

INVESTIGATION ON THE POZZOLANIC PROPERTY OF
PERLITE FOR USE IN PRODUCING BLENDED CEMENTS

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Tahir Kemal Erdem

ABSTRACT

INVESTIGATION ON THE POZZOLANIC PROPERTY OF PERLITE FOR USE IN PRODUCING BLENDED CEMENTS

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Perlite is a glassy volcanic rock that contains approximately 70-75% silica and 12-18% alumina.

There are very large perlite reserves in the world (~6700 million tons) and approximately two thirds of these is in Turkey.

Due to its high amounts of silica and alumina, at the beginning of such a study, it seemed that it would be worth first to find out whether perlite possesses sufficient pozzolanic property when it is a finely divided form and then to investigate whether it could be used as a pozzolanic addition in producing blended cements.

In this study, perlites from two different regions (İzmir and Erzincan) were tested for their pozzolanic properties. After obtaining satisfactory results, grindability properties of the clinker, perlites and their different combinations

were investigated. Several blended cements with different fineness values and different perlite amounts were produced by either intergrinding or separate grinding methods. The tests performed on the cement pastes and mortars containing the blended cements produced were as follows: Water requirement, normal consistency, setting time, soundness, compressive strength, rapid chloride permeability, resistance to sulfate attack and resistance to alkali-silica reactions.

The results showed that Turkish perlites possess sufficient pozzolanic characteristics to be used in cement and concrete industry. Moreover, the properties tested in this study satisfied the requirements stated in the standards for blended cements. The durability of the mortars was found to be improved by 20% or more perlite incorporation.

Keywords: Perlite, Pozzolan, Blended Cement, Cement Manufacturing, Grinding.

ÖZ

KATKILI ÇİMENTO ÜRETİMİNDE KULLANIMI İÇİN PERLİTİN PUZOLANİK ÖZELİĞİNİN ARAŞTIRILMASI

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Perlit, yaklaşık olarak %70-75 oranında silika ve %12-18 oranında alümin içeren camsı bir volkanik kayadır.

Dünyada çok büyük miktarda (~6700 milyon ton) perlit rezervi bulunmakta ve bunun yaklaşık üçte ikisi Türkiye’de yer almaktadır.

İçerdiği yüksek miktardaki silika ve alüminden dolayı, bu çalışmanın başında, ilk olarak perlitin yeterli miktarda puzolanik özeliğe sahip olup olmadığının bulunması ve sonra da katkılı çimento üretiminde puzolanik katkı olarak perlit kullanılıp kullanılamayacağının araştırılmasının önemli olacağı düşünülmüştür.

Bu çalışmada, iki farklı bölgeye (İzmir ve Erzincan) ait perlitin puzolanik özellikleri araştırılmıştır. Uygun sonuçların alınmasından sonra, klinkerin, perlitin ve bu iki malzemenin çeşitli miktarlardaki karışımlarının öğütülebilirlik özellikleri incelenmiştir. Beraber veya ayrı öğütme metotları kullanılarak,

değişik inceliklerde ve değişik miktarlarda perlit içeren birçok katkılı çimento üretilmiştir. Üretilen katkılı çimentolarla elde edilen çimento hamurlarına ve harçlara uygulanan deneyler şunlardır: Su ihtiyacı, normal kıvam, priz süresi, dayanıklılık, basınç dayanımı, hızlı klor geçirgenliği, sülfat hücumu ve alkali-silika reaksiyonlarına karşı direnç.

Deney sonuçlarına göre, Türkiye'deki perlitler, çimento ve beton endüstrisinde kullanılmaları için yeterli puzolanik özelliğe sahiptirler. Ayrıca, bu çalışmada denenen özellikler, katkılı çimentolarla ilgili standartlarda istenen özellikleri sağlamaktadır. 20% veya daha fazla perlit kullanılmasıyla perlit katkılı harçların dayanıklılığının arttırılabileceği bulunmuştur.

Anahtar Kelimeler: Perlit, Puzolan, Katkılı Çimento, Çimento Üretimi, Öğütme

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CHAPTER 1

INTRODUCTION

1.1 General

Pozzolans are siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties [1].

Volcanic ashes, volcanic tuffs (trasses), volcanic glasses, pumicites, calcined clays or shales, diatomaceous earths, fly ashes (the fine ashes obtained from the burning of pulverized coal in power plants for generating electricity), condensed silica fumes (the finely divided materials obtained as a by-product material in the manufacture of silicon metal or silicon alloys), and rice husk ashes are the commonly known materials that exhibit pozzolanic characteristics [2].

Pozzolanic materials can be used in concrete technology in two ways:

- 1) As a finely divided mineral admixture in concrete-making -- Finely divided pozzolan is added to the concrete mixture during or just before the batching operation in order to consist some part of the concrete. Usually,

the pozzolan added substitutes a certain amount of the reduced cement content.

- 2) As an addition in the production of blended cements -- Normally, portland cements are produced by intergrinding “clinker + gypsum”. Blended cements are produced either by intergrinding “clinker + pozzolan + gypsum” or by combining “cement + separately ground pozzolan”.

When pozzolan is used either as an admixture of concrete or as a part of the blended cement, the total amount of the cementitious materials in concrete consist of some amount of portland cement and finely divided pozzolan. Hydration of the portland-pozzolan materials takes place in such a sequence that first the cement reacts with water, and the calcium silicate compounds of the cement produces calcium hydroxide and calcium-silicate-hydrate gels that provide the binding effect in cement pastes; the pozzolan reacts with this calcium hydroxide, leading to the formation of new calcium-silicate-hydrate gels.

Not all kinds of pozzolans can be used in making pozzolanic concrete or blended cements. In order to possess sufficient pozzolanic activity, the amorphous materials should contain minimum 70% “ $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ” and they should be in a very finely divided form.

Whether the pozzolans are used as mineral admixtures in concrete making or as a material that consist some part of the blended cement, there are various advantages in their usage. Some of these advantages can be generally listed as follows:

- Improved workability
- Decreased bleeding and segregation
- Reduced temperature rise

- Reduced alkali - aggregate reaction
- Reduced permeability
- Reduced volume change
- Reduced creep
- Improved sulfate resistance
- Increased ultimate strength, and
- Economy

1.2 Object and Scope

Perlite is a glassy volcanic rock that contains approximately 70-75% SiO_2 and 12-18% Al_2O_3 . Its 2-6% chemically combined water causes it to expand and become a cellular material of extremely low bulk density when heated to a temperature of $\sim 900^\circ\text{C}$. Thus the expanded perlite is used in various constructional and industrial applications.

Due to its glassy structure and high SiO_2 and Al_2O_3 contents, perlite –in finely ground form- is a very good candidate for being a pozzolan. Although its pozzolanic characteristics have been mentioned in some limited numbers of technical papers [3-5], no investigation has so far been made on the use of perlite in manufacturing blended cements.

There are very large perlite deposits in the world (~ 6700 million tons) and approximately two thirds of these is in Turkey. However, the United States is estimated to be the largest producer of perlite and Turkey takes place its position after US, Greece, and Japan. The ratio of perlite reserves to perlite production is quite poor as compared to that in the other producer countries [6,7]. Therefore, investigations on the conformance of perlites to the requirements of the standard specifications for pozzolanic materials and their

effects on grindability during blended cement manufacturing are of vital importance.

The aim of this study is to examine the pozzolanic properties of Turkish perlites and, if appropriate, to investigate whether they can be used as a pozzolanic addition in producing blended cements.

For this purpose, perlites from two different regions of Turkey (İzmir and Erzincan) were tested to determine their conformance to the standard specifications for pozzolanic materials. After obtaining satisfactory results, grindability properties of the clinker, perlites and their different combinations were investigated. Several blended cements with different fineness values and different perlite amounts were produced by either intergrinding or separate grinding. The tests performed on the cement pastes or mortars containing the blended cements produced were as follows: Water requirement, normal consistency, setting time, soundness, compressive strength, resistance to sulfate attack, resistance to alkali-silica reactions, and rapid chloride permeability. All of the tests were made according to the pertinent ASTM standards.

CHAPTER 2

LITERATURE SURVEY ON PERLITES, GRINDABILITY OF MATERIALS AND SOME TESTS CONDUCTED IN THIS INVESTIGATION

In the first Section of this Chapter, a literature survey on “perlites” is given. Then, in Section 2.2, pertinent literature on the “grindability of materials” is summarized. In the last three Sections, general information and previous studies on the durability tests performed in this study, which are “rapid chloride permeability”, “alkali-silica reactions” and “sulfate attack”, are presented.

2.1 Perlite

Igneous rocks are formed by cooling and thus solidifying of the magma which is the molten material occurring in the depths of earth. This process is due to a decrease in temperature and pressure. The solidification of igneous rocks may take place either within the earth or on the surface of earth. The texture of these rocks is influenced greatly by the rate of cooling and by the volatile substance present. The rocks that have solidified within the earth are called intrusive rocks whereas those that solidified on the surface are extrusive rocks [8].

Obsidian is an extrusive type of rock. It is a rock that has formed by rapid cooling of the magma that flows through an environment which has active water coming from lakes, swamps, streams, or continuous rains. So, some amount of absorbed water can be held in obsidian. In the subsequent years, the obsidian alters into a glassy, gray-brown rock through hydration of obsidian caused by absorption of water during and after cooling. The amount of water in the hydrated obsidian can vary; but is typically less than 4%. Water absorption starts along cooling fractures in the obsidian and proceeds as concentric circles expanding away from the fractures toward the solid cores of unfractured rock resulting in the weakening and breakage of the bonds of the glass structure. This newly formed rock is known as “perlite” [6,9].

In brief, perlite is a form of altered obsidian which has some combined water in its structure. This glassy volcanic rock contains approximately 70-75% silica and 12-18% alumina [6,9].

Due to the resemblance of perlite -in broken form- to “pearl”, this material has been named as perlite. The color of perlite is generally light gray; but sometimes it may be black, light green or brown.

Most of the perlite ores are generally young (less than 50 million years old) [10]. Due to the youthfulness of the rock and closeness of it to the surface, mining the perlite is generally easy. Perlite can be mined by open pit methods at or near the surface. The fractured texture and brittleness of perlite makes it possible to minimize the drilling and blasting expenses [6,7,10,11].

The typical chemical analysis of perlite is given in Table 2.1 [11].

Perlite contains 2 to 6% combined water in its structure. Combined water in perlite is the water which did enter into the chemical composition of the volcanic glass as molecules, and consequently united with the volcanic glass.

The glass cannot be crystallized due the presence of active water in its structure [6].

Table 2.1 Typical Chemical Analysis of Perlite [11]

Compound			Content, %	Compound			Content, %
Silicon Dioxide	SiO ₂		73.8	Chlorine	Cl		<0.0005
Aluminium Oxide	Al ₂ O ₃		13.9	Chromium	Cr		<0.007
Sodium Oxide	Na ₂ O		4.7	Copper	Cu		<0.0015
Potassium Oxide	K ₂ O		4.3	Gallium	Ga		<0.05
Calcium Oxide	CaO		0.9	Lead	Pb		<0.001
Ferric Oxide	Fe ₂ O ₃		0.9	Manganese	Mn		<0.3
Magnesium Oxide	MgO		0.3	Molybdenum	Mo		<0.002
Water (moisture)	H ₂ O		<1.0	Nickel	Ni		<0.02
Arsenic	As		<0.001	Sulphur	S		<0.2
Barium	Ba		<0.1	Titanium	Ti		<0.1
Boron	B		<0.01	Zirconium	Zr		<0.003

The chemically bonded water held within the perlite glass structure expands on heating to create a cellular material of extremely low bulk density [7,10,11].

The particle must be heated quickly enough above its softening point ($\sim 870^{\circ}\text{C}$) so that it becomes soft enough to expand before the combined water in its structure vaporizes. The formed steam acts to expand the softened material, increasing the porosity of the structure and decreasing the original density so that, consequently, the rock expands creating many tiny bubbles. The resultant product is named as expanded perlite [6,10]. Bulk density of expanded perlite is $60 - 120 \text{ kg/m}^3$.

The expanded perlite is used widely due to its extremely low bulk density, high brightness, high absorption, low thermal and acoustical conductivity, and non-flammability. The uses of expanded perlite can be generally categorized as construction, horticultural, and industrial applications.

Total worldwide perlite reserve is around 6715 million tons. Approximately 70% of this reserve belongs to Turkey [11]. Perlite reserves in Turkey are given in Table 2.2. According to the report prepared by Turkish State Planning Organization [7], other than the regions given in Table 2.2, there is a significant amount of perlite reserve in Kars-Göle region.

The production rate of perlite is not directly related with the reserves. The United States is estimated to be the largest producer of perlite. Turkey takes place its position after US, Greece, and Japan. Although Turkey has rich reserves, the domestic consumption is limited. In Turkey, perlite is consumed mainly in three general categories: 60% in construction, 17% in horticultural and 20% in industrial applications [6,7].

