Digest 2009, December 2009 1337-1355

Portland Limestone Cement Part I - Preparation of Cements †

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ABSTRACT

This paper is the first part of a research project which was supported by TUBITAK titled "Determination of Optimum Limestone Content in Portland Limestone Cement Production from the View Point of Mechanical Performance and Sulfate Originated Durability Problems". In this stage, blended cements incorporating different amounts of limestone powders from 5 to 40% were prepared. The problems observed in the preparation stage of limestone blended cements and the effects of limestone replacement on the physical and mechanical properties were investigated. Increasing of limestone replacement ratios resulted in a wider particle size distribution. In contrast with the increases in Blaine values, fineness (residue at 32 μm) values of cements have also increased. Mortars had a sticky and cohesive consistency. Also, increasing the limestone incorporation caused decreases in unit weights and compressive strength values of mortars with a parallel increase in water absorption values at all ages.

Keywords: *limestone cement, grinding, fineness, compressive strength*

1. INTRODUCTION

Today, utilization of blended cements is usually preferred due to their economical 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. Nowadays, the production of blended cements incorporating limestone as major additive increased 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

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† Published in Teknik Dergi Vol. 20, No. 3 July 2009, pp: 4717-4736

cement are required when making cement nomenclature. For example, CEM II/A-M (S-V-LL) 32.5 R is the abbreviation of early strength Portland composite cement of 32.5 MPa strength class, incorporating 6-20% granulated blast furnace slag, siliceous fly ash and limestone (Total organic carbon content lower than 0.2%) by weight. Classification of limestone blended cements according to TS EN 197-1 standard is presented in Table 1 [1]. If the minor component is limestone, standard allows incorporation of 40% of limestone with a minimum 32.5 MPa 28 days strength value (CEM II/B-L 32.5 N). However, research is still in progress on how the high limestone replacement rates affect the durability properties of mortars and/or concrete prepared by using these blended cements. The mechanical properties and sulfate resistances of mortars prepared by using limestone blended cements incorporating 0, 5, 10, 20 and 40 % of limestone are investigated within the scope of this study. The determination of an optimum incorporation ratio of limestone for blended cements from the durability point of view was the main target of this study.

According to TS EN 197-1 standard, the $CaCO_3$ ratio 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 (TOC) content of limestone should be determined according to TS EN 13639 standard. High organic carbon contents may cause incompatibilities and problems when air entraining admixtures employed in concrete production. Limestone with an organic carbon content higher than 0.5% can not be used as cement additive. According to TS EN 197-1, limestone blended cements can be classified into two groups depending on their maximum TOC values as 0.5% (L) and 0.2% (LL).

Table 1. Classification of limestone blended cements according to TS EN 197-1 standard

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

1.1. Physical and chemical properties of limestone blended cements

Limestone blended cements present different properties compared to ordinary Portland cement and it is necessary to investigate their physical and mechanical properties with varying limestone contents. In this chapter, a brief literature survey about the effects of limestone content on grindability, consistency water demand, setting times, volume stability, heat of hydration and compressive strength evaluation will be presented.

1.1.1. Grindability

Limestone blended cements should be ground to very high Blaine values in order to obtain the desired strength values. However, the trend of fineness (retained amount on 32 micron sieve size) and Blaine values are not parallel to each other when high limestone replacement ratios are used. Studies which can be found in literature reported that increasing Blaine values result in wider particle size distributions [2,3,4]. Voglis et al. [3], compared the grindability of limestone with natural pozzolana and fly ash in blended (replacement ratio 15%) cements. Blaine values and grinding times that are required to reach the targeted compressive strength values (28 days) were compared (Table 2). According to their easier grindability the raw materials can be listed as limestone, fly ash, natural pozzolana and finally clinker. However, the targeted Blaine values in order to achieve required strength and grinding times were found highest in case of limestone blended cements. Cements incorporating limestone require higher grinding energy to obtain the same strength class [3].

Tsivilis et al. [4] investigated the grindability of limestone blended cements at different replacement ratios (10, 20, 30, 40 %) and at different grinding times (35, 50, 65, 85 minutes). Researchers reported that particle size distribution widens with increasing limestone ratios and increasing Blaine values. However, both the grindability of clinker and limestone were negatively affected in case of 40% limestone incorporation, and lower fineness values of limestone and clinker were measured when compared to 30% limestone replacement ratio.

Table 2. Grinding parameters of limestone, natural pozzolana and fly ash blended cements (15% replacement) and compressive strength values of samples prepared by using these cements

Cement type	Composition		Grinding time (min)	Blaine value (m^2/kg)	28 days compressive strength (MPa)
Portland cement	100% clinker	5%* gypsum	41	303	40.3
Limestone blended cement	85% clinker + 15% limestone	5%* gypsum	60	511	40.5
Natural pozzolana blended cement	85% clinker + 15% natural pozzolana	5%* gypsum	52	418	41.2
Fly ash blended cement	85% clinker + 15% fly ash	5%* gypsum	40	388	41.0

* by mass % of clinker

İnan Sezer [5] investigated the physical and mechanical properties of cements prepared by replacing 0-6-21 and 35% of clinker with limestone by intergrinding method. The time required to obtain a Blaine value of 330 m^2/kg has been determined. All other blended cements were ground at the same time interval, Blaine and fineness (retained amounts on 32-90 micron) values were measured. It was reported that, Blaine values of limestone blended cements and fineness values have increased (the amount of coarse material retained on sieve increased) at constant grinding times. Compressive strength values of mortars prepared by using these cements were also decreased by the increasing limestone replacement ratios. In conclusion, grinding periods seem to be insufficient. It is shown that making interpretations by only focusing on Blaine values of limestone blended cements may cause mistakes. At the second stage of the study, the relative performances of cements prepared by mixing the separately ground limestone and clinker were found better, however, a strength reduction is also reported with the increasing limestone ratios.

