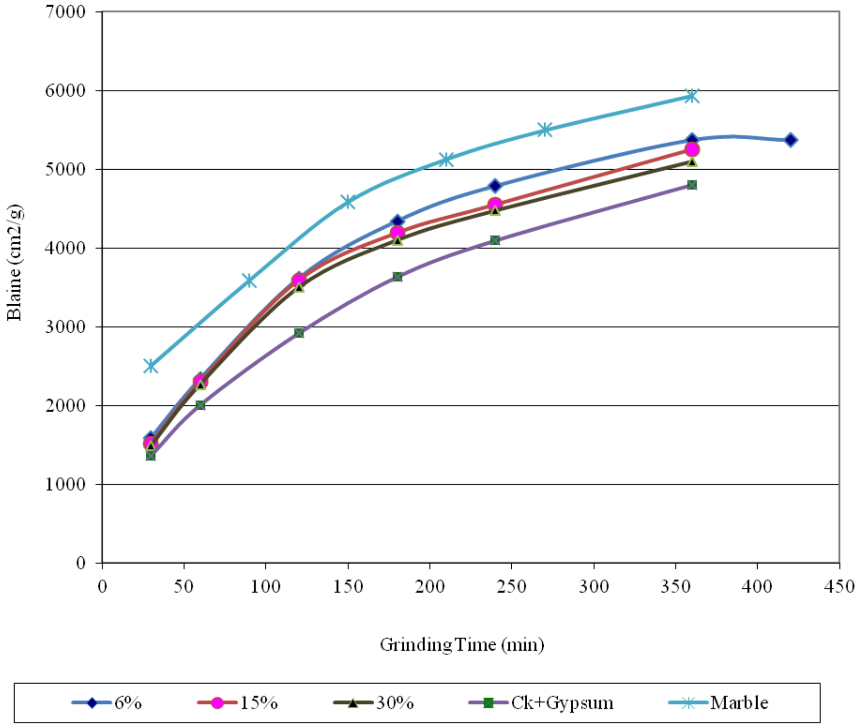


Figure 4.2. The grinding times vs. Blaine values of the marble and clinker compared with the clinker/gypsum/additive blend

Surprisingly, increasing marble content does not change the required grinding times of the cements much. One explanation for this outcome could be the observation that marble particles stick to the surface s of the steel charge in the mill. The hygroscopic nature of marble can prevent all of the moisture in the marble to be evaporated in the oven prior to milling. Fineness increases rapidly in the early stages of milling but later, this remaining hygroscopic water detaches from the marble and adheres onto the charge particles and the inner surface of the mill drum. Marble particles stick to these moist surfaces and create soft layers which hinder the size reduction [Tosun et al., 2009a and 2009b]. This is observed by the change in the slope of the blended cement curves in Fig. 4.2.

4.2 Particle Size Distributions of Different Cements

The particle size distributions of the twelve cements containing marble were determined using low-angle light scattering. Six of the cement mixtures had been prepared by intergrinding the marble, clinker, and gypsum, and the other six had been prepared by separately grinding the marble and the clinker/gypsum mixture to the same fineness. Two different overall finenesses and three different marble contents were evaluated. Figures 4.3. - 4.16. show the volumetric particle size distribution curves.