Table 2.2 Perlite Reserves in Turkey [7]

Region	Reserve (thousand tons)
Ankara (Çamlıdere, Çubuk, Kızılcahamam)	74.000
Balıkesir (Evrindi, Savaştepe-Sındırğa)	72.000
Bitlis-Adilcevaz-Tatvan-(Van-Erciş)	1.400.000
Çankırı-Orta	30.000
Çanakkale-Biga	3.400
Eskişehir-Seyitgazi	20.000
Erzincan-Merkez	27.000
Erzurum-Pasinler	100.000
İzmir-(Bergama, Dikili, Foça, Menderes-Cuma Ovası)	101.000
Kars -Sarıkamış	1.500.000
Manisa-(Demirci-Soma, Saruhanlı)	36.600
Nevşehir-(Acıgöl, Derinkuyu (Niğde-Gölcük))	1.212.000
Total	4.576.200

2.2 Grindability

2.2.1 General

In portland cement production, the calcareous and clayey raw materials are burned in a rotary kiln at 1400-1500 °C until obtaining a product called as “clinker”. On exit from the kiln, the clinker is cooled and then interground with

gypsum. In case of producing portland-pozzolan type of cement, some amount of pozzolan is also used besides the clinker and the gypsum, and these materials are interground. (Portland-pozzolan cement is also produced by combining some cement with separately ground pozzolans.)

The grinding operation is generally done in a ball mill consisting of several compartments with progressively smaller steel balls. Usually, a closed circuit system is used in the plants. The cement discharged by the mill is passed through a separator so that fine particles are removed to the storage silo by an air current, while the coarser particles are passed through the mill once again [12]. A significant portion of the electrical energy used in cement production is consumed during the grinding process and most of the energy input is lost as heat due to the friction of the ingredients [13].

Grindability is the measure of the ability to resist grinding forces. It is used to estimate the energy requirement for grinding the clinker to a given fineness. There are several different laboratory testing methods developed for determining the grindability of clinkers. The commonly used methods for this purpose are determination of (a) the energy requirement of the mill to produce a cement with a specified fineness, (b) revolutions of the mill necessary to produce a cement with specified fineness, (c) specific surface area of the ground clinker for a specified energy consumption of the mill, and (d) amount of ground clinker passing a specified sieve (usually 75 μm) per mill revolution [14].

Several variables can affect the efficiency and productivity of grinding circuit such as operating conditions of separators, air flow through the mill, ball sizes and ratio in the mill compartments, material filling, and speed of rotation [15].

2.2.2 Previous Studies on Grindability

Some of the studies on the grindability of clinker, mineral admixtures and blended cements are summarized below:

Chemical and mineralogical compositions of clinkers affect the grindability significantly [14]. It was found in different studies that grindability increases with decreasing C_2S and C_3A contents and with increasing C_3S , Al_2O_3 , Fe_2O_3 , C_4AF , K_2O , MgO contents [16-18]. Tokyay developed an exponential relationship between the grinding energy consumption and the specific surface area attained. The constants of the exponential function depended on the chemical composition of the clinkers. It was stated that a reasonable amount of energy savings can be obtained by careful adjustment of the chemical composition of the kiln feed [14].

Blended cements are produced by inclusion of mineral admixtures either by intergrinding or separate grinding. The grindabilities of blended cements depend on the grindability of the individual components [19]. However, the grindability of the mixtures is not simply the weighted average of the grindabilities of the ingredients [20]. This can be explained by the interactions between the particles of different components. Therefore, separate grinding yield a different particle size distribution than intergrinding [21].

Figure 2.1 shows the comparison of the grindabilities of limestone, clinker, slag and trass [22]. In this Figure, the required energy to reach certain fineness was taken as a measure of grindability. As seen from this Figure, clinker has a higher grindability than slag. On the other hand, trass and limestone are more easily grindable than the clinker.

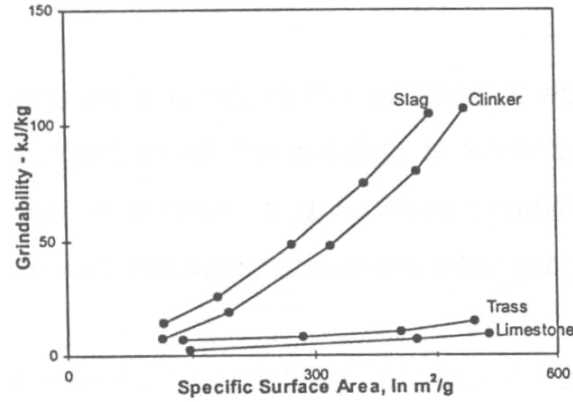


Figure 2.1 Comparison of the Grindabilities of Limestone, Clinker, Slag and Trass

Intergrinding and separate grinding of the cements containing natural pozzolan or ground granulated slag were compared by Erdoğan et al. [21]. For both mixtures, interground cements became relatively finer than the separately ground cements with increasing grinding energy consumption. It was shown that interactions between the ingredients during intergrinding were much more pronounced for higher particle size ranges. To reach a Blaine fineness of 3500 cm^2/g , intergrinding consumed more energy than separate grinding for slag-incorporated cements. The situation was reversed for the cements containing natural pozzolan, that is, energy consumption for intergrinding was less than separate grinding [21].

In case of intergrinding, harder particles can abrade the softer ones. For example, ground granulated blast furnace slag shows an abrasive effect on the clinker particles [19]. Similarly, clinker acts as a grinding media for the natural pozzolan particles [23].

According to the results of a study [24] in which grinding methods (intergrinding or separate grinding) are compared for blast furnace slag cement, separate grinding should be preferred in view of lower specific energy consumption, ease of manufacture, higher addition of slag (i.e., less environmental hazards) on top of higher flexibility in product quality arrangement according to the market requirements. It was stated that when the grindabilities of the components differ, their individual distributions are also different. In case of intergrinding, slag having lower grindability accumulates in coarser fractions; with the clinker having higher grindability accumulates in finer fractions. Therefore, although the two blast furnace slag cements produced by intergrinding and separate grinding have the same specific surface area, the harder component, slag, in the interground cement remains coarser than the slag in the cement ground separately. Since the contribution of a coarser slag to the reactions is slower, the strength values obtained for the interground cement were lower when compared to separately ground cement [24].

Opoczky suggested that in the production of slag cement, when the slag content is greater than 25%, separate grinding is more advantageous. This technology made it possible the slag to a suitable fine size thus enhancing its hydraulic activity. By separate grinding, cements with high strength and high slag content can be produced by adding even low-quality slag [25].

Erdoğan et al. [21] performed compressive strength tests on the natural pozzolan and slag-incorporated cements produced by intergrinding and separate grinding. The Blaine fineness values were the same for all of the cements. According to the results, intergrinding yielded higher strengths for both of the cements. This was explained by the finer particle size distribution of the interground cements when compared to the separately ground cements having the same composition. The difference between the strengths resulting from the grinding methods decreased with age [21].

More homogeneous products provided by intergrinding can be accounted for its advantages over separate grinding. Homogeneity can supply higher strength values [21]. Moreover, blending the separately ground components require additional equipment in plants.

It was found in a study [26] that it is difficult to control the particle size distribution of the blended cements produced by intergrinding method due to interaction between components during grinding. In the case of intergrinding the clinker together with a pozzolan which is more easily grindable, clinker may not be ground sufficiently. This phenomenon is more evident for the blended cements containing large amounts of an easily grindable natural pozzolan. Especially for relatively bigger particle sizes ($>15\mu\text{m}$), blended cements may be coarser than a typical Portland cement when their particle size distributions are compared, even if the Blaine fineness of blended cement is considerably higher than the Portland cement. Therefore not only the Blaine fineness method but also the particle size distribution data should be used to assess the fineness of blended cements produced by intergrinding [26].

According to a recent study on limestone incorporated cements [13], limestones can not be used by separate grinding technique for small addition amounts less than 20%, as separate grinding brings larger particle size distribution than intergrinding. To produce a portland limestone cement having the same Blaine fineness with a reference portland cement, the energy consumption was lower. However, the particle size distribution of the portland limestone cement have to be studied and monitored carefully. It was also stated that in production of portland limestone cement, feed size of limestone should be reduced as much as possible prior to the grinding [13].

Tsivilis et al. studied the intergrinding of clinker and limestone. Four clinker/limestone mixtures, containing 10, 20, 30 and 40% limestone respectively were ground to 4 different finenesses. It was concluded that the

presence of the easily ground limestone lead to a wider particle size distribution of the mixture. Moreover, they stated that limestone content over 30% obstructed the grinding of both clinker and limestone [27].

2.3 Rapid Chloride Permeability

2.3.1 General

One of the main problems in concrete structures has been chloride-induced corrosion [28]. Since the volume of the corrosion product is 2 - 3 times greater than the volume of the metal spent during corrosion, a great internal stress is created within the concrete. Development of such stress leads to cracking of concrete. Moreover, due to the reduction of the cross-section of the metal as a result of corrosion, its load carrying capacity is decreased [8].

Since 1970s, different organizations and professionals have tried to develop and implement rapid, inexpensive and reliable tests to measure the ability of concrete to resist the penetration of chloride ions. Whiting [29] developed the rapid chloride permeability test (RCPT) in the late 1970s, even though it is really a measure of electric conductivity. This test was adopted by AASHTO in 1983 as T277 and by ASTM in 1991 as ASTM C 1202 [28,29].

RCPT determines the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of chloride ions. The chloride ion resistance of concrete gives an indirect measure of its permeability and internal pore structure, as more current passes through a more permeable concrete. The results of this test can be used to assess the durability of concrete [30].

RCPT involves the application of a voltage between two sides of a concrete specimen with solutions of sodium hydroxide and sodium chloride on opposite

sides. The total charge passed during a six-hour period provides a measure of the permeability. It was stated that for concretes with w/c ratios between 0.4 and 0.75, RCPT results correlate well with both of the more conventional pressure methods used to measure permeability and total porosity [31].

The qualitative classification for concrete given by ASTM C 1202 [32] is shown in Table 2.3

Table 2.3 Chloride Ion Penetrability Based on Charge Passed [32]

Charge Passed (coulombs)	Chloride Ion Penetrability
> 4000	High
2000 - 4000	Moderate
1000 - 2000	Low
100 - 1000	Very low
<100	Negligible

Despite the view that RCPT can be used to evaluate the permeability [30,31,33-35], there are also studies in which it is concluded that this test may not be valid for evaluation of permeability of concretes containing different types of materials and proportions [36,37].

2.3.2 Previous Studies on Rapid Chloride Permeability

The effects of using mineral admixtures on rapid chloride permeability were examined in several studies. Some of these investigations will be summarized below:

Byung et al. [33] studied the influence of mixture proportions of concrete on the resistance to chloride penetration and tried to develop high-performance concrete having high resistance to chloride penetration and high durability. The variables in this study were water-to-binder ratio, type of cement, type and amount of mineral admixtures (silica fume, fly ash and blast-furnace slag), maximum size of aggregates and air-entrainment. According to the results, the concretes containing silica fume showed the best performance among the specimens in the rapid chloride permeability test. Concretes prepared by using fly ash also showed good performance. It was found that fly ash greatly decreased the permeability of concrete even though the strength of fly ash concrete at 28 days was not improved. The use of blast-furnace slag also decreased the chloride permeability since the secondary chemical reaction of blast-furnace slag contributed to make the microstructure denser. Using the appropriate type and amount of mineral admixtures was more effective than to use ordinary portland cement only or to decrease water-to-binder ratio.

Many properties of expansive-cement concrete containing silica fume and polypropylene fibers were investigated by Houssam and Toutanji [37]. Silica fume content used was 5 and 10% and fiber volume fraction was 0.10, 0.30, and 0.50%. The addition of polypropylene fibers caused an adverse effect on the chloride permeability of expansive-cement concrete. However, the addition of silica fume resulted in a significant decrease in permeability. Use of 5% silica fume combined with 0.30% fiber results in optimum mixture design for repair applications from the standpoints of workability, bond strength, length change and permeability.

The flow of electric current through a conductor generates heat. This heat is proportional to the quantity of electricity or charge passed through the conductor and to the applied potential. In RCPT, the problem with some concretes is that high current levels result in heating during the test. The temperature in the solution and concrete specimen increases during the test due to the flow of electric current generated by the relatively high applied voltage (60 V). The heating is more evident when the test is performed on young concretes or on those concretes with high water–cement ratios. An incremental change in temperature will increase the mobility of all ions that carry the current, which in turn will raise the total current flow producing more heat in a cyclic process. Since electrical conductivity is sensitive to temperature, heating will result in higher measured coulomb values [28].

The heat generated during the test may also alter the pore structure and accelerate the hydration. This effect is pronounced especially for young concretes [38].

This problem in RCPT was tackled by many researchers. They have modified the size of the cell, used a lower voltage or even proposed to run the test for only 30 min to reduce or eliminate the heating effect [28].

Due to the severe conditions during the test, both physical and chemical changes in the specimens can lead unrealistic values. Previously, good correlations between initial current and conductivity, initial current and charge passed, and conductivity and charge passed were obtained by taking measurements at the beginning of the test. These tests were for one type of concrete only. Then, Feldman et. al [38] studied the influence of concrete characteristics (type of binder, mix proportions, length of cure) on the mentioned correlations. The mixtures contained silica fume, blast furnace slag and fly ash. It was shown that it was possible to use simplified procedures,

which reduce the period of severe conditions and considerably shorten the length of time to perform the test.

Nehdi et. al [39] produced rice husk ash (RHA) by using a new technique and investigated its performance in concrete. It was shown that proportions of nonground RHA did not significantly change the rapid chloride penetrability classification of concrete stated in ASTM C 1202 [32]. However, using finely ground RHA reduced the rapid chloride penetrability of concrete from a “moderate” rating to “low” or “very low” ratings depending on the type and addition level of RHA. Such reductions were comparable to those achieved by silica fume.

As stated in the previous section, according to some studies [36,37], measuring the electrical conductivity is an inadequate method to indicate the permeability of concrete. The explanation given by Caijun [36] was as follows: The permeability of concrete depends on the pore structure of concrete, while electrical conductivity or resistivity of concrete is determined by both pore structure and the chemistry of pore solution. Factors that have little to do with the transport of chloride can have great effects on electrical conductivity of concrete. For example, mineral admixtures may have a significant effect on the chemistry or electrical conductivity of pore solution, depending on their alkali content and replacement level, which has little to do with the chloride permeability.