Various test results show that type of limestone and its incorporation ratios considerably changes the fineness and the grindability properties of blended cements.

1.1.2. Consistency water requirement and setting time

As well known, consistency water requirement and setting time of cements can be determined by Vicat probe and needle. Theoretically, in order to achieve the same strength values, limestone blended cement should be ground finer compared to ordinary Portland cement, which ands up with a high specific surface area. An increase in consistency water requirement is also expected. However, some researchers reported that increasing limestone contents decreased the consistency water requirement [2,3,4,5]. For example, İnan Sezer [5], showed that consistency water demand decreases when limestone and clinker are interground together. In this study, grinding time was kept constant for all cements. Blended cements with higher Blaine values were found coarser compared to cement without any additive. This situation was found when the retained amounts on sieves 32 and 90 microns were investigated. Furthermore, gypsum amount used in the formation of cement composition, microporosity of limestone and morphological properties (surface roughness formed by grinding process) may affect the consistency water demand. For example, Erdoğdu [6], prepared blended cements with 5-10-20 and 30% limestone replacement ratios, and reported that consistency water demand decreases with the increasing limestone replacement. The decrease in consistency water content was attributed to the smooth surface and lower porosity of limestone particles after grinding. However, strength values of blended cements were found lower than the required strength in particular at higher limestone replacement rates. As suggested by the author, limestone blended cements must be ground finer.

Dhir et al. [7], studied the effects of limestone replacement at the ratios of 15-45% and their results are presented in Table 3. Limestone replacement is performed by separate grinding before mixing the ingredients. The required consistency water in order to get a probe penetration depth to 30±5 mm was found in the range of 26-27%.

Table 3. Effect of limestone replacement ratio on physical and mechanical properties

Physical and mechanical properties		Limestone replacement ratio (by mass)				
		0%	15%	25%	35%	45%
Penetration of Vicat probe (mm)		28	30	34	31	35
Consistency water (%)		26.5	26.8	26.8	26.8	27
Initial setting time (min)		105	128	128	122	118
Strength class (MPa)		42.5	42.5	32.5	32.5	-
Compressive strength (MPa)	2 days	30.6	25.3	21.6	17.7	14.1
	7 days	45.8	37.7	33.0	28.5	22.4
	28 days	63.5	45.0	40.1	34.7	26.9
Volume stability (mm)		0.5	0.5	0.5	0.5	0

1.1.3. Volume stability

As the limestone replacement ratio increases, no significant change is reported in volume stablity determined by the Le Chatelier method [2, 5, 7]. However, higher water absorption values are reported for mortars prepared by using high amounts of limestone replacement. Open porosity ratio increases as the limestone ratio increases and absorbed water causes some reversible swelling.

1.1.4. Heat of hydration

At the early ages of hydration, the evolution of heat of hydration of cements prepared with limestone replacement ratio of 5% is faster than samples prepared with only Portland cement. Similar results are also reported from the view point of total heat of hydration. However, heat of hydration tends to decrease at higher replacement ratios due to reduction in total cement content [6]. Until a definite ratio, finely ground limestone particles serves as nucleus for the formation of calcium silicate hydrate and calcium hydroxide which accelerate the rate of hydration. Furthermore, it is reported that formation of hemicarbonate, monocarboaluminate and calcium tricarboaluminate in the presence of limestone addition increase the heat of hydration at early ages [8].

In Self Compacting Concrete (SCC) applications which became widespread in recent years, high amounts of limestone addition is preferred in order to maintain high viscosity as well as high segregation resistance which is also due to both the economical suitability of limestone and beneficial rheological properties of paste phase by its incorporation [9]. Poppe and Schutter [10] investigated the differences between heat of hydration of SCC's incorporating 240 kg/m^3 limestone and traditional concrete by using the isothermal and adiabatic methods. They have prepared a model by using the data derived from experimental studies and determined that utilization of high amounts of limestone increased the heat of hydration. However, it should be noted that relatively low water/powder ratios of SCCs compared to conventional concrete can be another reason for this increase. The results of this study may be discussed from this point of view.

Similar studies on this topic have been performed by Bentz [11], he studied the effects of limestone powder on cement hydration and performed some computer simulations and models by using CEMHYD3D program. In these models, degree of hydration, evaluation of microstructure and strength has been modelled as a function of time. CEMHYD3D program was modified by taking the effect of limestone addition into consideration. It was determined that, W/C ratio was the most dominant factor in demonstrating the effectiveness of limestone powder replacement up to 20%. Under the W/C ratio of 0.4, limestone addition serves as a hydration triggering and an accelerating agent, however, at higher W/C ratios, it loses its effectiveness.

Rahhal and Tolero [8], studied the mechanism of hydration at early ages in case of finely ground limestone and quartz powder intermixed with Portland cements with different compositions. For this purpose; calorimetric activity, hydraulic activity (Frantini test) and XRD analysis were performed. They have determined that both of these inert admixture additions activated or slowed down the hydration rate at different intensities depending on the cement compositions. In particular, when cement with high C_3A content is used, hydration reactions speed up for both of two types of fillers, and it was determined that these fillers act as nucleus for rapid formation of hydration products. However, in case of low C_3A content cements, both filler additions retarded the hydration.