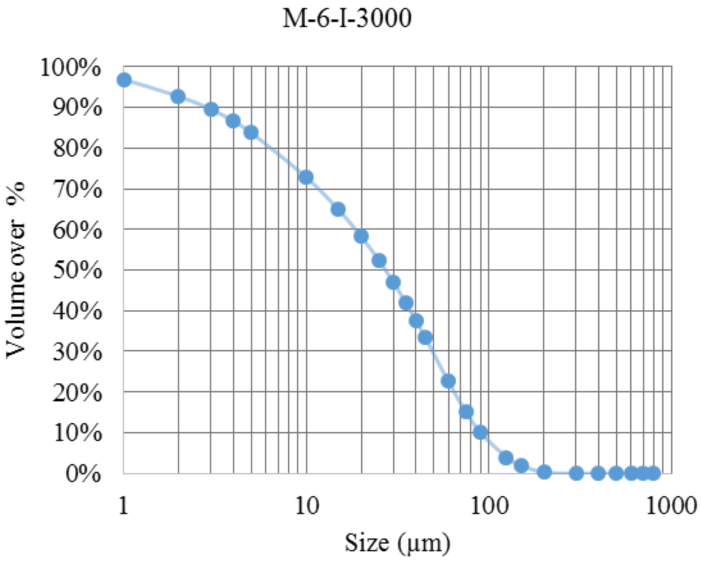


Figure 4.3. Particle Size Distribution for the sample coded as M-6-I-3000

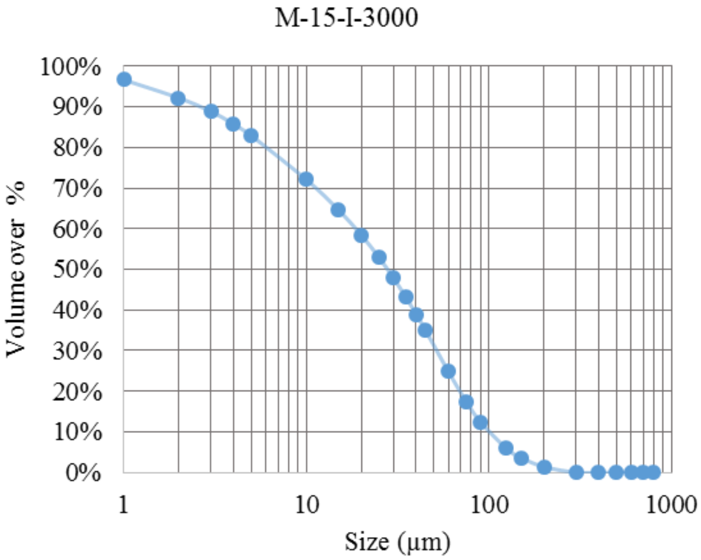


Figure 4.4. Particle Size Distribution for the sample coded as M-15-I-3000

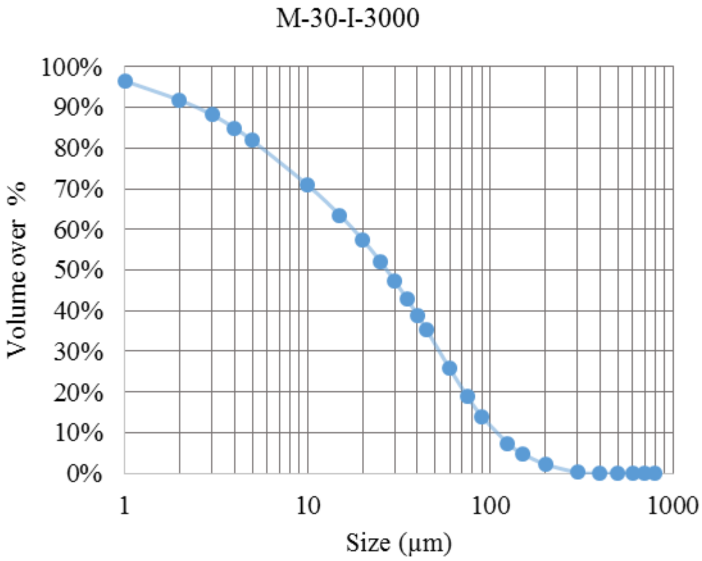


Figure 4.5. Particle Size Distribution for the sample coded as M-30-I-3000

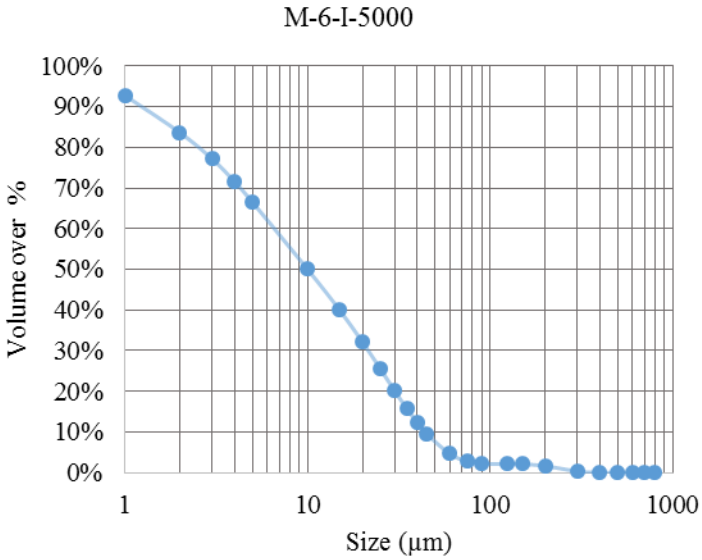


Figure 4.6. Particle Size Distribution for the sample coded as M-6-I-5000

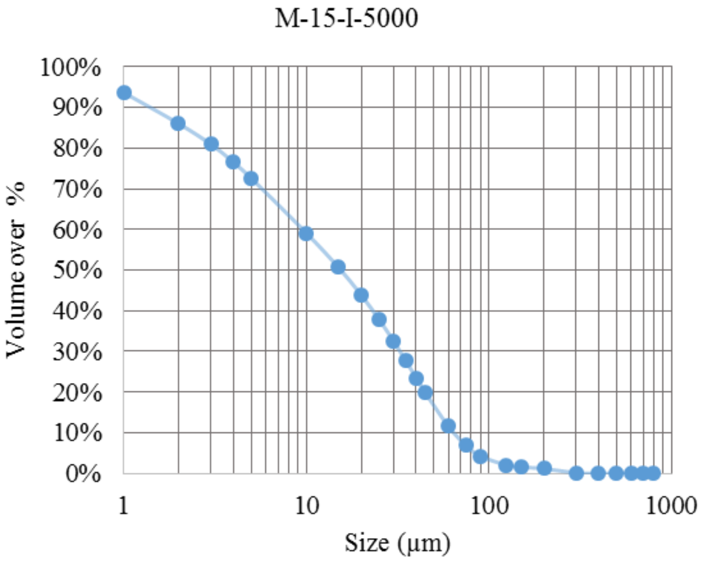


Figure 4.7. Particle Size Distribution for the sample coded as M-15-I-5000

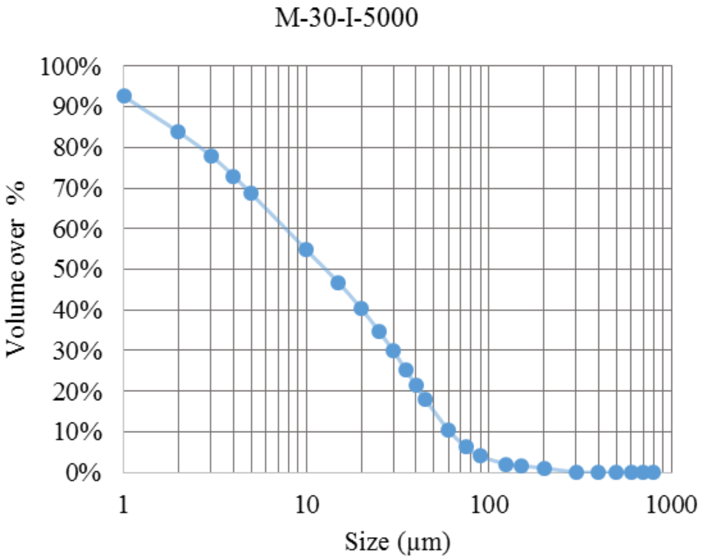


Figure 4.8. Particle Size Distribution for the sample coded as M-30-I-5000

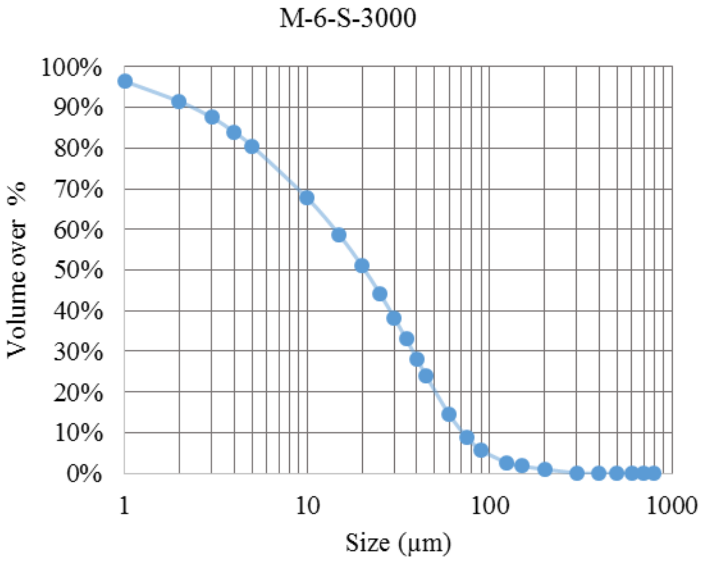


Figure 4.9. Particle Size Distribution for the sample coded as M-6-S-3000

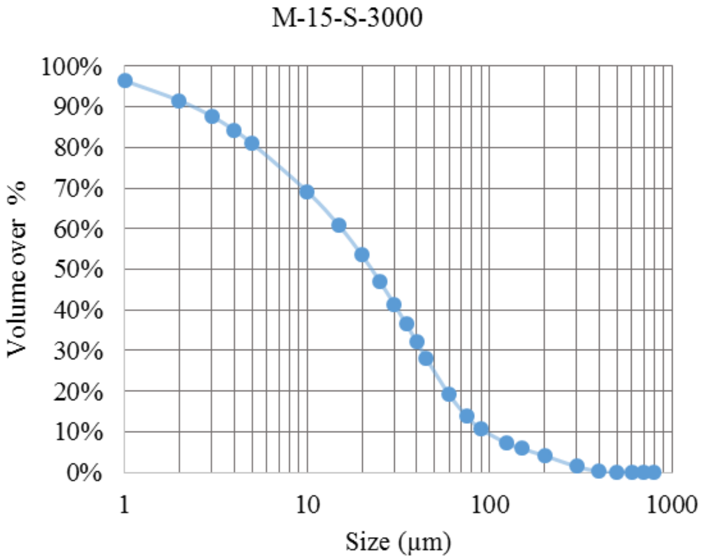


Figure 4.10. Particle Size Distribution for the sample coded as M-15-S-3000

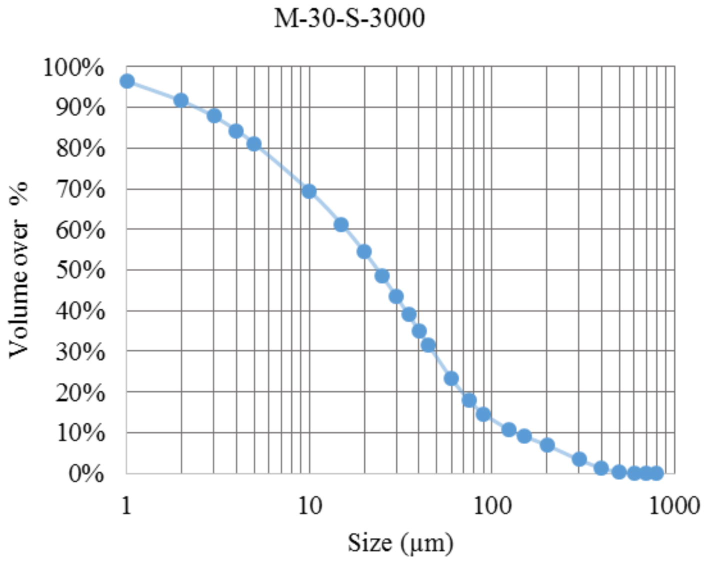


Figure 4.11. Particle Size Distribution for the sample coded as M-30-S-3000

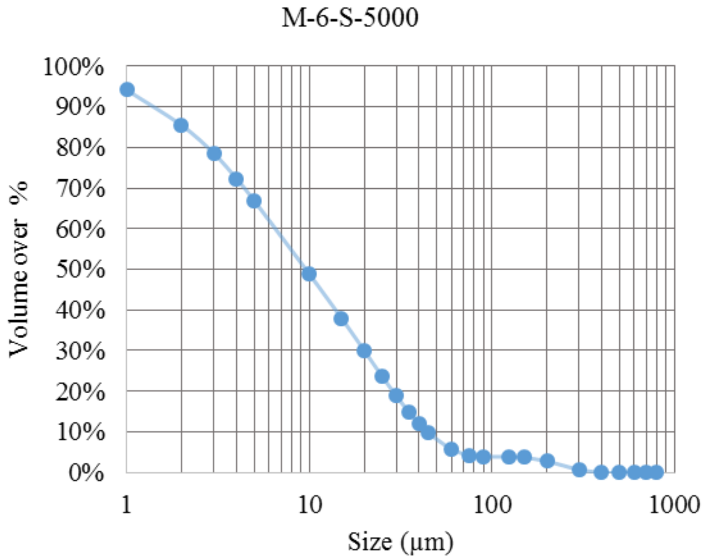


Figure 4.12. Particle Size Distribution for the sample coded as M-6-S-5000

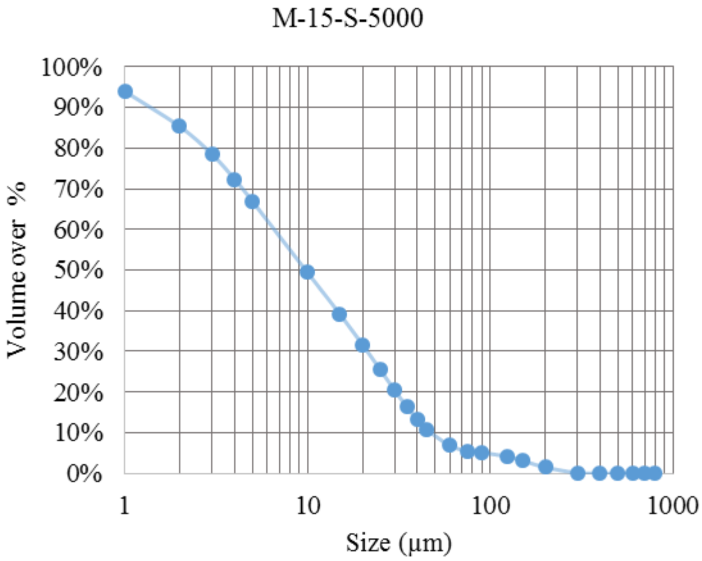


Figure 4.13. Particle Size Distribution for the sample coded as M-15-S-5000

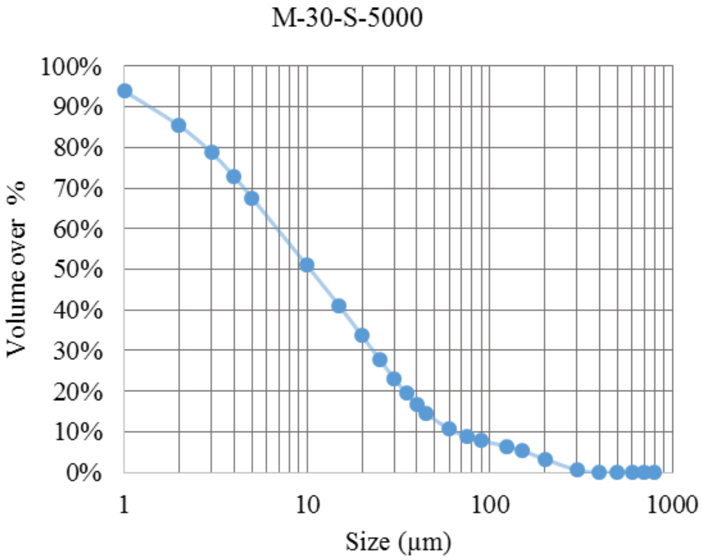


Figure 4.14. Particle Size Distribution for the sample coded as M-30-S-5000

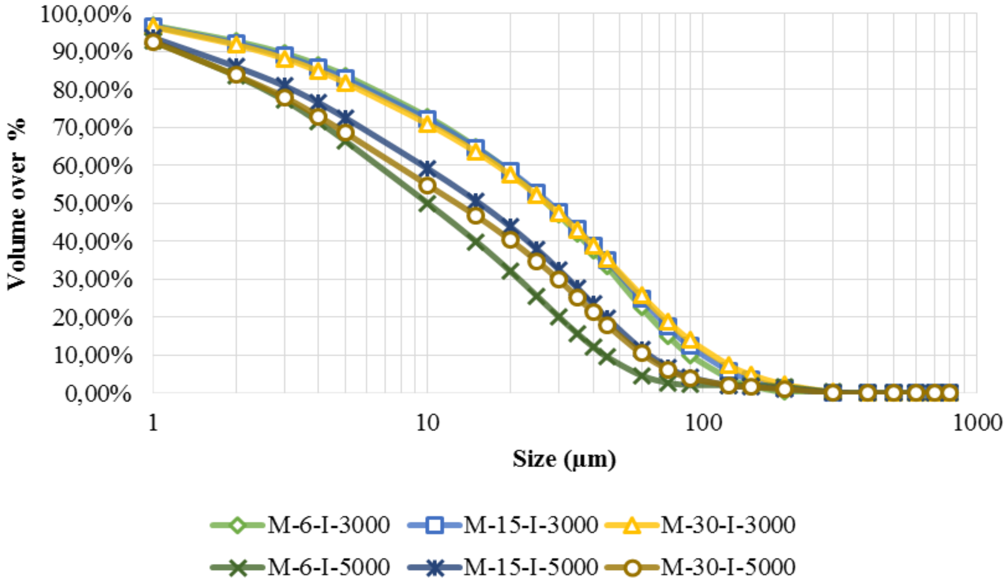


Figure 4.15. Particle Size Distribution for the interground samples