2.4 Alkali-Silica Reactions

2.4.1 General

There are three types of alkali-aggregate reactions: alkali-carbonate reaction, alkali-silicate reaction and alkali-silica reaction. In general terms, these

reactions involve chemical interaction between alkali-hydroxides, which are generally derived from the cement, and reactive components in the aggregates. The most common reaction among these is the alkali-silica reaction [40,41].

Alkali-silica reaction starts with the attack on the siliceous minerals in the aggregate by the alkaline hydroxides in pore water derived from the alkali oxides, Na_2O (N) and K_2O (K), in the cement. The reactive forms of silica (opal, calcedony and tridymite) occur generally in opaline or calcedonic cherts, siliceous limestones, rhyolites, dacite, andesite, and phyllites. As a result of the reactions, an alkali-silica gel (N-S-H or K-S-H) is formed either in planes of weakness or pores in the aggregate (where reactive silica is present) or on the surface of the aggregate particles [12, 42]. This gel has an unlimited swelling capacity: It imbibes water and increases the volume. The confinement of the gel by the surrounding hydrated cement paste causes internal pressures which may lead to expansion, cracking and disruption of the paste [12].

As the water content in the gels increases, the product turns to a liquid containing colloidal particles. This system reacts with calcium hydroxide (CH) in the paste, then sets in the cracks in the aggregates and concrete, and covers the aggregate particles. This process causes expansions in the aggregates and in the cracks in concrete [42].

Alkali-silica reaction is a very slow process which may spread over years.

The pattern of surface cracking induced by the alkali-silica reaction is irregular and resembles a spider's web. Sometimes, the colloidal system may exude from the cracks and causes white stains and aesthetical problems. Alkali-silica reactions may cause severe cracking, which can promote further durability problems [42].

The major factors that affect the expansion induced by alkali-silica reactions can be listed as: nature of the reactive silica, amount of reactive silica, particle size of reactive material, amount of available alkali, and amount of available moisture [31].

One of the possible measures to control the expansions resulting from the alkali-silica reactions is to use cements with low alkali content. ASTM C 150 [43] limits the “ $\text{Na}_2\text{O} + 0.66\text{K}_2\text{O}$ ” content of the portland cement to maximum 0.6%. Alternatively, non-reactive aggregates should be selected in preparing the concrete mix [42]. Use of pozzolanic admixtures is another possibility to prevent the expansions. This can be explained by the reduction in the alkali content of the cementitious blend and the reduction in pH of the solution. Also, the C-S-H formed in the pozzolanic reaction can absorb alkali-ions to a greater extent than formed by hydration of the calcium silicates alone [31].

The measures that reduce the permeability are also effective to prevent several durability problems including alkali-silica reactions. Permeability can be reduced by using lower water-binder ratio, applying proper compaction and curing, and employing mineral admixtures. A lower permeability reduces the mobility of aggressive agents which may be present within the concrete and which may ingress into the concrete [12].

2.4.2 Previous Studies on Alkali-Silica Reactions

In the United States, there were many reported failures of concrete structures built during the late 1920s to the early 1940s. These failures were due to the overall cracking throughout the structure manifested at the surface as extensive map cracking. The cracks were accompanied by gel exuding from the cracks or surface popouts and spalling. Stanton [44] diagnosed the failures in 1940s as being due to expansions caused by a chemical reaction between the alkalis in

the cement and reactive silica within the aggregate [31]. Since then, many studies have been carried out on alkali-aggregate reactions. In this text, only those investigating the effects of pozzolans will be summarized.

Replacement of portland cement partly by fly ash, or blast furnace slag, silica fume or rice husk ash reduces the expansion as a result of alkali-aggregate reactions [45]. The explanations for this are generally centered on the type of C-S-H formed during the hydration of cement. When the CaO/SiO₂ ratio of the C-S-H formed is approximately 1.2 or lower, this product is suggested to have an increased capacity for accommodating Na₂O and K₂O in its structure, thereby reducing the hydroxyl ion concentration [46]. During normal hydration without the mineral admixture this ratio is about 1.5 [45].

Perry and Gillott have studied the effect of silica fume to control alkali-silica reactions at temperatures of 25, 38 and 50°C. Amounts of cement replaced by the silica fume ranged from 0 to 40% by weight. Results of the experiments performed at 50°C showed that replacement of cement by silica fume significantly reduced expansion, but 20% replacement was necessary to control the reaction. Moreover, it was found that superplasticizer addition at 15% replacement level of silica fume might influence expansion in a negative manner [45,47].

The presence of superplasticizers may increase alkali-silica reactivity. Mortar bars made containing 0, 6 and 12% silica fume and superplasticizer showed greater early reactivity and ultimate magnitude of expansion than the corresponding bars with no superplasticizer [48].

Within the various pozzolans, silica fume is particularly effective because the silica reacts preferentially with the alkalis. Although the reaction product is the same as that between the alkalis and the reactive silica in the aggregate, the

reaction takes place at the very large surface of the fine particles of silica fume. In consequence, the reaction does not result in expansion [12, 49].

Fly ash or slag incorporation reduces the alkali-silica reaction expansions. The test results obtained by Lane and Özyıldırım [50] can be used to illustrate the benefits of using these mineral admixtures. Figures 2.2 (a) and 2.2 (b) show the expansions over time for several replacement levels, respectively, for fly ash and slag.

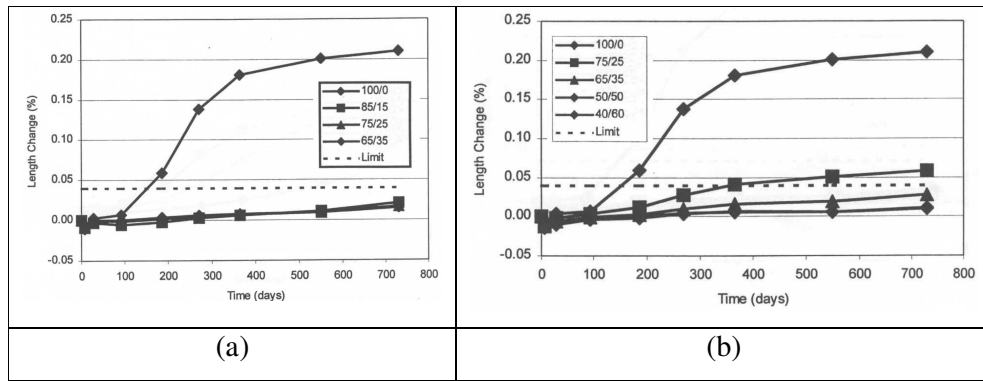


Figure 2.2 (a) ASR Expansions for PC-Fly Ash Concretes (Portland Cement/Fly Ash), (b) ASR Expansions for PC-Slag Concretes (Portland Cement/Slag) [50]

The effects of alkali and CaO content in fly ash were also studied. According to the results obtained using 20 fly ashes, it was found that, the expansion of concrete prisms generally increased as the CaO or alkali content of the fly ash increased or its silica content decreased. Consequently, the minimum level of replacement required to control expansion increased as the CaO or alkali content of the fly ash increased [51]. Moreover, in other studies it was found

that small additions of fly ash may increase expansion, whereas larger amounts may reduce expansion. This was attributed to the alkali contribution from fly ash [52]. It should be pointed out that fly ash itself contains alkalis, but typically only about one-sixth of the total alkali content in the fly ash is water soluble, and therefore potentially reactive, the remainder being combined [12,53].

By using the accelerated mortar bar method, the effectiveness of slag with low alkali (0.68% Na_2O_e) and high alkali (1.37% Na_2O_e) cements was studied by Monterio et al [54]. Great reductions were achieved when used <45% and <60% slag replacements with low and high alkali cements, respectively.

The performance of ternary blends (portland cement + silica fume + fly ash and portland cement + silica fume + slag) was evaluated by Lane and Özyıldırım [50]. It has already been stated that fly ash or slag can improve the alkali-silica reaction resistance (Figures 2.2 (a) and 2.2 (b)). However, high replacement levels may cause low strength values at early ages and some problems in the construction. It was stated by Lane and Özyıldırım that incorporating small amounts of silica fume with ordinary portland cement and fly ash or slag in ternary systems can be used to counterbalance the negative effect of fly ash or slag replacement level on early strength and low replacement level on durability [50].

Natural pozzolans were also found to be a possible measure to control the expansions [54,55]. In a study involving the use of Santorin Earth (a volcanic ash) in the range of 0-30%, it was stated that as the amount of natural pozzolan increased, the expansion values decreased [55].

ASTM C 1260 [56] is based on the NBRI (National Building Research Institute) Accelerated Test Method [57]. In this test, the specimens are exposed to 1N NaOH solution. Therefore, it was stated that the alkali content of cement

is not a significant factor in affecting expansions [56]. ASTM C 1260 provides a means of detecting the potential of an aggregate intended for use in concrete for undergoing ASR resulting in potentially deleterious internal expansion. However, this method is found to be very successful also in screening different mineral admixtures for their effectiveness in preventing expansions induced by ASR. It has the advantage that it can be applied to specific aggregate/mineral admixture combinations. Moreover, this test method is relatively easy to carry out and provides results in a short period of time (16 days) [58]. However, a longer period (30 days), in some cases, was also suggested for more reliable results [41]

2.5 Sulfate Attack

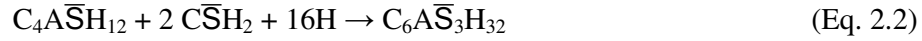
2.5.1 General

Sulfates are often present in groundwater, particularly when high proportions of clay are present in the soil. Groundwater may have local concentrations of sulfate in the vicinity of industrial wastes such as mine tailings, slag heaps, and rubble fills. Sulfates present in rainwater from air pollution, or produced by biological growth, may cause slow deterioration even in concrete above ground [31].

As known, the hydration products of portland cement are calcium silicate hydrates (C-S-H gels), calcium hydroxide (CH), calcium sulfoaluminates ($C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$). When concrete is exposed to sulfates such as sodium sulfate (Na_2SO_4 or $N\bar{S}$) or magnesium sulfate ($MgSO_4$ or $M\bar{S}$), CH in the hardened cement paste reacts with the sulfates to produce gypsum ($C\bar{S}H_2$). The reaction for $M\bar{S}$ is given as:



Then, metastable $C_4A\bar{S}H_{12}$ in the hydrated cement paste reacts with gypsum produced from the sulfate attack causing the formation of ettringite ($C_6A\bar{S}_3H_{32}$):



Formation of gypsum in Eq. 2.1 causes some expansion in the hardened cement paste. However, expansion resulting from Eq. 2.2 is greater than that was caused by Eq. 2.1.

The consequences of sulfate attack include not only disruptive expansion and cracking, but also loss of strength of concrete due to the loss of cohesion in the hydrated cement paste and of adhesion between the paste and aggregates. Moreover, sulfate attack can also cause disintegration and loss of stiffness [59]. Concrete attacked by sulfates has a characteristic whitish appearance. The damage usually starts at edges and corners and is followed by progressive cracking and spalling which reduce the concrete to a friable or even soft state [12].

As discussed above, both sodium sulfate and magnesium sulfate cause the production of gypsum and ettringite. On the other hand, magnesium sulfate can be even more aggressive since it can decompose C-S-H gels. Therefore, the binding property of the cement is reduced. Fortunately, magnesium hydroxide (MH) produced from the reaction of magnesium sulfate with CH or C-S-H can deposit in the pores and partially close them. This prevents further diffusion of the sulfates to concrete [31, 42]

Following measures can be taken to prevent or reduce the deterioration caused by the sulfate attack [8,42]:

- Exposure to sulfates should be reduced: For this purpose, the concrete surface can be sealed with a proper coating. Moreover, a less permeable concrete also reduces the exposure to sulfates. For low permeability, water/(cementitious materials) ratio should be low, and the concrete should be placed, compacted and cured adequately.
- C_3A content should be low: Ettringite amount can be reduced when C_3A content in the cement is low. This can be achieved through using commercially available sulfate resisting cements. Alternatively, partial replacement of cement with a pozzolan or slag decreases the cement and, therefore, C_3A content.
- CH content should be low: As discussed previously CH is one of the reactants in the formation gypsum (Equation 2.1). Using cements with relatively lower C_3S/C_2S ratios reduces the CH content in the paste since C_3S produces a higher amount of CH than C_2S . Alternatively, pozzolans or slag can be used as a partial replacement material for portland cement to decrease the amount of C_3S and C_2S , which are the main compounds that produce CH. Moreover, pozzolans or slag can decrease the CH content through pozzolanic reactions. As it is known, pozzolanic materials react with CH resulting from the hydration of calcium silicates to produce additional C-S-H gels.

2.5.2 Previous Studies on Sulfate Attack

There are a large number of studies on sulfate attack in literature. Extensive reviews can be found in References [60-64]. The studies generally concentrate on the w/c ratio, use of pozzolans, type and amount of mineral admixtures, cement type (mainly C_3A amount), sulfate concentration, type of sulfate, the chemistry of the attack, microstructure, pH of the solution, testing methods,

monitoring the damage, etc. Since this thesis is on the use of perlite as a pozzolanic material, some of these studies involving the use of pozzolans will be summarized below:

A study by Cao et.al. [65] reports the results of tests on sulfate resistance of Portland cements and blended cements. Blended cements containing fly ash, ground granulated blast furnace slag and silica fume and four Portland cements of different characteristics were used in this work. The pH of the sulfate solutions were remained at different levels ranging from 3 to 12. It was found that sulfate resistance of cementitious materials was dependent on its composition and on the pH of the environment. The performance of the Portland cement with low C_3A and low C_3S was well in all sulfate solutions. Fly ash, silica fume and slag improved the performance. However, the mineral admixture type and its amount becomes more critical as the pH of the sulfate solution decreases. A good overall sulfate resistance was achieved by 40% fly ash blend and 5% silica fume blend. For slag blended cement, this was obtained when the replacement percentage was higher than 60%.