1.1.5. Compressive strength

There is no direct positive effect of limestone incorporation on compressive strength. Only the filler function can be pronounced. It is also accepted that limestone possesses no pozzolanic property [8]. It is known that, if 5% limestone is used as additive, early strength can be slightly increased by its indirect hydration accelerating effect. However higher rates of limestone incorporation usually reduce the compressive strength [5-8].

2. EXPERIMENTAL STUDY

Within the scope of experimental studies, limestone blended cements at 4 different replacement ratios (0-5-10-20-40%) have been prepared by using intergrinding method. After the detailed fineness characterization of cements, effects of limestone replacement on consistency, mechanical performance and physical properties of cement mortars have been investigated.

2.1. Materials and method

2.1.1. Preparation of cement samples

Clinkers used in the production of limestone blended cements were procured from a cement plant. Clinkers are coded as no III, since they were the products of the third furnace. The chemical analysis (XRF) of clinkers and theoretical phase ratios calculated by Bogue formulae are presented in Table 4. The clinkers taken from coolers were reduced to sand size (below 4 mm) by using jaw and double cylinder crushers.

Table 4. Chemical analysis (XRF) of clinkers and theoretical phase ratios calculated by using the Bogue formulae

	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	Cl	Na_2O	Free CaO	Immeasurable	Eq. alkali
III (%)	0.91	5.01	21.68	0.55	0.52	66.78	3.63	0.001	0.24	0.18	0.69	0.58

	C_3S	C_2S	C_3A	C_4AF
III (%)	67.47	11.27	7.13	11.03

After the preparation of clinkers, limestone samples have been dried and ground to sand size. The chemical composition of limestone has been found to be 55% CaO and with a loss on ignition value of 43.6%. Furthermore, some impurities such as MgO, K_2O, Fe_2O_3, SO_3, SiO_2 and Al_2O_3 has been determined where their total amount is lower than 1%. The total organic carbon content of limestone has been determined as 0.25% according to TS EN 13639 standard. As stated by TS EN 197-1 standard, capital L is used for cements labeled where this limestone is used (Group L: between 0.5% and 0.2%, group LL: lower than 0.2%). According to TS EN 197-1 standard, it is possible to classify these cements as CEM II/A-L (limestone replacement ratio up to 20%) and CEM II/B-L (limestone replacement ratio higher than 20%). However, strength classes should be determined according to the criteria based on 32.5 and 42.5 MPa 28 days compressive strength values. By using the strength values, classification will be performed in the next stages.

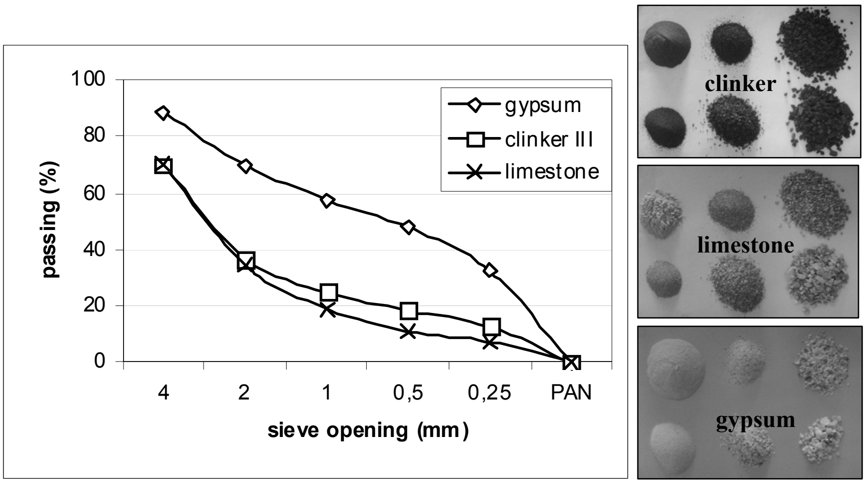


Figure 1. Sieve analysis of clinker, limestone and gypsum before grinding

Another ingredient, gypsum that will be added in the grinding stage has also been dried. Gypsum was pre-processed by crusher and for this reason; it is used at the same particle size distribution. The SO_3 content of gypsum was 40%. The particle size distributions of clinker, limestone and gypsum before grinding can be seen in Figure 1.

Cement samples have been prepared by using 0%, 5%, 10%, 20% and 40% of limestone additions. Laboratory type mill was used in the preparation of cement. Mill was equipped with 60 kg total weight of ball at varying diameters (20, 30, 40, 50 and 60 mm). For each mixture, 5 groups of cement samples each weighing 2.5 kg have been prepared. A constant 5% of gypsum by weight of clinker has been added to each cement mixture.

Control cement mortars (without limestone) and incorporating 5% of limestone were ground for 30 minutes, and their Blaine and fineness values were measured in conformity with TS EN 196-6 standard. The aim of this procedure was to compare the grindability properties of clinkers at constant periods. In order to determine the proper amount of cement to fill the Blaine cell, the specific gravity of cements were measured by using a nitrogen picnometer. Furthermore, two grams of cement samples were vacuum sieved from 32 micron sieve, and the cement amounts retained on the sieve were measured. In addition to the determination of Blaine values and amount of material retained above 32 micron sieve, Laser diffraction scattering (LDS) measurements were performed to observe changes in the particle size distribution by limestone addition. These measurements were conducted using Malvern Mastersize 2000 apparatus. Particle size distribution was determined in the range of 0.1 to 800 micron by using "particle with equivalent diameter" principle. Furthermore cumulative particle diffraction graphs were plotted for each measurement. Results will be presented in "Results and Discussion (3.2) section.