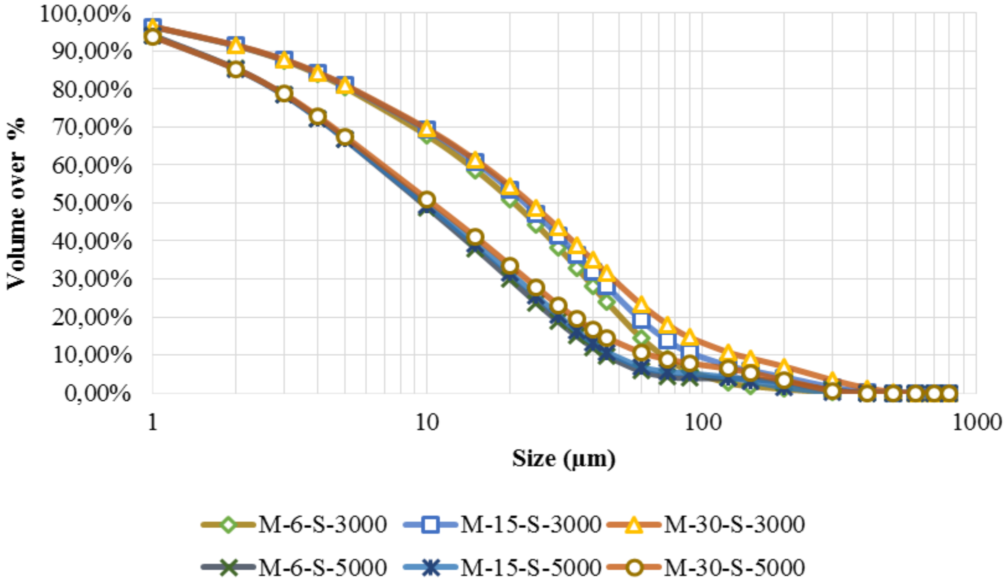


Figure 4.16. Particle Size Distribution for the separately ground samples

The midsections of the cumulative particle size distribution graphs for the 5000 Blaine mixtures have more constant slopes than the 3000 Blaine mixtures, indicating wider particle size distributions. This is similar to what was observed by Tosun et al. (2009a, 2009b).

Table 4.1 shows the D10, D50, and D90 values (in percent) for the twelve different cement mixtures. Here Dx is the particle size below which x % of the total material lies. So D50 is the median diameter for a cement.

Table 4.1. The D10, D50, and D90 values for the cements used

	Marble %	G	Blaine	D10 (µm)	D50 (µm)	D90 (µm)
1	6	I	3000	2.86	27.15	90.18
2	15	I	3000	2.65	27.86	99.78
3	30	I	3000	2.49	27.19	107.95
4	6	I	5000	1.23	10.01	44.03
5	15	I	5000	1.39	15.45	64.15
6	30	I	5000	1.22	12.78	61.32
7	6	S	3000	2.37	20.72	71.54
8	15	S	3000	2.39	22.64	94.26
9	30	S	3000	2.41	23.78	135.06
10	6	S	5000	1.42	9.57	44.34
11	15	S	5000	1.40	9.77	47.06
12	30	S	5000	1.39	10.40	64.45

It can be seen that the D50 values of the interground cements are significantly higher than the D50 values of the separately-ground cements. Later, this will be related to the lower strength of mortars made with the interground cements.

Although an analysis of the individual size distributions of the marble and clinker phases of the cements is not available, it is likely that the softer marble particles get finer, sooner and the clinker particles remain coarser than in the separately ground case.