When mineral admixtures such as silica fume are used, CH is consumed through the pozzolanic reactions. Thus, magnesium sulfate attack can proceed quickly to the stage where the decalcification of the CSH gel occurs. This leads to a poorer performance of the systems containing silica fume than Type I cement [66,67]. However, the use of mineral admixtures can overcome this negative effect through the reduction in permeability and the refinement of the pore structure. It is, therefore, essential to determine critical dosage of mineral admixtures to maximize their benefits [64].

Monterio and Kurtis [68] found that increase in w/c ratio and C_3A content reduces the time to failure, as measured by expansion. Failure did not occur within the 40-year exposure period when the w/c was below 0.45 and C_3A content was 8% or less. According to the results of expansion tests, cements

with high amounts of C_3S may lead to premature failure of concrete, even when moderate w/c ratios are used. Samples containing 25% and 45% fly ash showed significantly less expansion when compared to the mixtures containing no pozzolans.

The performance of the mortars containing ground brick and portland cement when exposed to synthetic seawater was investigated by O'Farrell et.al [69]. It was found that as the amount of ground brick increased up to at least 30% replacement, the resistance of mortar to expansion was generally increased and the strength loss was reduced. Ground bricks having high CaO content, low glass content, and low sulfate content reduced the sulfate resistance, and increased expansion and degradation. A layer of brucite formed on the surface of the mortar and a layer of gypsum was observed below this. Formation of these surface layers reduced for higher replacement levels. The build up of these surface layers inhibited sulfate attack and retarded expansion.

Sulfate resistance of high-performance concrete containing natural pozzolan and silica fume was studied by Shannag and Shaia [70]. Visual observations, ultrasonic pulse velocity measurements, and relative strength determinations showed that the concrete mix containing 15% natural pozzolan, and 15% silica fume showed the best protection in sulfate solutions and sea waters. After one year of storage in sulfate solutions and sea waters, more than 65% of its strength was retained. The superior sulfate resistance of that mix is attributed to the pore refinement process and further densification of the transition zone as a result of pozzolanic reactions. It was recommended that for better performance in severe sulfate environments, silica fume should be used in combination with natural pozzolan.

Strength development, drying shrinkage, sulfate resistance, and alkali-silica activity of the portland pozzolan cements containing 10, 20, or 30% Santorin earth were investigated by Mehta [55]. Highest compressive strengths at 1 year

were obtained for the cement containing 20% pozzolan, and the cements containing 20 or 30% pozzolan showed the least permeability and best sulfate resistance. It was concluded that the enhanced strength and durability of portland pozzolan cements were due to the process of pore refinement associated with pozzolanic reactions.

Based on the findings of many researchers, ASTM C 989 [71] contains the following summary of the state of the art on the sulfate resistance of blended cements containing ground granulated blast furnace slag:

“The use of slag will decrease the C_3A content of the cementing materials and decrease the permeability and CH content of the mortar or concrete. Tests have shown that the alumina content of the slag also influences sulfate resistance, and that high alumina content can have a detrimental influence at low slag replacement percentages. The data from these studies of laboratory exposure of mortars to sodium and magnesium sulfate solutions provide the following general conclusions [60, 71]:

The combinations of slag and portland cement in which the slag content was greater than 60-65% had high sulfate resistance, always better than the portland cement alone, irrespective of the Al_2O_3 content of the slag. The improvement in sulfate resistance was greatest for the cement with higher C_3A contents.

The low-alumina (11%) slag increased the sulfate resistance independently of the C_3A content of the cement. To obtain adequate sulfate resistance higher percentages were necessary with the higher C_3A cements. The high-alumina (18%) slag adversely affected the sulfate resistance of portland cements when blended in low percentages (50% or less).”

ASTM C 1012 [72] is a suitable method for both portland and blended cements [60]. In this method, mortar bars are immersed in a sulfate solution for 6

months. Obviously, such a long period is an important drawback of this test. Moreover, loss of stiffness and strength is not evaluated [60]. Another drawback of the method is that continuous immersion of the specimens does not represent the field conditions: In laboratory testing, pH of the solution changes from ~7 to ~12 due to the leaching of the alkalis, and the sulfate concentration in the solution decreases during continuous immersion. In general, laboratory specimens are able to withstand the attack longer than the corresponding field exposure specimens. This is attributed to the fact that the field specimens are subjected to atmospheric effects such as wetting and drying, in addition to the attack by a sulfate solution of an almost constant concentration [64].

Improving the test methods and standards for sulfate attack has been the subject of several studies. Clifton et al. presented a comprehensive review of the test methods, and provided recommendations for improving the current standards [73].

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Introduction

As previously expressed in Section 1.2, the aim of this study was to investigate the pozzolanic properties of Turkish perlites and, if appropriate, to investigate whether perlite can be used as a pozzolanic addition in producing blended cements.

For this purpose, perlites from two different regions of Turkey (İzmir and Erzincan) were tested for determining their general characteristics and conformance to the standard specifications for pozzolanic materials. After obtaining satisfactory results on the conformance of perlites to the standard specifications for pozzolanic materials, further tests were conducted on grindability and on blended cements produced by using perlites. Several blended cements with different fineness values and different perlite amounts were produced by either intergrinding or separate grinding. Following tests were performed on the cement pastes or mortars: water requirement, normal consistency, setting time, soundness, compressive strength, resistance to sulfate attack, resistance to alkali-silica reactions, and rapid chloride permeability. All of the tests were made according to the pertinent ASTM standards. The details of the experimental study will be given in the following Sections.

3.2 Materials

The materials used in this study constitute portland cement clinker, gypsum, perlite from İzmir (P1), perlite from Erzincan (P2), and fine aggregates. While chert was used for only alkali-silica tests, the mortars for all of the other tests were prepared from standard RILEM sand. The properties of the perlites and clinker were determined upon grinding in a medium described in Section 3.4.1. The tests performed on these materials were the determination of density (ASTM C 188 [74]), fineness by Blaine air permeability (ASTM C 204 [75]), fineness by 45 µm sieve (ASTM C 430 [76]), X-ray diffraction (XRD), and X-ray fluorescence (XRF).

3.2.1 Portland Cement Clinker and Gypsum

The portland cement clinker and gypsum used in producing portland cements and blended cements were obtained from SET Cement Plant in Ankara.

In order to determine the properties of the clinker and gypsum, they were crushed, and sieved through 3/8" sieve (9.5 mm) before the grinding operation. Gypsum needed to be dried at 40 °C prior to crushing.

For all of the cement types to be used in this study, gypsum/clinker ratio was 4/96 by weight.

The oxide composition of the interground “clinker + 4% gypsum” (that is, portland cement) obtained by XRF is shown in Table 3.1. The compound composition of the portland cement shown in the Table was calculated by Bogue’s equations.

Table 3.1 Oxide Compositions of the Materials Used in the Research

Oxides	PC, %	P1, %	P2, %
SiO ₂	21.00	76.57	75.30
Al ₂ O ₃	4.98	9.99	9.35
Fe ₂ O ₃	3.57	0.96	1.36
CaO	63.58	0.51	0.60
MgO	1.86	0.03	0.05
Na ₂ O	0.14	0.00	0.00
K ₂ O	0.74	5.58	4.82
SO ₃	2.52	0.04	0.06
C ₃ S	53.49		
C ₂ S	20.04		
C ₃ A	7.16		
C ₄ AF	10.86		

The specific gravity of the portland cement (PC) in relation to grinding time and fineness is given in Table A.1 in Appendix.

3.2.2 Perlites

Two different Turkish perlites, one from İzmir (P1) and the other from Erzincan (P2) were used throughout the investigation. The properties of the perlites were determined on the ground samples. Before grinding, they

were dried at 110 °C, crushed and sieved through ASTM No. 4 sieve (4.75 mm).

The chemical compositions of the ground perlites determined by XRF are given in Table 3.1.

The specific gravity values of the perlites in relation to grinding time and fineness are given in Table A.2 in Appendix.

3.2.3 Fine Aggregates

Standard RILEM Cembureau sand was used for the preparation of mortars in the water requirement, strength activity index, compressive strength, sulfate attack and rapid chloride permeability tests.

The aggregate used in the tests for alkali-silica reactions was chert obtained from Kazan- Ankara. The aggregate had been proven to contain reactive silica and cause expansions in a previous study [77]. The color of the chert was light brown - brown. It was containing thin calcite bands. According to the results of semi-quantitative analysis based on its XRD trace, the mineral contents were as follows: 92.6% quartz and 7.4% calcite [77].

3.3 Determination of Pozzolanic Properties of Perlites

3.3.1 Conformance of the Perlites to ASTM C 618

ASTM C 618 (Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete) [1] was taken as a basis to investigate the pozzolanic properties of

the perlites. As it is stated in this specification, the tests were performed according to ASTM C 311 [78].

The Blaine fineness of P1 and P2 type perlites used for these tests was 370 ± 5 m²/kg. Clinker and gypsum were interground to produce a portland cement with 320 ± 5 m²/kg Blaine fineness.

3.3.2 Insoluble Residue and XRD Tests to Investigate the Pozzolanic Properties of Perlites

Insoluble Residue -- In a previous study by Tokyay [79], the pozzolanic reactions for fly ashes were studied by solving the portland cement, fly ash and blended cement pastes in hydrochloric acid (HCl). This method was based on the assumption of the insolubility of the pozzolanic materials and solubility of the hydrated portland cements in HCl. Moreover, the products of pozzolanic reactions resemble those of portland cement hydration and are also soluble in HCl. Therefore, this leads that once the amount of pozzolan incorporation is known, the insoluble portion of the PC-pozzolan paste can be used to prove the presence of pozzolanic reactions.

The idea given here can be expressed for perlite as:

$$S_t = S_{PC} + S_{perlite} + S_{pozz}$$

where,

S_t = Total solubility of PC+perlite paste, %

S_{PC} = Solubility of portland cement fraction, %

$S_{perlite}$ = Solubility of perlite fraction, %

S_{pozz} = Solubility due to the pozzolanic reactions, %

In this study, insoluble residue was determined instead of solving the materials in HCl. The procedure of the test is given below:

- a) For control mixes, 300 g of PC was mixed with 90 g of water to produce a cement paste with a w/b ratio of 0.30. In the blended cement pastes, by replacing 20% of the PC with perlite (P1 or P2), 240 g of PC and 60 g of perlite were mixed with 90 g of water. The fresh pastes were placed into cylindrical plastic molds with 1 cm height and 3 cm diameter. After moist curing at 22 °C for 1 day, the specimens were demolded, put in a wet towel and placed into a closed container. The specimens were cured in the container for 90 days.
- b) By following a similar procedure applied by Lam et.al. [80], at the end of each curing period, the specimens were broken into small pieces and stored in acetone for 7 days to stop hydration. Then, they were dried at 60 °C in an oven for 24 hours. The dried samples were ground in a mortar and sieved through 150 μm sieve. Afterwards, the ground materials were kept at 110 °C for 24 hours.
- c) After cooling of the ground pastes, the insoluble residue values of the following materials were determined:
 - ground PC paste (W_{PC}),
 - ground PC+P1 paste ($W_{\text{PC+P1}}$),
 - ground PC+P2 paste ($W_{\text{PC+P2}}$),
 - P1 with particles smaller than 150 μm (W_{P1}),
 - P2 with particles smaller than 150 μm (W_{P2}).

X-Ray Diffraction -- It is a well known fact that the pozzolanic materials should possess amorphous silica. In order to investigate the amorphousness of the perlites, their X-ray diffractograms were obtained.

3.4 Cement Production and Types of the Cements Produced

3.4.1 Grinding of the Materials

As a preliminary operation for producing cements, following processes were applied to the clinker, gypsum and the perlites before grinding:

The clinker and gypsum were crushed, and sieved through 3/8" sieve (9.5 mm). Gypsum needed to be dried at 40 °C prior to crushing. The perlites were dried at 110 °C, crushed and sieved through ASTM No. 4 sieve (4.75 mm). The purpose of sieving was to keep the uniformity between each grinding operation through using the same feed sizes.

A laboratory type grinding-mill which has a length of 450 mm and a diameter of 420 mm was used for the grinding of materials. The speed of the mill was 30 rev/min.

The charge of the grinding mill consisted of steel spherical balls and cylpebs. The total weight (98 kg) and the gradation of the charge, which is given in Table 3.2, were kept constant in all of the grinding operations.

The amount of material to be ground was kept constant at 7 kg in all of the grinding processes. Therefore, total weight in the mill was $98+7=105$ kg and the material/charge ratio was $7/98 = 0.71$.

Table 3.2 Grading of the Grinding Mill Charge

Charge type	Dimensions	Weight (kg)
Spherical balls	70 mm	14.1
	65 mm	3.0
	60 mm	10.0
	55 mm	9.7
	50 mm	12.0
	40 mm	13.4
	30 mm	21.8
Cylpebs	A combination of 30x30 mm, 20x20 mm and 10x10 mm particles	14.0
Total :		98.0

3.4.2 Types of the Cements Produced

The portland cements used in this study were produced by intergrinding the clinker and 4% gypsum to 320 m²/kg or 370 m²/kg Blaine fineness. The portland cements having 320 m²/kg or 370 m²/kg fineness were denoted with PC/320 or PC/370.