2.1.2. Preparation of cement mortar specimens, consistency tests and test setup

Standard mortar mixtures have been prepared by using five sets of cements (with limestone replacement of 0, 5, 10, 20 and 40%). Mortar mixtures with sand/cement/water ratios of 3/1/0.5 (by weight) were prepared in conformity with TS EN 196-1 standard. Consistency tests have been performed for each mixture by using a tilting table in conformity with ASTM C 230 standard. 50 mm cubic specimens have been prepared to determine the 56 days compressive strength value and the long term effect of environmental conditions on compressive strength. Furthermore, 2 prismatic specimens of 25x25x285 mm have been prepared and studs were attached to the end of specimens for length measurements. All samples were kept at standard curing conditions for the first 56 days. During this period the compressive strength values at 1, 7, 28 and 56 days have been determined by using some of the cube samples. Furthermore, some of the physical properties of limestone blended mortar samples have been determined. After 56 days of water curing, saturated surface dry unit weights, 56 days water absorption values and length changes of specimens in water curing conditions have been determined. All these physical tests have been performed in order to determine the effect of limestone addition on cement mortars.

3. RESULTS and DISCUSSION

3.1. Results and discussion related with the grinding process

During grinding process, laboratory ball mill has been stopped at definite fixed times and both the Blaine and fineness values of 32 micron have been measured. By this way, fineness of cement was determined as a function of time. The test results of cements without limestone and 5% limestone incorporation have been presented in Table 5 and 6, respectively. It is shown that Blaine values tend to increase and 32 micron fineness values decrease parallel with grinding. However, in the case of mixtures incorporating 10% limestone, amount of material retained on 32 micron sieve did not decrease even at increased grinding times. As clearly seen from Table 7, the fineness values (amount retained on 32 micron sieve) of cements prepared by using high volumes of limestone increased in line with their increasing Blaine values. Observation of the coarse portion retained on 32 micron sieve revealed the existence of coarse limestone particles in the clinker powder (Figure 2). This situation became more pronounced with increasing limestone ratios. At first glance, an increase in the amount of material retained on 32 micron sieve, in contrast with the increasing Blaine values can be accepted as an unexpected result. High Blaine values may be an indicator of proper grinding process. However, some limestone particles remained coarser. Similar situation was observed when more sieves with wider openings were used. For example, the amount of material retained over 500 micron and 250 micron for the mixture incorporating 40% of limestone after grinding were 2.5% and 10%, respectively.

Table 5. Variation of Blaine and fineness values of control cement by grinding time

time	III-K	
	Blaine (m^2/kg)	32 micron fineness (%)
18 min	241	37
25 min	317	22
30 min	358	19

Table 6. Variation of Blaine and fineness values of blended cements with 5% of limestone replacement

time	III-%5	
	Blaine (m^2/kg)	32 micron fineness (%)
18 min	240	36
25 min	355	24
30 min	399	21
33 min	442	21

Table 7. Blaine and fineness values at mill discharge

Grinding time	Cement	Blaine (m^2/kg)	32 micron fineness (%)
36 min	III-%10	432	30
40 min	III-%20	466	37
45 min	III-%40	494	40

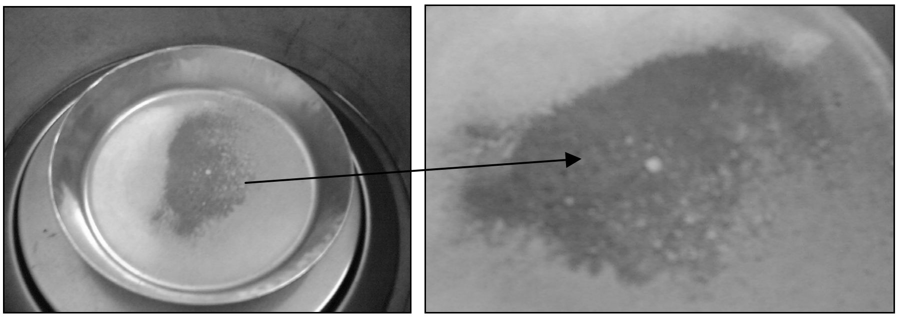


Figure 2. Coarse limestone and clinker particles retained over 32 micron sieve after grinding

In general, limestone particles were softer than clinker particles. However, in order to provide ease of grinding, limestone should be in bone-dry condition. Even after drying of sand size limestone, limestone particles tend to stick to the surfaces of the mill and grinding balls (Figure 3). Stickiness of limestone may be due to the hygroscopic water content that can not be driven off from the structure by oven drying at 100^{o}C for long periods. However, during the initial periods of grinding, the fineness of both limestone and clinker particles increase. At the following stages, hygroscopic water bound in the structure of limestone particles is detached due to grinding energy and adhered onto the surfaces of mill and balls. Adhesion of limestone particles on the surfaces of balls and membrane create soft layers. When balls crash at the membrane, these soft layers reduce the fracture and grinding efficiency of the mill.

Some of the limestone types such as used in this study contain hygroscopic water and this situation may cause problems at the intergrinding stage of limestone with cement. A doctoral thesis related to the investigation of different types of limestone focused on this topic can be found in literature [6]. Cements incorporating limestone types which contain hygroscopic water were prepared in scope of this thesis. Similar grinding problems may be observed in cement production if limestone incorporating hygroscopic water is used as an ingredient.