4.3. Chemical Compositions of the Marble-Blended Cements

The chemical compositions of the different cements produced by intergrinding and by separate grinding of marble, and clinker/gypsum, are provided in Table 4.2.

Table 4.2. Chemical compositions of the marble-blended cements produced

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
M-6-I-3000	18.64	5.15	3.20	64.20	2.10	1.83	0.68	0.32	3.53
M-15-I-3000	17.45	4.74	2.96	63.47	1.93	2.10	0.63	0.21	6.47
M-30-I-3000	15.40	4.28	2.66	62.57	1.83	1.75	0.57	0.26	10.62
M-6-I-5000	18.58	5.20	3.11	64.32	2.08	1.88	0.67	0.33	3.49
M-15-I-5000	17.53	4.87	2.91	63.59	2.01	1.90	0.63	0.22	6.31
M-30-I-5000	15.73	4.40	2.62	62.34	1.89	1.80	0.60	0.29	10.29
M-6-S-3000	19.03	5.26	3.18	64.16	2.12	2.13	0.70	0.23	3.17
M-15-S-3000	17.86	5.00	3.05	62.96	2.04	2.03	0.66	0.22	5.63
M-30-S-3000	16.55	4.53	2.80	61.67	1.88	1.74	0.62	0.25	9.60
M-6-S-5000	19.11	5.20	3.10	64.06	2.08	2.00	0.68	0.25	3.36
M-15-S-5000	17.93	4.96	2.92	63.25	2.00	1.97	0.65	0.25	5.95
M-30-S-5000	16.64	4.55	2.68	61.75	1.86	1.77	0.62	0.26	9.79

It is clear that, as the marble content of a mixtures increases the CaO, SiO_2, Al_2O_3, and Fe_2O_3 contents of the mixtures all decrease. The loss on ignition (LOI) increases for all cements. It would be expected that there would be no real difference between the interground cements containing the same amount of marble but ground to different finenesses. This difference is indeed