In this study, several types of blended cements were produced by:

- using two types of perlites (P1 and P2),
- intergrinding or separate grinding and mixing the materials,

- using different finenesses ($320 \text{ m}^2/\text{kg}$ and $370 \text{ m}^2/\text{kg}$), and
- changing the replacement amount of PC with perlite (5%, 20%, and 30%, by weight).

In the intergrinding method, all materials (clinker, gypsum and P1/P2) were ground together to obtain the aimed fineness values.

In the separate grinding method, first the clinker and gypsum were ground to the aimed fineness values, then, the perlites were ground to the aimed fineness values. Finally, 5%, 20% or 30% perlite was mixed with the ground “clinker+gypsum” mixture (that is, PC).

For all of the cement types in this study, gypsum/clinker ratio was kept constant at 4/96 (by weight).

The specific gravity values of the interground blended cements produced in relation to grinding time and fineness are given in Table A.2 in Appendix.

Table 3.3 shows the description of the abbreviations used in naming the cements listed in Tables 3.4 and 3.5.

Table 3.4 gives the cement types produced for normal consistency, setting time, soundness and compressive strength tests, and their descriptions. The cement types used in the sulfate attack, alkali-silica reactions and rapid chloride permeability tests, and their descriptions are given in Table 3.5.

Table 3.3 The Description of the Abbreviations Used in Cement Names

Type of Grinding:

I = Intergrinding

S = Separate grinding

Source of Perlite:

P1 = İzmir Perlite

P2 = Erzincan Perlite

First number following the source of perlite:

Percent of perlite by weight of cement

Number(s) following the slash sign:

- For interground cements: Blaine fineness of the cement in m^2/kg
 - For separately ground cements: If there is only one number following the slash sign, it shows the fineness of PC and the fineness of perlite in m^2/kg . If there are two numbers separated with a dash sign, the first number shows the fineness of PC and the second one shows the fineness of perlite in m^2/kg .
-

Table 3.4 Description of the Cements Used for the Normal Consistency, Setting Time, Soundness, and Compressive Strength Tests

Cement Type	Description
PC/320	Ordinary portland cement with Blaine fineness of 320 m ² /kg.
I P1-20/320	Blended cement produced by intergrinding the clinker, gypsum and 20% P1 to Blaine fineness of 320 m ² /kg.
I P2-20/320	Blended cement produced by intergrinding the clinker, gypsum and 20% P2 to Blaine fineness of 320 m ² /kg.
S P1-20/320	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 20%. Both P1 and PC have a Blaine fineness of 320 m ² /kg.
S P2-20/320	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 20%. Both P2 and PC have a Blaine fineness of 320 m ² /kg.
I P1-30/320	Blended cement produced by intergrinding the clinker, gypsum and 30% P1 to Blaine fineness of 320 m ² /kg.
I P2-30/320	Blended cement produced by intergrinding the clinker, gypsum and 30% P2 to Blaine fineness of 320 m ² /kg.
S P1-30/320	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 30%. Both P1 and PC have a Blaine fineness of 320 m ² /kg.

Table 3.4 (continued)

S P2-30/320	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 30%. Both P2 and PC have a Blaine fineness of 320 m ² /kg.
S P1-20/320-370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 20%. Blaine fineness values of PC and P1 are 320 and 370 m ² /kg, respectively.
S P2-20/320-370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 20%. Blaine fineness values of PC and P2 are 320 and 370 m ² /kg, respectively.
S P1-30/320-370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 30%. Blaine fineness values of PC and P1 are 320 and 370 m ² /kg, respectively.
S P2-30/320-370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 30%. Blaine fineness values of PC and P2 are 320 and 370 m ² /kg, respectively.
PC/370	Ordinary portland cement with Blaine fineness of 370 m ² /kg.
I P1-20/370	Blended cement produced by intergrinding the clinker, gypsum and 20% P1 to Blaine fineness of 370 m ² /kg.
I P2-20/370	Blended cement produced by intergrinding the clinker, gypsum and 20% P2 to Blaine fineness of 370 m ² /kg.

Table 3.4 (continued)

S P1-20/370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 20%. Both P1 and PC have a Blaine fineness of 370 m ² /kg.
S P2-20/370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 20%. Both P2 and PC have a Blaine fineness of 370 m ² /kg.
I P1-30/370	Blended cement produced by intergrinding the clinker, gypsum and 30% P1 to Blaine fineness of 370 m ² /kg.
I P2-30/370	Blended cement produced by intergrinding the clinker, gypsum and 30% P2 to Blaine fineness of 370 m ² /kg.
S P1-30/370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 30%. Both P1 and PC have a Blaine fineness of 370 m ² /kg.
S P2-30/370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 30%. Both P2 and PC have a Blaine fineness of 370 m ² /kg.

Table 3.5 Description of the Cements Used for the Sulfate Attack, Alkali-Silica Reactions and Rapid Chloride Permeability Tests

Cement Type	Description
PC/320	Ordinary portland cement with Blaine fineness of 320 m ² /kg.
S P1-5/320-370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 5%. Blaine fineness values of PC and P1 are 320 and 370 m ² /kg, respectively.
S P2-5/320-370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 5%. Blaine fineness values of PC and P2 are 320 and 370 m ² /kg, respectively.
S P1-20/320-370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 20%. Blaine fineness values of PC and P1 are 320 and 370 m ² /kg, respectively.
S P2-20/320-370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 20%. Blaine fineness values of PC and P2 are 320 and 370 m ² /kg, respectively.
S P1-30/320-370	Blended cement produced by separately grinding and mixing P1 and PC. Perlite amount is 30%. Blaine fineness values of PC and P1 are 320 and 370 m ² /kg, respectively.
S P2-30/320-370	Blended cement produced by separately grinding and mixing P2 and PC. Perlite amount is 30%. Blaine fineness values of PC and P2 are 320 and 370 m ² /kg, respectively.

3.5 Determination of Grindability Properties

As explained in Section 2.2.1, there are various methods to determine the grindability properties of the materials. In this study, grindability was measured by obtaining the fineness values of the materials for various grinding times while keeping the grinding medium unchanged. For this purpose, during the grinding procedure, the mill was stopped at every 30 minutes and samples of approximately 100 g were taken. These samples were used to determine the specific gravity and fineness values of the materials. Fineness was determined by measuring the Blaine fineness (ASTM C 204 [75]) and amount of material retained on 45 μm sieve (ASTM C 430 [76]). At the end, “grinding time - Blaine fineness” and “grinding time - % retained on 45 μm sieve” curves were obtained for PC, perlites and blended cements.

The particle size distributions of perlites and cements with Blaine fineness of 320 m^2/kg and 370 m^2/kg were also determined by using Malvern Mastersizer laser particle size analyzer for better understanding of the grinding performance.

3.6 Tests on Cement Pastes and Mortars

Normal consistency, setting time and soundness (autoclave expansion) tests were performed on the pastes containing the cement types given in Table 3.4 according to ASTM C 187, C 191 and C 151 [81-83], respectively.

Compressive strength and flow values of the mortars containing the cements in Table 3.4 were determined according to ASTM C 109 [84]. In these tests, 500 g of cement and 1375 g of Standard RILEM sand were used. PC mortars were prepared with 242 ml of water whereas the water content of the blended cement mortars were adjusted to give a flow of 110 ± 5 . The compressive

strength of the mortars was determined at 2, 3, 7, 28, 56 and 91 days. Three 5 cm x 5 cm x 5 cm cube specimens were tested for each day.

Rapid chloride permeability tests (RCPT) were performed on the mortars containing the cement types given in Table 3.5. ASTM C 1202 [32] was followed for the tests although this standard test method is, in fact, for concrete specimens. For each cement type, mortars (containing 500 g cement, 1375 g standard RILEM sand and 242 ml water) were prepared several times to produce three 10 cm x 20 cm cylindrical specimens for testing one specimen at each testing age (28 days, 3 months and 6 months). At each age, three slices with 10 cm diameter and 5 cm height were cut from a specimen by using a saw. After the slices were placed in a vacuum desiccator, the vacuum pump was run in dry condition for 3 hours and in wet condition for 1 hour. The set-up of the vacuum operation is shown in Figure 3.1. Following the soaking under water for 18 hours, each slice was placed between two testing cells and sealed (Figure 3.2) with silicon. One of the cells was filled with 3.0% NaCl solution while the other was filled with 0.3N NaOH solution. After making the electrical connections, the test was started (Figure 3.3). The current was recorded by the testing machine at every 30 minutes. The test was terminated after 6 hours.

The resistance of the perlite mortars to alkali-silica reactions were investigated by using the cements given in Table 3.5 according to ASTM C 1260 [56]. In these tests, the first step was the preparation of the aggregates (chert) to satisfy the grading requirements given in the standard. Then, mortars with w/b of 0.47 were prepared with 440 g of cement and 990 g of chert. 3 mortar bars (25 mm x 25 mm x 285 mm) were cast for each cement type. The bars were first moist cured at 22 °C for 24 hours, and then, they were immersed in a hard-plastic container with sufficient tap water. The container was kept in a water bath at 80 °C for 24 hours. At the end of this period, the initial lengths of the bars were measured by using a comparator with 0.0025 mm precision. Afterwards, the

specimens were placed in a container with 1N NaOH at 80 °C. The container was again placed in the water bath at 80°C and stored there for 22 days. Length measurements were taken at 3, 7, 10, 14, 17 and 22 days.



Figure 3.1 Set-up of the Vacuum Operation



Figure 3.2 A Sealed Slice



Figure 3.3 RCPT Test Set-up

In order to investigate the sulfate resistance of the mortars containing perlite, the cements given in Table 3.5 were used. The tests were performed in accordance with ASTM C 1012 [72]. In this text, only a brief summary of the procedure applied will be presented: For each cement type, mortar mixes were prepared to produce 15 cubes (5 cm x 5 cm x 5cm) and 6 bars (25 mm x 25 mm x 285 mm). 2 cubes were tested under compression at several ages to check whether the strength reached 20 MPa or not. During this period, the bars and the remaining cubes were stored in lime-saturated water at 23 °C. When the compressive strength of the cubes reached 20 MPa, the lengths of the mortar bars were measured, and then, they were immersed in sulfate solution ($\text{pH} = 7 \pm 1$) containing 352 moles of Na_2SO_4 per m^3 (50g/L). The length changes of the mortar bars were determined at 1, 2, 3, 4, 8, 13, 17, 26 and 39 weeks after the bars were placed in the sulfate solution. The measurements were taken by using a comparator with 0.0025 mm precision. The solutions were refreshed at each testing age. The pH value of the fresh solutions was always 7 ± 1 .

CHAPTER 4

TEST RESULTS AND DISCUSSIONS

4.1 Determination of Pozzolanic Properties of the Perlites

4.1.1 Conformance of the Perlites to ASTM C 618

Since perlites contain high amount of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and have an amorphous structure, the aim of this study was to find out whether they possess sufficient pozzolanic property in order to find out whether they could be used in making portland-pozzolan type of cements. Therefore, at the beginning of the experimental study, the conformance of the perlites to ASTM C 618 [1] was checked. Table 4.1 gives the results of the tests performed for this purpose as well as the requirements prescribed in this standard specification.

As can be seen from Table 4.1, both P1 and P2 satisfy the physical and chemical requirements stated in ASTM C 618. Moreover, it has to be noted that P2 is slightly more reactive than P1 since the strength activity index of P2 is higher than that of P1.

Generally, increase in the water requirement can be an important problem associated with the natural pozzolans. However, according to Table 4.1, the perlites do not have such a drawback since they cause no or little increase in the water requirement.

Table 4.1 Conformance of the Perlites to ASTM C 618.

	P1	P2	ASTM C 618
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , %	87.52	86.01	min. 70.0
SO ₃ , %	0.04	0.06	max. 4.0
Loss on ignition, %	4.22	4.13	max. 10.0
Fineness:			
amount retained when			
wet-sieved on 45 µm sieve, %	31	31	max. 34
Strength activity index			
7-d (% of control)	80.3	85.1	min. 75
28-d (% of control)	81.9	85.9	min. 75
Water requirement			
(% of control)	103	100	max. 115
Soundness			
autoclave expansion or contraction, %	0.05	0.07	max. 0.8

4.1.2 Results of the Insoluble Residue Tests and XRD Patterns to Determine the Pozzolanic Properties of the Perlites

Insoluble Residue -- The solubility of a PC+pozzolan paste is composed of the solubility of PC (and its hydration products), solubility of the pozzolan itself and the solubility of the products of the pozzolanic reactions. Considering this information, following expression can be established:

$$S_t = S_{PC} + S_{perlite} + S_{pozz}$$

where,

S_t = Total solubility of PC+perlite paste, %

S_{PC} = Solubility of portland cement fraction, %

$S_{perlite}$ = Solubility of perlite fraction, %

S_{pozz} = Solubility due to the pozzolanic reactions, %

The expression above can be rewritten as:

$$S_{pozz} = S_t - (S_{PC} + S_{perlite})$$

The presence of pozzolanic reactions can be proved when the following statement is shown to be true:

$$S_{pozz} > 0, \text{ or}$$

$$S_t - (S_{PC} + S_{perlite}) > 0$$

While the values of S_{pozz} greater than zero show pozzolanic reactions, when $S_{pozz} = 0$, perlite can be regarded as an inert material.