In another thesis, the amount of material retained on 32 micron sieve increased even though increasing Blaine values by grinding limestone blended cements [5]. However, the coarse particles were clinker in contrast to limestone. This situation possibly arises from the fact that limestone used in that study contains no hydroscopic water. This type of limestone is easily ground and passes through sieves without the sticking problem.

The situation described above was observed in many studies for limestone blended cements prepared in small mills at laboratory conditions. However, in case of full scale mills, the hygroscopic water evaporates at the stage of grinding due to the inner mill temperatures exceeding 100^{o}C and sticking problem may not be observed. The effect of hygroscopic water content on grindability of limestone and clinker decreases in cement production. On the contrary, it is not possible to reach the required temperatures to evaporate the hygroscopic water content of limestone in a laboratory mill.

Figure 3. Limestone coated steel balls at the mill, where cements with limestone replacement ratio of 10% and higher have been ground.

Furthermore, cements ground at full-scale mills usually pass through separators which filter the coarse clinker and/or limestone particles. However, there is no filtering process in case of laboratory mills. In scope of this study, blended cement mixtures incorporating 10% limestone and more were initially ground in the mill and then sieved by means of 250 micron sieve to simulate industrial conditions. In this way, the filtration process conducted by separators was artificially performed. Separated coarse particles were reduced to less than 250 micron diameter by re-grinding in a small ball mill and mixed with cement mixture. After mixing of 5 sets of cements in a homogenizer, the fineness (32 and 90 microns) and Blaine values of cements were measured again. The final (after re-sieving) physical properties of cements are presented in Table 8. There is a slight change (compared to Table 7) on the initial fineness and Blaine values of mixtures incorporating 10-20 and 40% of limestone as seen in Table 8. This is due to the addition of previously coarse portion of ground and sieved materials after re-grinding. Even though the sieving, grinding and re-mixing processes are performed, the amount of material retained on 32 and 90 micron sieves increased with the increasing limestone content. In conclusion, the grindability of limestone blended cements with replacement ratio of 10% and more were negatively affected by the limestone used in this study (due to the hygroscopic water content). Furthermore, sufficient grinding periods have also increased in the case of blended cements.

Table 8. The physical properties of cements prepared by the addition of re-grinded coarse portion of each mix.

Cement code	Material amounts for 2.5 kg mill batches (g)			Grinding time (min)	Specific gravity	Fineness retained on 90 micron (%)	Fineness retained on 32 micron (%)	Blaine values (m^2/kg)
	Clinker	Gypsum	Limestone					
III-K	2375	125	-	30	3.12	0	19	358
III-5%	2255	120	125	33	3.10	1	21	442
III-10%	2135	115	250	36	3.06	1,5	26	452
III-20%	1900	100	500	40	3.02	4	31	465
III-40%	1425	75	1000	45	2.94	9	36	505

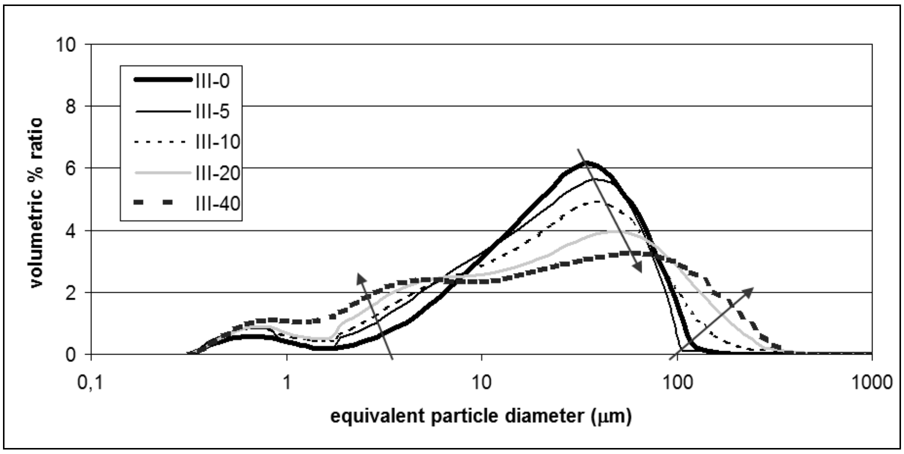
Increase in the amount of particles retained on 32 micron sieve, with increasing Blaine values seems to be in contrast with some of the previous studies. This result may be attributed to;

- grinding performance reducing effect of hygroscopic water content of limestone used in this study which cause adherence of blended cement on mill membranes and ball surfaces.
- differences between the laboratory mill conditions and industrial mill conditions (temperature and filtration differences in the mill) which can be related to non-evaporable hygroscopic water and dispersion of poor ground coarse particles from the cement mixture.