less than a few percent between such cement pairs. The difference between interground and separately-ground cements of the same composition and fineness is, however, greater. The CaO and Fe_2O_3 contents are higher for the interground cements while the SiO_2 and Al_2O_3 contents are lower. Slight differences in alkali oxide contents can also be noted.

4.4. Comparison of the Compressive Strengths of the Interground and Separately Ground Marble-Containing Mortar Mixtures

The compressive strength development of the marble-blended Portland cement mortars was investigated up to 28 days. The results are shown in Table 4.3.

Table 4.3. Compressive strength development of the interground and separately-ground marble-containing mortar mixtures

				Compressive Strength (N/mm2)		
	Marble %	**Grinding**	**Blaine fineness (cm2/g)**	**2-day**	**7-day**	**28-day**
6-I-3000	6	I	3000	17.6	32.3	41.7
15-I-3000	15	I	3000	16.4	31.1	38.3
30-I-3000	30	I	3000	13.5	26.3	34
6-I-5000	6	I	5000	27.4	41.8	49.1
15-I-5000	15	I	5000	19.4	33.5	39.7
30-I-5000	30	I	5000	18	30.9	35.4
6-S-3000	6	S	3000	20.6	35.1	43.3
15-S-3000	15	S	3000	19.1	33.8	42.4
30-S-3000	30	S	3000	16.4	31	37.7
6-S-5000	6	S	5000	31.7	46.9	53.4
15-S-5000	15	S	5000	29.6	44.3	51.5
30-S-5000	30	S	5000	24.3	38.5	44.4
CONTROL	**-**	**-**	**3000**	**20.3**	**37.6**	**50.5**
CONTROL	**-**	**-**	**5000**	**26.7**	**45.4**	**57.8**

Figures 4.17 and 4.18 show the compressive strength development of the interground and separately-ground marble blended cements.