In these expressions, solubility of the materials can be calculated as follows:

$$S_t = (100 - W_{PC+P1}) \text{ or } (100 - W_{PC+P2})$$

$$S_{PC} = a(100 - W_{PC})$$

$$S_{perlite} = b(100 - W_{P1}) \text{ or } b(100 - W_{P2})$$

where,

W_{PC+P1} = Insoluble residue of ground PC+P1 paste

W_{PC+P2} = Insoluble residue of ground PC+P2 paste

W_{PC} = Insoluble residue of ground PC paste

W_{P1} = Insoluble residue of P1

W_{P2} = Insoluble residue of P2

a = Weight fraction of PC = 0.80

b = Weight fraction of P1 or P2 = 0.20

Table 4.2 shows the test results.

Table 4.2. Insoluble Residue of the Materials

	Insoluble Residue (%)
W_{P1}	93.18
W_{P2}	92.59
W_{PC}	0.60
W_{PC+P1}	17.36
W_{PC+P2}	16.88

By using the equations above, solubility due to the pozzolanic reactions of P1 and P2 can be calculated as:

$$\text{For P1: } S_{\text{pozz}} = (100 - 17.36) - [0.8(100 - 0.60) + 0.2(100 - 93.18)] = 1.76$$

$$\text{For P2: } S_{\text{pozz}} = (100 - 16.88) - [0.8(100 - 0.60) + 0.2(100 - 92.59)] = 2.12$$

As shown, S_{pozz} values for both P1 and P2 are greater than zero. Therefore, it can be concluded that perlite shows pozzolanic reactions.

The results also show that the S_{pozz} value of P2 is greater than that of P1, which reveals that P2 is more reactive than P1.

X-Ray Diffraction (XRD) Patterns of the Perlites -- The pozzolanic materials should possess amorphous silica. The amorphousness of the perlites was investigated by XRD. The XRD patterns of P1 and P2 are shown in Figures 4.1 and 4.2, respectively.

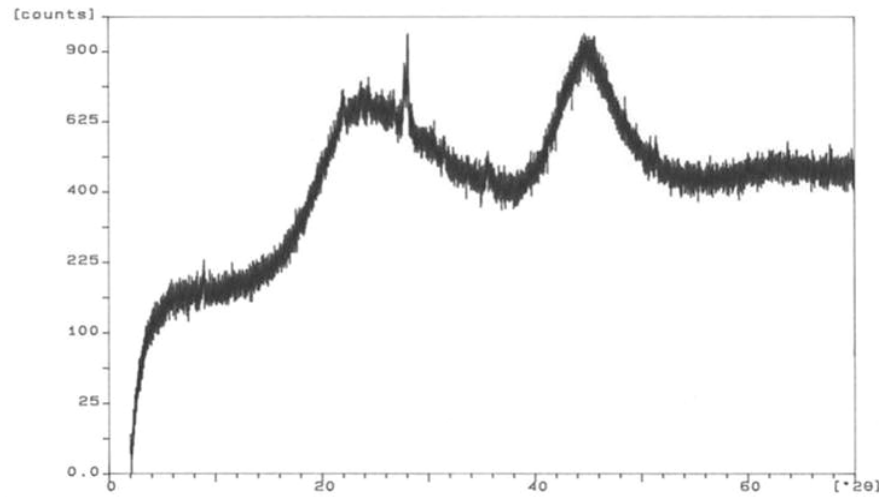


Figure 4.1 X-Ray Diffractogram of P1

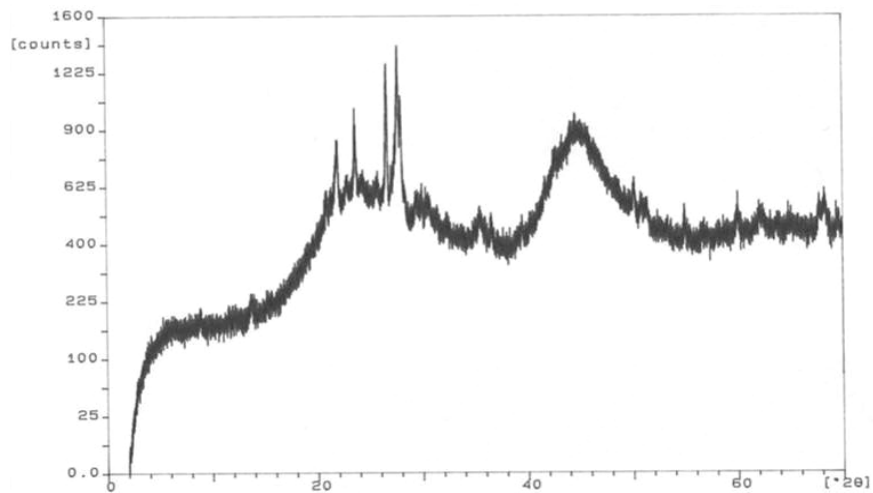


Figure 4.2 X-Ray Diffractogram of P2

High background trends in the XRD patterns of P1 and P2 show the amorphousness of the perlites. (This amorphous or poorly crystalline structure prevented the identification of the minerals existing in the perlites by XRD. Therefore, the peaks in the Figures could not be assigned to any mineral.)

4.2 Grindability

In making portland-pozzolan type of cements, the pozzolanic material is either interground with portland cement clinker and a small amount of gypsum or it is separately ground and combined with the already ground portland cement clinker and small amount of gypsum. In both cases, the grindability of the pozzolanic material is considered to be an important parameter.

The grindability properties of the materials can be determined by several methods as explained in Section 2.2.1. In this investigation, grindability was measured by obtaining “grinding time-fineness” relations.

Fineness of cements and pozzolans are generally evaluated by Blaine surface area, amount retained on a sieve (such as 45 μm sieve) or by determining the particle size distribution with laser diffraction. All these methods have some advantages and disadvantages in showing the fineness of the materials:

Blaine air-permeability method (ASTM C 204 [75]) may cause misleading values especially for porous materials [85]. Moreover, in this method, only the continuous paths through the bed of cement contribute to the measured surface area [12].

On the other hand, determination of the amount retained on a sieve may be insufficient to evaluate the fineness since this method provides only a single

value and supplies no information on the size of grains smaller than the opening of that sieve [12].

A more informative method is the determination of particle size distribution by laser diffraction [31]. However, this technique is based on volumetric measurements and it is difficult to compare the data with the results of conventional sieve analysis [13].

Since all of the above three methods had their advantages and disadvantages for determining the fineness of cements and pozzolans, all of these methods were decided to be used in this investigation.

4.2.1 Grindability of the PC and the Perlites

The change of Blaine fineness of PC, P1 and P2 in relation to grinding time is shown in Figure 4.3 (The data plotted in Figure 4.3 are also given in Table A.1 in Appendix). As seen from this Figure, for the same grinding time, PC resulted in the lowest fineness value, and P2 was finer than both P1 and PC. In other words, the required time (or energy) to achieve a given fineness was greatest for PC and least for P2. Further examination of Figure 4.3 also reveals that PC required more time to increase the fineness of the product when compared to P1 and P2. For example, the time necessary to increase the fineness from 320 to 370 m²/kg was 30 min for PC, and it was 10 and 15 min for P1 and P2, respectively. This fact can also be observed from the milder slope of the curve for PC. In the same way, the shapes of the curves in Figure 4.3 show that as the grinding time increased, the curve for PC approached a horizontal line indicating that it became harder and harder to make the PC finer. In other words, the efficiency of grinding operation decreased with time. However, such a behaviour was not observed for the perlites until a grinding

time of 180 min. Therefore, the above discussions yield that the grindability of P2 was better than P1, and PC was less grindable than both perlites.

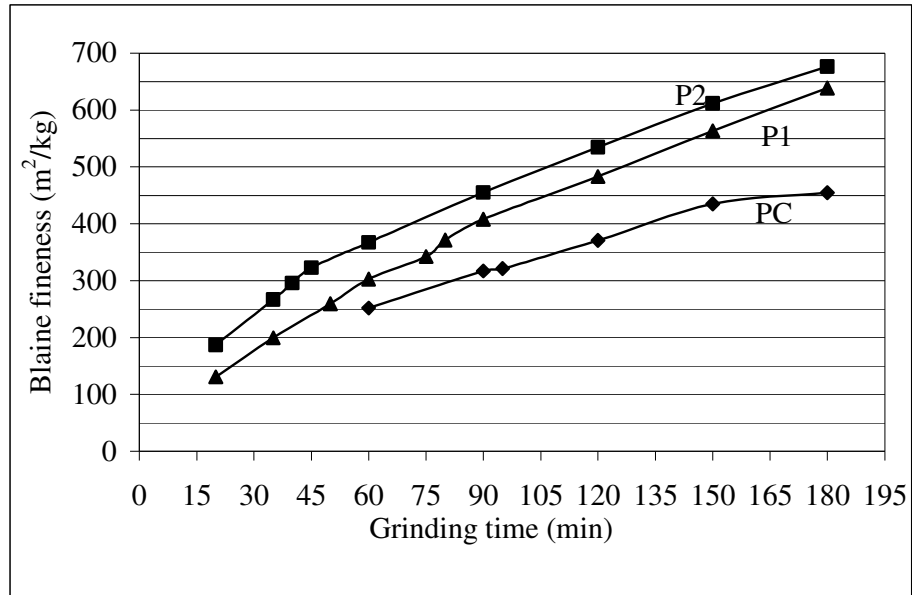


Figure 4.3 “Grinding Time - Blaine Fineness” Relationships for P1, P2 and PC

The “grinding time-amount of material retained on 45µm sieve” relationships for PC, P1 and P2 are shown in Figure 4.4 and given in Appendix A.1. These curves revealed that P2 was softer than both P1 and PC. While the grindabilities of P1 and PC were similar at early stages, grinding P1 became easier than grinding PC in time.

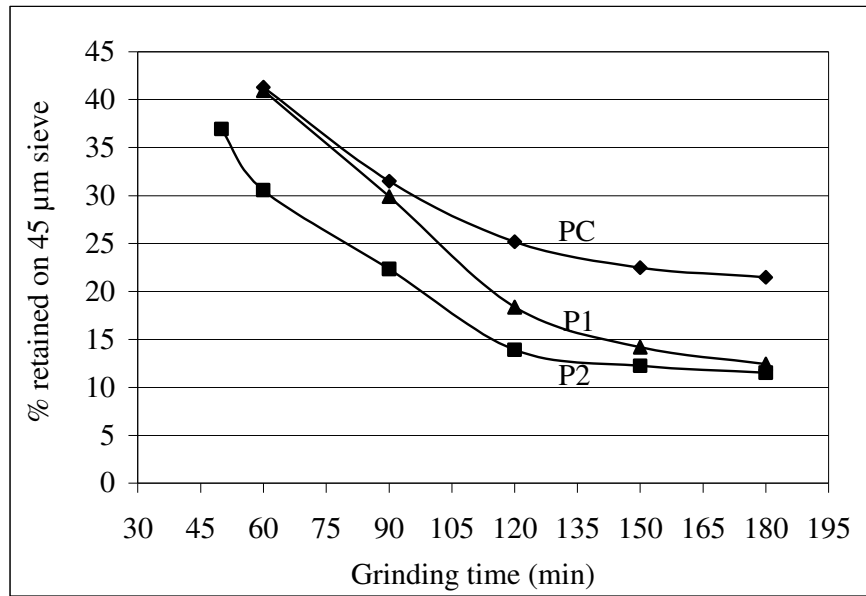


Figure 4.4 “Grinding Time - Amount of Material Retained on 45μm Sieve”
Relationships for P1, P2 and PC

Particle size distribution of the materials was obtained by laser particle size analyzer. A summary of the results for fineness values of 320 and 370 m^2/kg are given in Table 4.3. (The complete particle size distribution of them is given in Tables A.3 and A.4 in Appendix). As observed from this Table, although the materials had the same Blaine fineness, their particle size distributions were significantly different from each other. P2 was finer than P1, and both perlites were coarser than PC for a given Blaine fineness. However, the difference in particle size distribution becomes less for smaller sizes.

Table 4.3 Particle Size Distribution of PC, P1 and P2

	>93 μm	>59 μm	>44 μm	>30 μm	>15 μm	>5 μm
PC/320*	4.0	15.8	26.7	39.8	58.8	84.4
P1/320	13.9	30.1	40.6	52.0	68.5	87.9
P2/320	12.4	28.7	39.4	51.2	68.1	87.0
PC/370*	3.2	12.2	20.6	32.1	51.8	80.5
P1/370	9.8	23.9	34.4	46.1	63.9	86.0
P2/370	5.8	16.1	25.2	36.8	56.3	82.7

* The numbers 320 and 370 show the Blaine fineness of the materials in m^2/kg .

4.2.2 Grindability of the Blended Cements

The “grinding time-Blaine fineness” relationships for the PC and the interground blended cements are shown in Figure 4.5 and tabulated in Tables A.1 and A.2 in Appendix. This Figure shows that interground cements containing P1 yielded a similar curve to that of PC. However, for the same grinding duration, blended cements containing P2 were finer than PC and blended cements with P1. This shows that replacement with P2 increased the efficiency of the grinding operation and promoted the grindability as it enabled to reach higher fineness values in shorter grinding periods resulting in lower energy requirement. This result was consistent with the results of a research by Opoczky in which the grindabilities of several composite cements were better than that of the clinker [19].