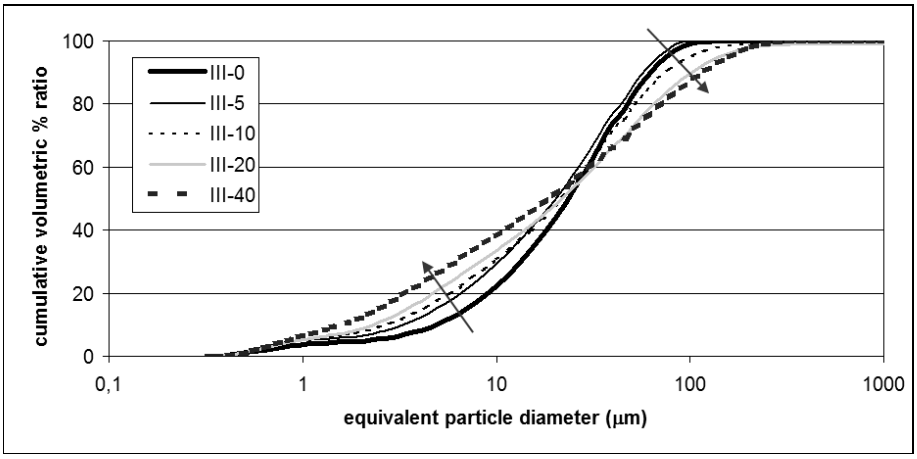
3.2. Particle size distributions of cements and relation with consistency of cement mortar

Due to the contradictory results of Blaine and fineness values of cements obtained from limestone blended mixtures, particle size distributions of all cement mixtures have been determined according to the method previously described in Section 2.1.1. Particle size distributions of cements are presented in Figure 4.

Volumetric % presence of particles at each equivalent particle diameter can be seen in Figure 4a. Particle size distribution widens by increasing limestone replacement. Both coarser and finer volumetric portion of particles increased and the peak portion of distribution function flattened. At the same time, the equivalent particle diameter which corresponds to the maximum volumetric amount of material (peak point of function) increased with limestone replacement. All these results showed that some particles became finer and some particles remained coarse. The velocity of air passing around particles is measured in Blaine test. Due to the very small size particles present in the system, the passing velocity of air decreases (even at the presence of small amounts of coarse particles). By this way the Blaine values of blended cements significantly increased with limestone replacement. However, particle size distribution results proved that coarse particles can also be present in the system. From this point of view, Blaine test seems to be an insufficient method to determine the fineness properties of limestone blended cements. The cumulative volumetric ratios can be seen in Figure 4b. In case of cements prepared by solely clinker and gypsum, the volumetric portion of material which has a particle diameter greater than 100 micron is in negligible amounts. However, the amount of particles higher than 100 micron increases by limestone replacement. On the other side, the amounts of particles with diameter less than 5 micron have also increased by increasing limestone replacement. The particle size distribution widening effect of limestone on blended cements which was previously mentioned by other researchers has been observed [3, 8].



(a)



(b)

Figure 4. Effects of limestone replacement on particle size distribution of cements. Equivalent particle diameter distribution graphs a) by volume and b)by cumulative volume

(III-0 indicates the particle size distribution of cement prepared by using clinker no III without any limestone addition. In case of limestone blended cements, limestone replacement ratios have been presented.)

Table 9. Flow diameters of mortar mixtures

Limestone replacement ratio	%0	%5	%10	%20	%40
Flow diameters (mm)	125	124	125	125	125
Consistency difference as of 0% limestone.	-	softening	gumming	gumming	gumming

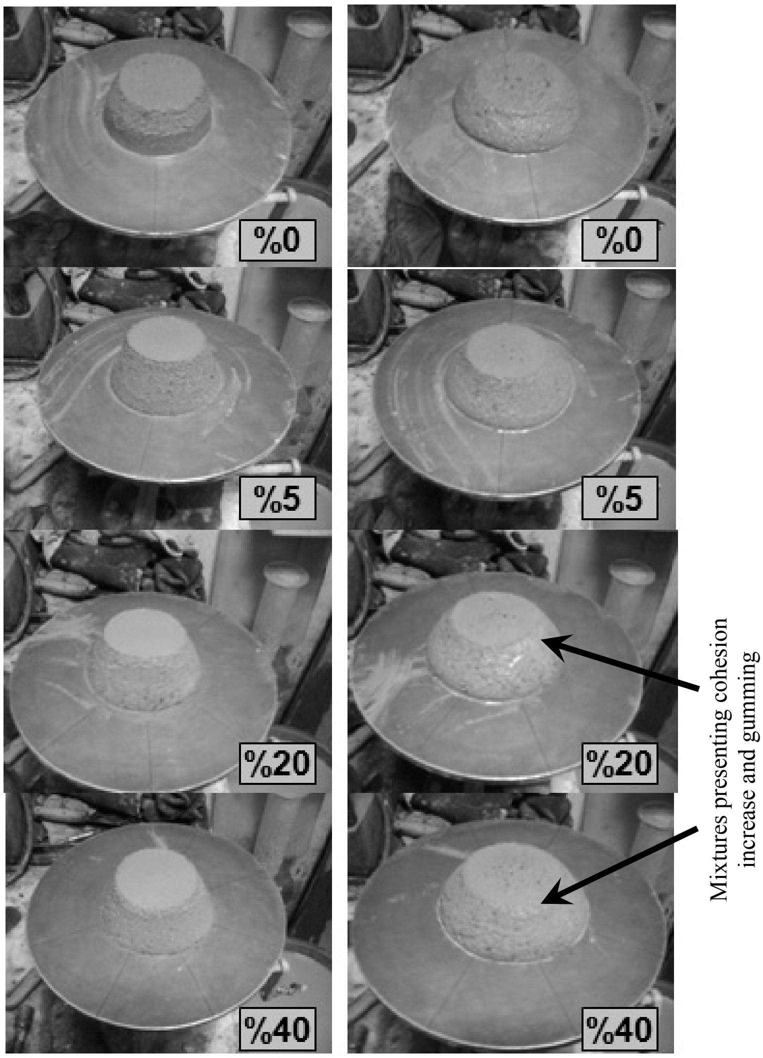


Figure 5. Effect of limestone replacement on consistency properties of cement mortars
(Photos in the left have been taken before tilting and in the right after tilting. Limestone replacement ratios have been presented at the right bottom edges of photos.)