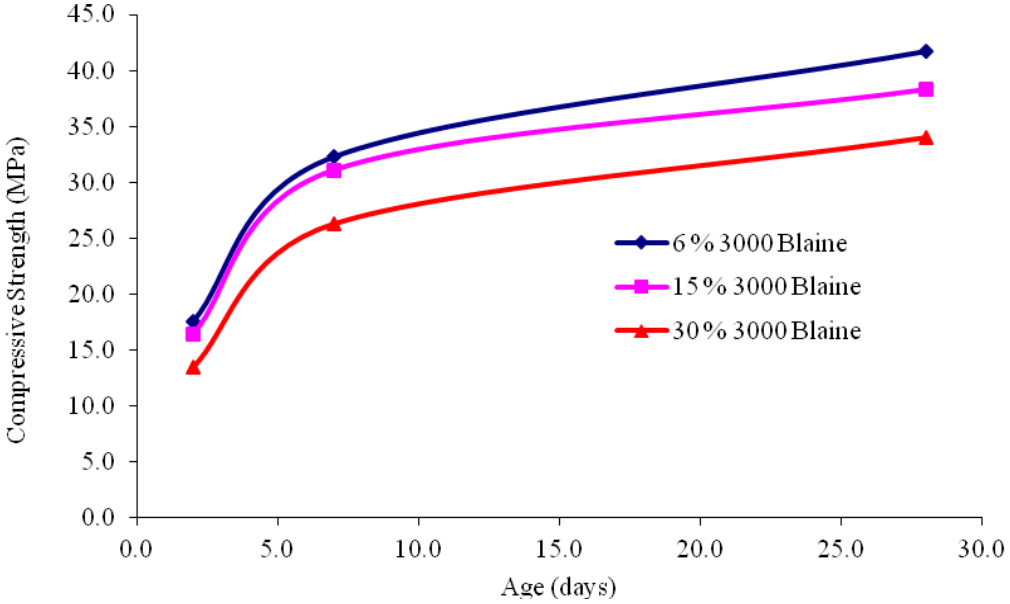


Figure 4.17. Compressive strength development of the interground blended cements with Blaine fineness 3000 cm^2/g

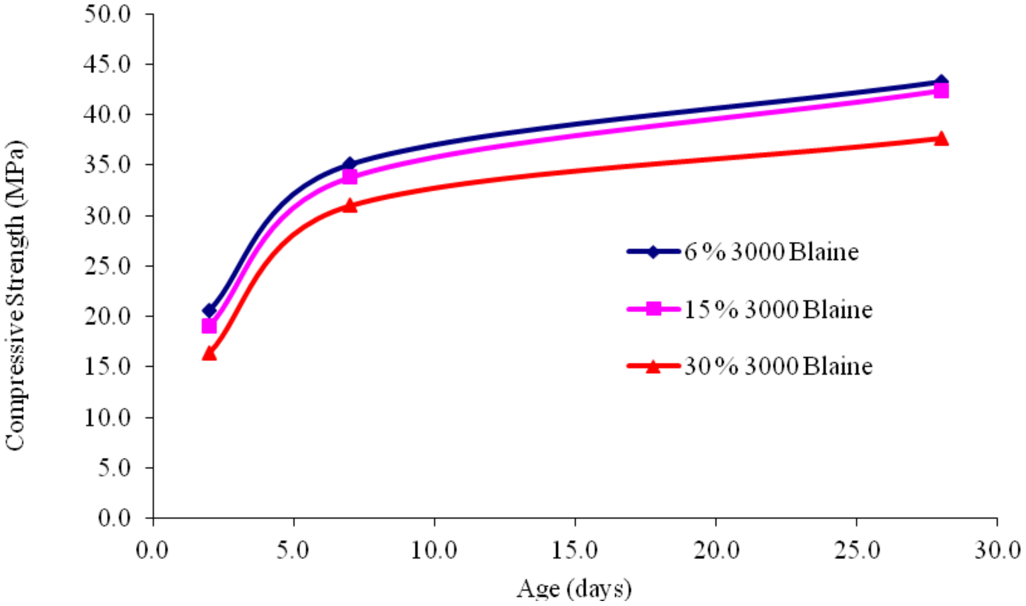


Figure 4.18. Compressive strength development of the separately-ground blended cements with Blaine fineness 3000 cm^2/g

It can be seen that increasing marble content causes a decrease in the compressive strength values at all ages. This decrease corresponds to about 20 % for the interground mixtures and about 15 % for the separately-ground mixtures, at 28 days, for 30 % cement marble content. The 2-day strength of all

3000 cm^2/g fineness mixtures are all above ~12 MPa, even for 30 % cement marble addition. The strength development for the interground and separately-ground 5000 cm^2/g Blaine mixtures is shown in Figures 4.19. and 4.20.