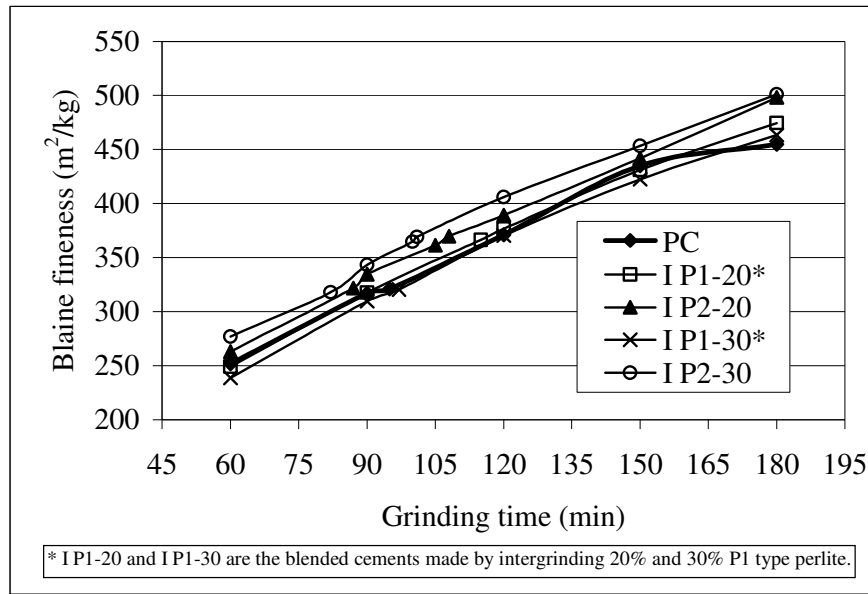


Figure 4.5 “Grinding Time-Blaine Fineness” Relationships for the PC and Interground Blended Cements

Similar to the discussions put forth for Figure 4.5, “grinding time- amount of material retained on 45 μm sieve” relationships, which is given in Figure 4.6 (and in Tables A.1 and A.2 in Appendix), reveals that the interground blended cements containing P2 (especially for 30% replacement) was generally finer than the PC and the blended cements with P1. Moreover, the curve for PC remained above the other curves for all of the grinding times, that is, PC was found to be always coarser than the blended cements.

A summary of the particle size distribution of the blended cements with Blaine fineness values of 320 and 370 m^2/kg is given in Table 4.4. (The complete particle size distribution of the cements is given in Tables A.3 and A.4 in Appendix). The values for separately ground blended cements were calculated by the weighted sum of the size fractions of the PCs and perlites given in Table

4.3. To illustrate, for S P1-20/3200, the amount of material having particles greater than 93 μm was calculated as: $4.0 \times 80\% + 13.9 \times 20\% = 6.0$, where 4.0 and 13.9 were the values belonging to PC/3200 and P1/3200 for 93 μm (see Table 4.3), and 80% and 20% were the percentages of PC and P1.

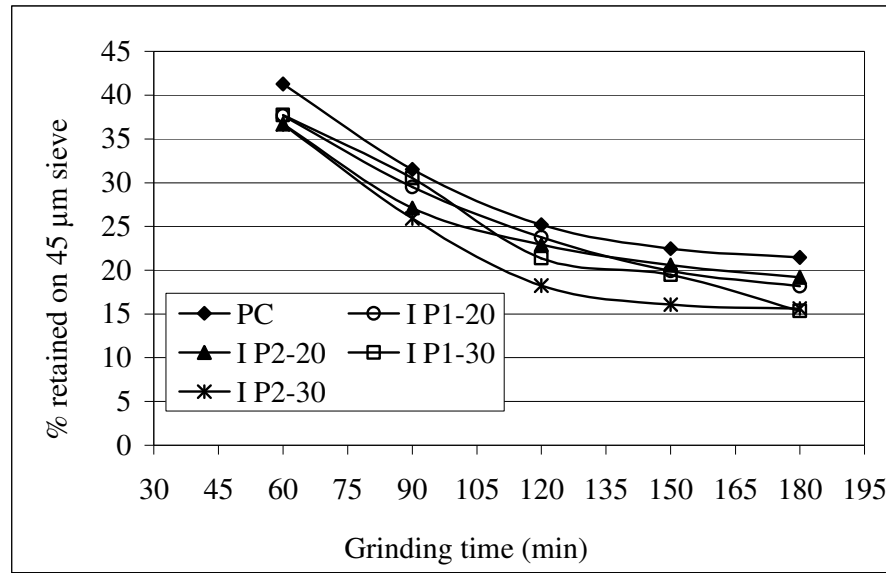


Figure 4.6 “Grinding Time - Amount of Material Retained on 45 μm Sieve”
Relationships for PC and the Interground Blended Cements

In order to compare the particle size distribution of the interground cements and separately ground cements, in Table 4.5, the values for separately ground cements taken from Table 4.4 were expressed as percentages of those for interground cements having the same fineness and composition. For example, the number 92 calculated for S P1-20/3200 and for 93 μm was obtained from $(6.0/6.5) \times 100$, where 6.0 and 6.5 were the values belonging to I P1-20/320 and S P1-20/320 for 93 μm (see Table 4.4).

Table 4.4 Particle Size Distribution of the Blended Cements

	>93 μm	>59 μm	>44 μm	>30 μm	>15 μm
I P1-20/320	6.5	18.0	27.2	39.2	58.7
S P1-20/320	6.0	18.7	29.5	42.3	60.7
I P2-20/320	4.3	15.0	25.0	37.8	57.3
S P2-20/320	5.7	18.4	29.2	42.1	60.7
I P1-30/320	5.7	17.5	27.4	39.8	58.8
S P1-30/320	7.0	20.1	30.9	43.5	61.7
I P2-30/320	5.1	16.4	26.2	38.3	57.5
S P2-30/320	6.5	19.7	30.5	43.3	61.6
I P1-20/370	2.7	11.8	21.0	33.5	53.4
S P1-20/370	4.5	14.5	23.3	34.9	54.2
I P2-20/370	2.6	10.9	20.2	32.7	52.4
S P2-20/370	3.7	12.9	21.5	33.1	52.7
I P1-30/370	3.2	12.6	21.4	33.3	52.7
S P1-30/370	5.2	15.7	24.7	36.3	55.4
I P2-30/370	2.2	11.9	21.7	35.0	55.9
S P2-30/370	4.0	13.3	22.0	33.5	53.2

Table 4.5 Relative Particle Size Distribution of the Separately Ground
Cements with respect to Interground Cements

	>93 μm	>59 μm	>44 μm	>30 μm	>15 μm
I P1-20/320	100	100	100	100	100
S P1-20/320	92	104	108	108	103
I P2-20/320	100	100	100	100	100
S P2-20/320	134	123	117	111	106
I P1-30/320	100	100	100	100	100
S P1-30/320	122	115	113	109	105
I P2-30/320	100	100	100	100	100
S P2-30/320	128	120	117	113	107
I P1-20/370	100	100	100	100	100
S P1-20/370	165	123	111	104	101
I P2-20/370	100	100	100	100	100
S P2-20/370	144	118	107	101	101
I P1-30/370	100	100	100	100	100
S P1-30/370	159	125	115	109	105
I P2-30/370	100	100	100	100	100
S P2-30/370	180	112	101	96	95

As seen from Table 4.5, the values for separate grinding were generally higher than 100%. This indicates that separate grinding yielded coarser particles when compared to intergrinding. The difference in the particle size distribution of the separately ground and interground cements proves the interactions between the ingredients, that is clinker and perlite, during intergrinding. In this study, these interactions affected the final product positively since interground blended cements had finer particles while their Blaine fineness values were the same.

The interactions originate from the differences in the grindabilities of the constituents. Previous studies have shown that the harder component (clinker, in case of clinker-natural pozzolan mixes; or slag, in case of slag-clinker mixes) act as a grinding medium to the softer one [19,23,24]. In the light of this information, the finer particle size distribution of the interground cements can be explained as follows: as shown in Table 4.3, for a given Blaine fineness, the perlites had a coarser particle size distribution when compared to the clinker. When ground clinker (e.i, PC) and ground perlite were mixed, the perlite remained coarser than PC. On the other hand, during intergrinding the perlite was ground not only by the steel charges but also by the clinker. These interactions eliminated the relatively coarser perlite particles and yielded a finer particle size distribution for interground cements.

Table 4.5 also shows that although the difference between intergrinding and separate grinding was high for larger sizes, it decreased as the particle size got smaller. Such a trend was an indication of the higher interactions for larger particles [21].

As seen from Table 4.4, for a given fineness and perlite amount, interground cements containing P1 was slightly coarser than those containing P2. Further investigation of the table shows that 20% and 30% replacement resulted in almost the same particle size distribution for the interground cements with the same fineness and perlite type.

4.3 Normal Consistency, Soundness and Setting Time

The results of the normal consistency, setting time and soundness tests that were conducted according to ASTM C 187 [81], C 191 [82] and C 151 [83] are shown in Table 4.6 and Figures 4.7 and 4.8. The data presented in these Figures are also presented in tabular form in Table A.5 in Appendix.

Table 4.6 Water/binder (w/b) Ratios for Normal Consistency and the Results of the Soundness Tests

Cement	w/c	Exp. (%)	Cement	w/c	Exp. (%)
PC/320	0.234	0.07	PC/370	0.235	0.06
I P1-20/320	0.240	0.05	I P1-20/370	0.248	0.04
S P1-20/320	0.242	0.05	S P1-20/370	0.248	0.04
I P2-20/320	0.242	0.06	I P2-20/370	0.248	0.06
S P2-20/320	0.243	0.07	S P2-20/370	0.248	0.06
I P1-30/320	0.243	0.02	I P1-30/370	0.252	0.02
S P1-30/320	0.242	0.02	S P1-30/370	0.254	0.02
I P2-30/320	0.248	0.05	I P2-30/370	0.254	0.04
S P2-30/320	0.247	0.06	S P2-30/370	0.254	0.04
S P1-20/320-370	0.240	0.05	S P2-20/320-370	0.244	0.06
S P1-30/320-370	0.245	0.02	S P2-30/320-370	0.250	0.05

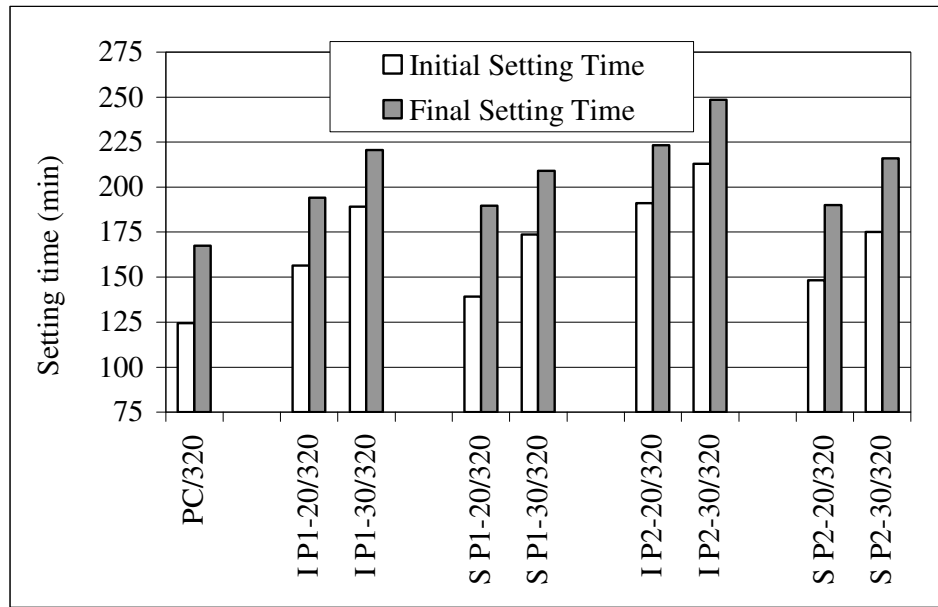


Figure 4.7 Setting Time of the Cements Having 320 m²/kg fineness

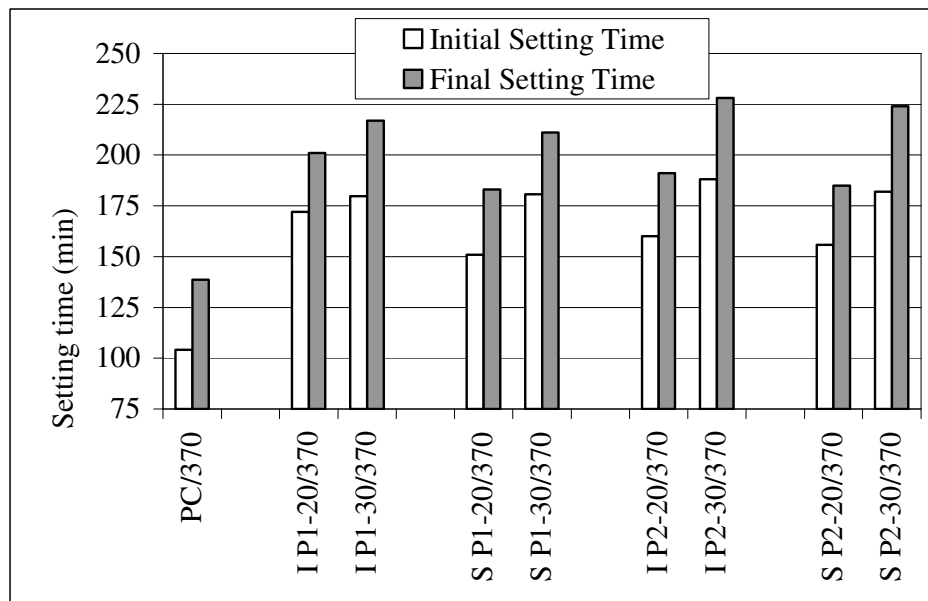


Figure 4.8 Setting Time of the Cements Having 370 m²/kg fineness

As seen from Table 4.6, the water requirements of all of the blended cements were higher when compared with PC. Moreover, as expected, the cements containing 30% perlite required more water than those containing 20% perlite. The water requirements of the cements with 370 m²/kg fineness were higher than those of the cements with 320 m²/kg fineness since more water is necessary for wetting higher surface areas. The amount of water necessary for the cement pastes to have normal consistency did not change significantly with the perlite type and method of grinding.