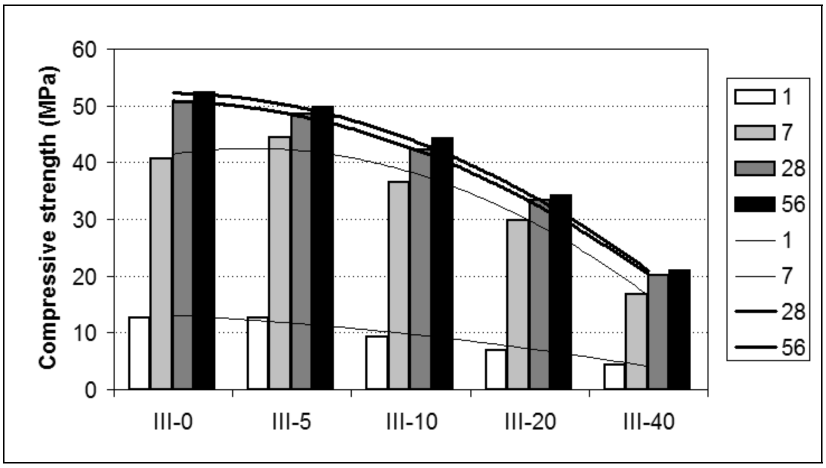
In order to determine the effect of particle size distribution differences of limestone blended cements on consistency of fresh mortars, mixtures have been prepared by using the mixture proportions given in Section 2.1.2. The flow diameters of these mixtures have been measured. The flow diameters of cement mortars prepared at constant water/cement ratios are in the range of 124-127 mm and results of each mixture are presented in Table 9. The relative difference in consistency can be directly related to the limestone replacement due to the constant mixing water content. Limestone replacement ratio did not significantly affect the flow diameter values, however a sticky and gummy fresh state structure has been observed by limestone addition. There were differences in the flow forms of mortars after the flow tests. After the flow tests, visual changes in the flow form of mortars with increasing limestone replacement percentages are presented in Figure 5. In fact, the change in the form of mortar that can not be measured by flow diameter seems to be an indicator of increasing plastic viscosity.

Data summarized above shows that there is a relationship between the particle size distribution and flow properties. Particle size distribution widens with increasing limestone replacement percentages. While the finer and coarser portions of system increase, percentage of the average diameter size decreases by limestone replacement. This situation leads to a surface area increase at constant consistency water content which increases the cohesion of mortars by limestone replacement. Due to the insufficiency of flow diameter test, the cohesion differences of mortars can not be determined by only measuring the flow values. However, change of cohesion is evident when mixtures are poured into their molds and compacted. In practice, the cohesion changes of concretes prepared by using limestone blended cement may increase the required water contents for a desired workability. It may be difficult to mix a sticky mixture in practice. On the other hand, in some cases, compatibility problems between the limestone blended cements and superplasticizing admixtures which are one of the most important ingredient of concrete production should be taken into consideration. Compatibility of admixtures should be checked by pre-trial tests.

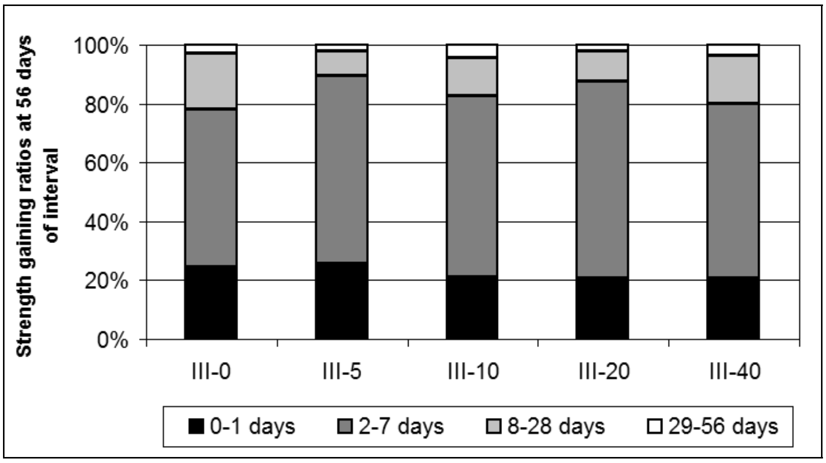
3.3. Effect of limestone replacement on compressive strength development of cement mortars

The compressive strength development of mortars by increasing limestone replacement ratio is presented in Figure 6a. No significant effect of limestone incorporation on compressive strength was seen at 5% replacement ratio. In fact, the compressive strengths of samples at early ages were slightly higher. However, increasing replacement ratio decreased the strength values at all ages. Bar charts illustrating the ratio of strength gain at different time intervals are given in Figure 6b. Early age strength gain ratio is somewhat higher for samples with 5% limestone replacement ratio. The reason for early age strength enhancement may be attributed to the nucleus forming effect of $CaCO_3$ particles for CH crystals at low concentration and accelerating effect of limestone particles to the formation of CSH [8]. At the same time, limestone particles contribute to the strength development by forming new hydration products like carboaluminate phases and by reducing the pore ratio [6]. However no additional strength increase is observed by limestone replacement in the long term (between 28-56th days). This conclusion proved that limestone has no pozzolanic property as stated in literature [8]. 28 days compressive strength of blended cements with

5% and 10% limestone replacement ratio are higher than 42.5 MPa. These cements can be classified as CEM II/A-L 42.5, if the values obtained from 50 mm cube and 40 mm cube specimens are to be accepted as similar. Cements prepared with limestone replacement ratio of 20% can be accepted as CEM II/B-L 32.5 class. The strength values of cements with highest limestone replacement ratio were under the values that are required by standards. However, due to their strength that is comparable with masonry cements, these cements are included in the test program for comparison purposes.