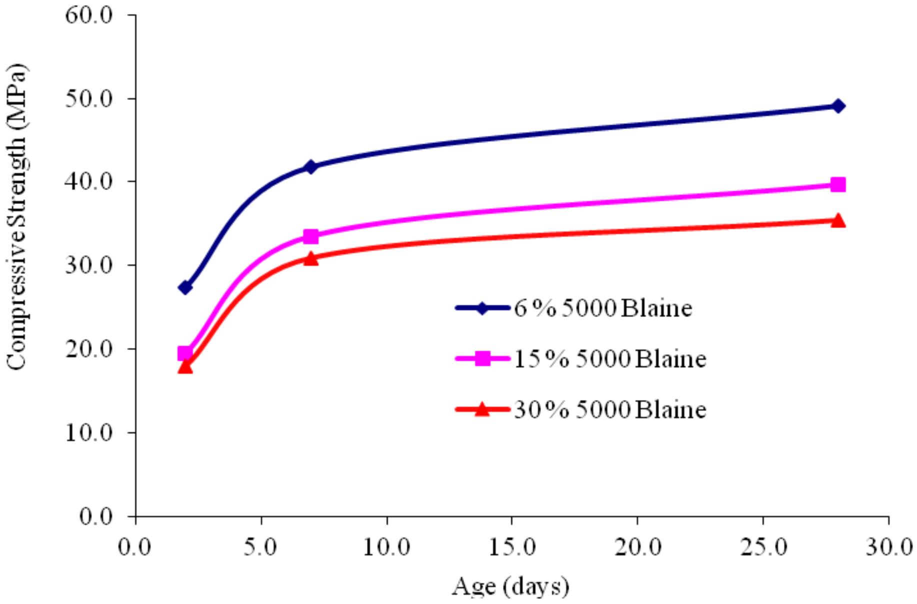


Figure 4.19. Compressive strength development of the interground blended cements with Blaine fineness 5000 cm^2/g

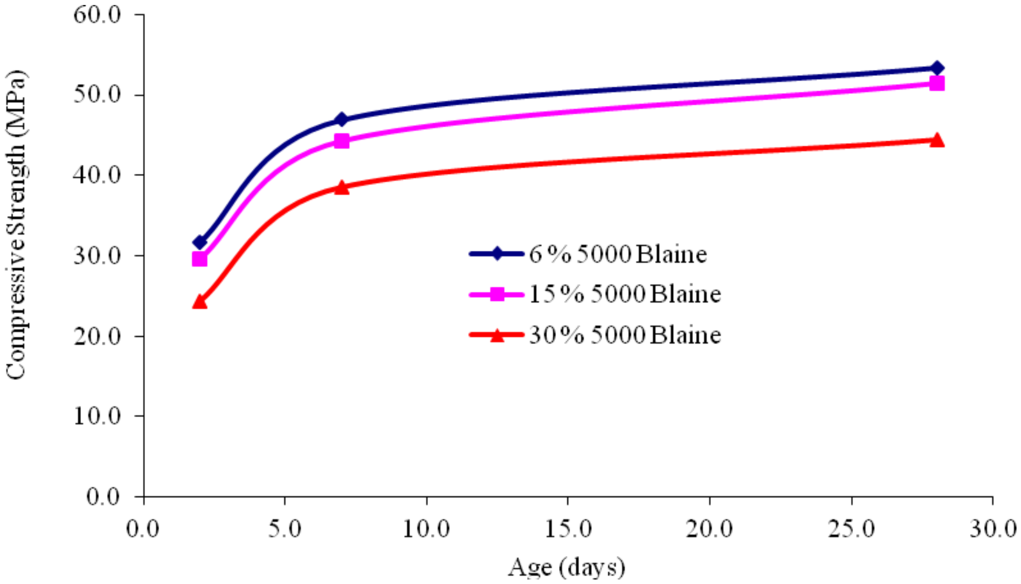


Figure 4.20. Compressive strength development of the separately-ground blended cements with Blaine fineness 5000 cm^2/g

Increasing the fineness of the blended cements can increase the 2-day strengths to 20 MPa. Once again, the decrease in strength at any chosen age is greater for the interground cements than for the separately-ground ones.

The most important observation made is that separately-ground cement mortars always give higher strengths than the interground cement mortars. This is no doubt due to differences in the size distribution of the cements, particularly the differences in the mean sizes of the clinker and the marble within a blended cement. In separate grinding to a selected Blaine fineness value the fineness of both the clinker and the marble are approximately the chosen fineness value. Hence, the mean or medium particle diameter is similar for both raw materials. In intergrinding however, the difference in the hardnesses of the two raw materials lead to different grinding behavior and the softer marble tends to accumulate more in the smaller sizes. The clinker tends to remain coarser than it would otherwise. Since the marble do not contribute much to the strength of the mortar, especially at early ages, the coarser-ground clinker reacts less at early ages and less overall. The effect on ultimate strength is more difficult to interpret as it depends on the chosen fineness. As the overall cement fineness increases, the median diameters of both the marble and the clinker decrease. For very high fineness, a large fraction of even the coarser clinker particles can hydrate, given enough time, contributing to ultimate strength gain. For lower overall fineness, the part of the clinker that remains unhydrated will be greater and the ultimate strength will be low in addition to the low early strength.

When the strengths of the various mortars are compared to the control mortars containing 100 % Portland cement, it is seen that some of the separately-ground marble blended cements give higher 2-day strengths. At both 3000 and 5000 cm^2/g Blaine, the strengths of the 6 % marble-containing mixtures exceed the strengths of the control mortars. This amount of exceeding is very small for the lower fineness case but greater than 15 % for the higher-fineness mortar. In fact, even the 7-day compressive strength of the 6 % marble-containing 5000 cm^2/g Blaine mortar exceeds the strength of the portland cement-only control at the same age (46.9 MPa > 45.4 MPa). While all 28-day compressive strengths are lower than that of the control, the separately-ground blend mortars come within 8 %.