(a)

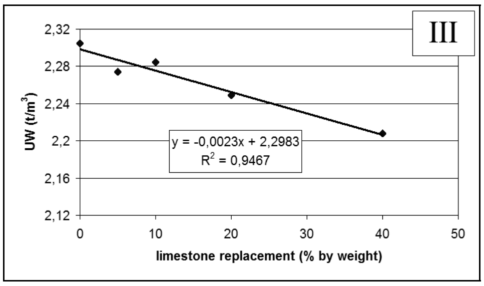


(b)

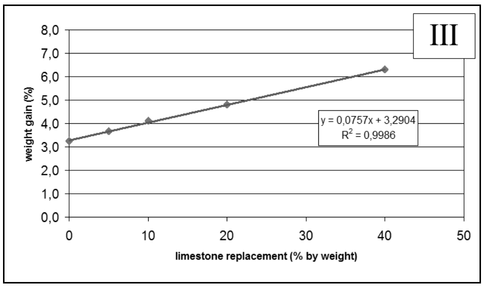
Figure 6. a) Time dependent strength increases, b) strength gaining ratios at different time intervals of cement mortars depending on limestone replacement ratio.

3.4. Effect of limestone replacement on unit weight and water absorption of cement mortars

The effect of limestone replacement on unit weights was investigated by weighing 50 mm cement mortar cubes. After 56 days of water curing these samples have been surface dried, weighed and by dividing their weights by theoretical volumes, saturated surface dry (SSD) unit weights (UW) have been determined. This method is not a standard method due to the negligence of the surface roughness of samples. However, this method gives approximate results on the unit weight changes of samples by limestone replacement. Saturated surface dry UW changes by limestone replacement can be seen in Figure 7a. Each point has been obtained by using the average values of 12 samples. From the graphs, it can be seen that decrease in the average UW values was approximately 100 kg/m^3 for the samples prepared by using 40% limestone replacement. Decrease in unit weights decreased the compressive strength values at the same time. In order to determine the water absorption values, samples that are used to determine the UW values were oven dried and weighed. The water absorption values are determined by taking the de-molding weights into consideration. The average water absorption values of 12 samples for each point are given in Figure 7b. As the limestone replacement ratio increased, the water absorption values also increased. The amount of water absorption was doubled for samples incorporating 40% of limestone. Test results revealed that the open porosity of limestone blended cement mortars increased and water ingress became easier. Determination of water absorption potentials is quite important from the view point of durability of limestone blended cement mortars [7]. Limestone addition increased the water absorption values that lead to decreasing of durability of cement mortars.



(a)



(b)

Figure 7. Effects of limestone replacement ratio on physical properties of cement mortars, a) unit weight, b) water absorption

4. CONCLUSIONS

In the first section of this two staged study, limestone blended cement mortars have been prepared with varying amounts of limestone from 5% to 40%. Problems encountered within the grindability of limestone blended cements were discussed, and the effects of limestone replacement on the physical and mechanical properties of blended cements were investigated. Results are presented as follows:

- Grindability problems have been observed for limestone replacement ratios at 10% and over. This situation arises from the existence of hygroscopic water that appears at the stage of grinding and adherence of wet limestone onto the balls.
- Limestone replacement changed the particle size distribution of blended cements. The resulting change can not be determined clearly by only using the standard Blaine method or by weighing amount of material retained on 32 micron sieve. Determination of particle size distribution by laser diffraction method will be more appropriate. A wider particle size distribution can be pronounced for limestone blended cements compared to ordinary cements without blending. This situation reveals that both the amounts of finer and coarser fractions increased with limestone addition.
- The consistency of mortars prepared by using limestone blended cements changed significantly, a more cohesive and sticky mortar has been obtained for the same spread values. The fresh state consistency changes which can not be differentiated by standard workability tests are attributed to the effect of limestone on particle size distribution of blended cements.
- Unit weights of cement mortars decreased with increasing limestone replacement ratios, and water absorption values increased at the same time. All these results showed that open porosity of cement mortars increased with limestone replacement ratio. This situation revealed that limestone replacement negatively affects the durability of cement mortars.
- Compressive strength development results of cement mortars showed that all mixtures with limestone replacement ratio above 5% resulted in strength loss. A slight early strength enhancement compared with control mortar can be pronounced for samples with limestone replacement ratio of 5%. This strength increment can be attributed to the effect of limestone particles on hydration kinetics by forming nuclei for precipitation of calcium hydroxide. If solely strength factor was to be taken into consideration, optimum limestone replacement ratio seems to be around 5-10%. However, other factors like cement fineness, clinker-limestone compatibility and hygroscopic water content of limestone may change the optimum limestone replacement ratio for a suitable blended cement production.

Acknowledgements

The support of TUBITAK on “Determination of Optimum Limestone Content in Portland Limestone Cement Production from the view point of Mechanical Performance and Sulfate Originated Durability Problems” through project (MAG-104I083) is acknowledged by authors and also the industrial partners of the project; İzmir ÇİMENTAŞ Türk A.Ş. and ÇİMBETON A.Ş. which provide the materials and experimental infrastructure throughout the study are greatly acknowledged.

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