Another observation about strength development is that separately-ground cement mortars achieve a greater fraction of their ultimate strength sooner i.e. their 2-day strengths are a greater fraction of their 28-day strengths. There exists a 20 to 25 % difference between the 28-day strengths of the 5000 Blaine cement mortars and the 3000 Blaine cement mortars, for the separately ground mortars. A possible explanation for this could be that much of the clinker in the 3000 Blaine cements is too coarse and does not react, keeping the degree of hydration low but in the case of the 5000 Blaine cements, this coarse clinker is reduced sufficiently in size and starts to react within the 28-day period.

Yet another observation is that the drop in strength with increasing marble content is steeper for the interground blends than it is for the separately-ground blends.

The setting behaviors and of the different blended cements are presented in Table 4.4. Also shown, are the water requirements of the mortar mixtures i.e. the amount of water in percentage of the mass of powder materials, needed to achieve “normal consistency”.

Table 4.4. Initial and final setting times, and normal consistency water requirements of the interground and separately-ground marble-containing mortar mixtures

			Blaine (cm^2/g)	**% water for normal consistency**	**Initial set (min)**	**Final set (min)**
6-I-3000	6	I	3000	24.6	231	298
15-I-3000	15	I	3000	24.6	233	294
30-I-3000	30	I	3000	24.4	222	293
6-I-5000	6	I	5000	25.4	161	202
15-I-5000	15	I	5000	24.6	170	216
30-I-5000	30	I	5000	24.8	171	222
6-S-3000	6	S	3000	24.4	203	264
15-S-3000	15	S	3000	24.4	192	243
30-S-3000	30	S	3000	24.2	197	253
6-S-5000	6	S	5000	25.4	131	162
15-S-5000	15	S	5000	25.8	124	170
30-S-5000	30	S	5000	25.8	135	165

In accordance with their lower compressive strengths, the interground cement mortars set slower than their separately-ground counterparts. The difference between mortars with identical marble contents is 30 to 40 minutes, both for initial setting time and for final setting time. Both initial and final setting correspond to some mass-based degree of hydration completion and the coarser clinker in the interground cases achieves these critical hydration completion percentages later.

Increasing fineness results in earlier setting. From 3000 cm^2/g to 5000 cm^2/g, both initial and final setting time shorten by about one hour. As for the influence of increasing marble content on setting time, it is insignificant. The uncertainty in determining the setting time values is probably greater than the actual differences observed between the different cases.

Set retardation due to marble use has been attributed to the retardation of the hydration of C_3A. It is believed that the $CaCO_3$ increases the set retardation efficiency of gypsum by altering the surface of C_3A by forming carboaluminates [Ramachandran and Chun-mei, 1986].

CHAPTER 5

CONCLUSIONS

5.1 Summary

This study investigated the use of industrial waste marble cuttings as a source of $CaCO_3$ in marble-containing blended cement production. The blended cements were of the types CEM II/A-L and CEM II/B-L according to TS EN 197-1. Two different grinding methods were employed: separate grinding of the marble and the clinker/gypsum, and intergrinding. The gypsum-to-clinker ratio was kept constant for all cements while the marble-to-clinker ratio was varied. Two different ultimate cement finenesses were targeted and the ease of grinding of the different cases were compared. Then, mortar prism samples were prepared with the cements produced and some of their fresh and hardened properties were compared up to 28 days.

5.2 Conclusions

The following conclusions were reached as a result of this thesis study:

1) The marble is softer than the clinker and is therefore easier to grind. Mixtures of marble and clinker offer intermediate resistance as they are softer than the clinker but harder than the marble. Surprisingly, however, the marble content does not influence the overall cement grindability very much probably due to the hygroscopic marble hindering the grinding by coating the charge and insides of the mill.
2) The 5000 cm^2/g Blaine fineness cements have broader particle size distribution peaks than the 3000 cm^2/g cements. The D50 (median) values of the interground cements are significantly higher than those of the separately-ground cements.
3) Increasing marble content causes a decrease in the compressive strength of the mortars at all ages. This difference is ~20 % for the interground mixtures and ~15 % for the separately-ground mixtures, as 28 days for a marble content of 30 %. Despite this, the ultimate strengths of even the 30 % marble mixtures are acceptable.
4) Increasing the fineness of the cements increases the achieved compressive strength.
5) Separately ground cements always give higher strengths than interground ones with the same fineness and mineral additive content. This is attributed to differences in the resulting relative sizes of the clinker and additive in the two grinding methods. In addition, separately-ground cement achieve a greater percentage of their ultimate strength, sooner, meaning their 2-day to 28-day compressive strength ratios are higher than for the interground cements.
6) The early-strength of the mortars up to 7 days is not reduced much and even improved for the separate grinding case for a replacement level of 6 %. At higher replacement levels, both early and ultimate strengths are diminished. The drop in strength with increasing marble content is steeper for the interground cements.
7) The setting times, both initial and final, of the interground cements are longer than their separately-ground counterparts. This difference is slightly more than half an hour for both

setting times. This is in accordance with the strength development shown by the cements. Increasing fineness leads to shorter setting times, as expected. Marble content, however, does not seem to affect setting time noticeably.

5.3 Recommendations for Future Studies

Based on the results of this study, the following recommendations can be made for research along the same lines:

- The hydration and mechanical property development of $CaCO_3$-containing blended cements can be supported by x-ray diffraction studies performed on hydrating samples taken at closely-spaced intervals to observe the formation and disappearance of crystalline phases.
- Thin section analysis of the marble used can be done.
- Scanning electron microscopy and x-ray techniques can be employed to distinguish the particle size distributions of the mineral additive, the clinker, and the gypsum following intergrinding.
- The heat evolution of interground and separately-ground cements of the same Blaine fineness further sieved into several size fractions can be measured to assess the contribution of different sized particles to the overall property development and to relate size with composition.
- A greater number of calcareous mineral additives can be used and their performances compared.

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