Blended cements must conform either to ASTM specification C 595 [86] or the performance-based specification ASTM C 1157 [31,87]. While the latter is a purely performance-based specification with no compositional limits, the former provides for some limits. According to C 595, the cements produced in this study are classified as “type IP (portland-pozzolan)” since the pozzolan constituent is between 15 and 40% (by mass) of the blended cement. When C 1157 is considered, the cements produced can be classified as “type GU (general use)”.

The standard specifications C 595 and C 1157 allow an autoclave expansion value of maximum 0.80%. Table 4.6 shows that the results for the blended cements were below this limit. It can be stated that incorporation of PC with perlite reduced the expansions. In addition, the increase in the perlite content decreased the expansion values.

The standard specifications C 595 and C 1157 limit the initial setting time to minimum 45 min and final setting time to maximum 420 min. As seen from Figures 4.7 and 4.8, all cement types satisfied these requirements. Due to the lower clinker content, the setting time values of the blended cements containing 20% perlite were longer than those of PC, and 30% replacement with perlite increased the values further. For a given fineness and composition, the interground cements had longer setting times when compared to separately

ground cements. This may be explained by the relatively coarser clinker particles in the interground cements [23].

4.4 Water Requirement and Compressive Strength

Mortars for compressive strength tests were prepared in accordance with ASTM C 109 [84].

Portland cement mortars were prepared with a water/binder ratio (w/b) of 0.48 as stated in the standard. The flow values found for PC/320 and PC/370 were 97 and 100, respectively.

Mortars with blended cements were produced to have a flow value of 110 ± 5 as stated in the standard. Of course, depending on the blended cement type used, different w/b values were obtained for a flow of 110 ± 5 .

Portland cement and blended cement mortars were subjected to compressive strength tests at 2, 3, 7, 28, 56 and 91 days. Table 4.7 shows the w/b and compressive strength values at these ages. Standard deviations are given in Table A.6 in Appendix.

Perlite type (whether P1 or P2) and the method of grinding (whether using intergrinding or separate grinding) did not affect the amount of water required for a given constant flow which was 110 ± 5 in this case. For example, as can be seen from Table 4.7, w/b ratios of I P1-20/320, S P1-20/320, I P2-20/320 and S P2-20/320 are 0.50. On the other hand, for the cements having the same Blaine fineness, 30% replacement increased the water requirement slightly with respect to 20% replacement. This increase was thought to be due to the absorbed water by the perlites, and it was not due to differences in the particle size distribution since the particles of the cements with 20% or 30% perlite had almost the same grading as discussed in Section 4.2.2.

Table 4.7 Water/binder Ratios and Compressive Strengths of PC and Blended Cements

	w/b	Compressive Strength (MPa)					
		2-d	3-d	7-d	28-d	56-d	91-d
PC/320	0.48	22.5	24.4	35.5	49.6	51.5	53.6
I P1-20/320	0.50	17.5	20.8	29.1	39.6	46.8	51.3
S P1-20/320	0.50	17.5	21.7	26.1	41.8	47.2	50.2
I P2-20/320	0.50	17.7	21.5	29.5	42.8	46.0	51.7
S P2-20/320	0.50	17.9	21.8	26.6	38.1	47.6	50.4
I P1-30/320	0.51	15.1	15.9	26.9	40.3	44.3	46.3
S P1-30/320	0.51	13.7	16.6	27.6	34.7	40.1	42.6
I P2-30/320	0.51	14.1	18.7	27.9	35.5	44.3	46.5
S P2-30/320	0.51	12.6	17.5	27.0	35.3	42.4	45.3
S P1-20/320-370	0.51	16.9	21.8	29.3	42.7	48.4	52.0
S P2-20/320-370	0.51	19.4	21.2	28.3	40.4	49.2	51.7
S P1-30/320-370	0.51	15.7	17.1	27.7	39.8	44.2	47.4
S P2-30/320-370	0.51	14.2	17.9	27.2	37.6	42.8	46.6
PC/370	0.48	25.4	28.5	38.5	50.8	52.8	54.2
I P1-20/370	0.50	22.0	22.8	30.4	44.9	47.8	53.4
S P1-20/370	0.50	17.8	22.3	30.0	43.3	48.1	53.4
I P2-20/370	0.50	18.9	24.4	32.1	47.7	50.3	56.7
S P2-20/370	0.50	20.7	22.7	31.7	43.7	50.4	53.1
I P1-30/370	0.52	16.9	19.9	30.6	41.0	45.3	48.6
S P1-30/370	0.52	16.7	19.1	28.6	40.0	46.0	48.2
I P2-30/370	0.52	19.1	18.9	30.6	41.9	47.0	50.7
S P2-30/370	0.52	18.6	19.5	28.3	39.8	44.6	49.8

ASTM C 595 [86] states that compressive strengths of type IP cements at 3, 7 and 28 days should be minimum 13, 20 and 25 MPa, respectively. As seen from Table 4.7, the strength requirements stated in C 595 were satisfied by all of the blended cements. According to C 1157 [87], the strengths of type GU (General Use) cement should be between 10 and 20 MPa at 3 days, and between 17 and 30 MPa at 7 days. The strength values of the blended cements were even higher than the limits stated in the standard.

Figures 4.9 – 4.12 show the strength development of the blended cements with respect to the portland cements. In these Figures, the strengths of the blended cements were expressed as percentages of the portland cement having the same fineness.

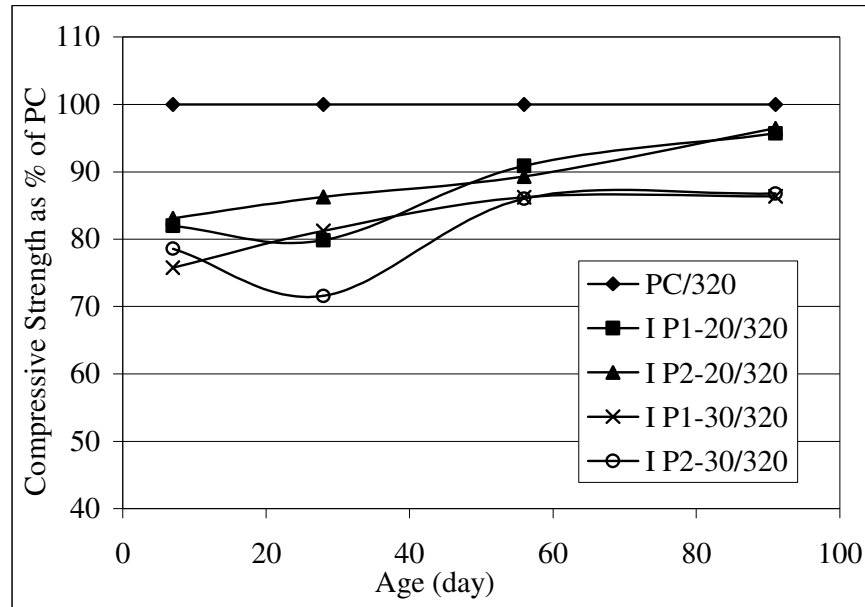


Figure 4.9 Compressive Strength of the Interground Blended Cements as % of PC (Fineness = 320 m²/kg)

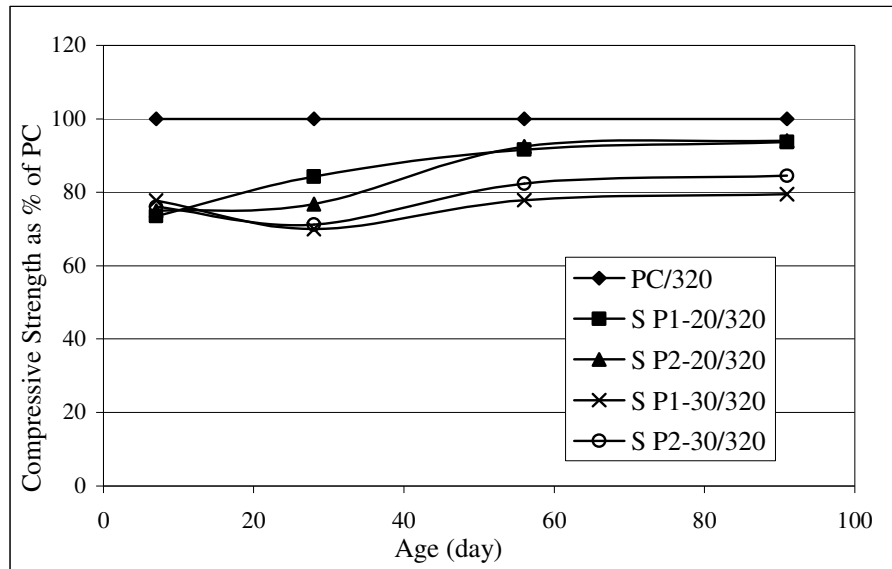


Figure 4.10 Compressive Strength of the Separately Ground Blended Cements as % of PC (Fineness = 320 m²/kg)

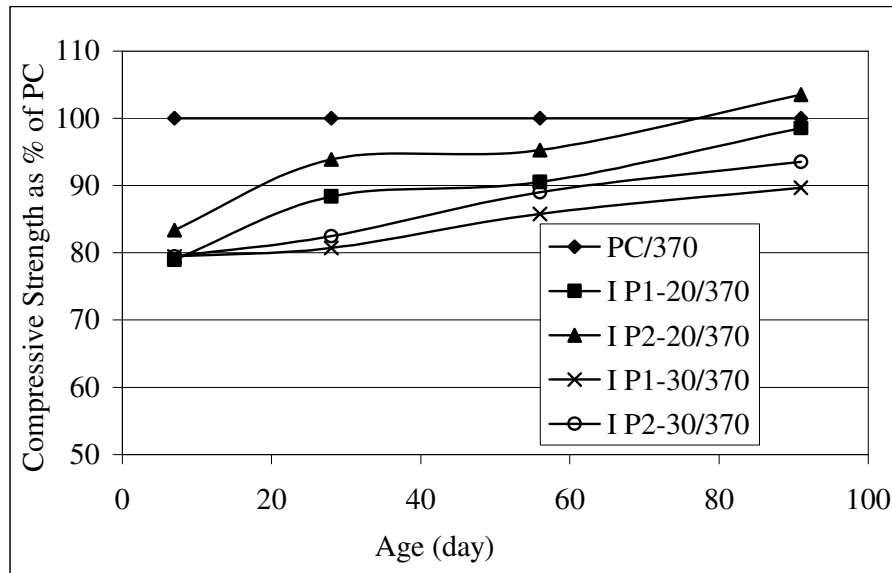


Figure 4.11 Compressive Strength of the Interground Blended Cements as % of PC (Fineness = 370 m²/kg)

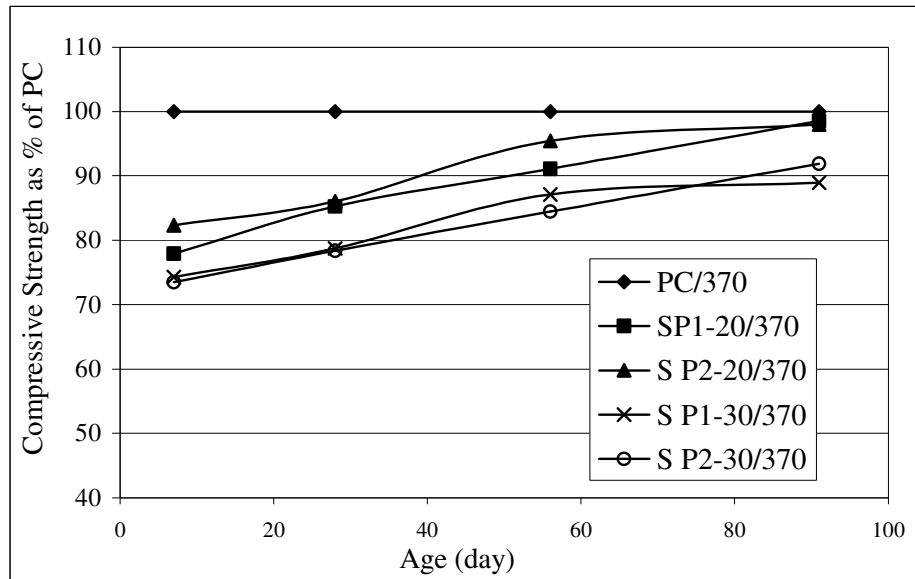


Figure 4.12 Compressive Strength of the Separately Ground Blended Cements as % of PC (Fineness = 370 m²/kg)

It can be seen from the Figures 4.9 – 4.12 that the strengths of blended cements were lower than those of PC. However, the differences became smaller in time due to the pozzolanic reactions of the perlite in the blended cements.

Table 4.7 shows that for a given Blaine fineness and composition, the strengths of the mortars made with interground cements were generally higher than those made with separately ground cements. The higher strengths of the interground cements were due to their finer particle size distribution when compared to separately ground cements (Table 4.5). Another possible reason may be due to the more homogeneous products provided by intergrinding [21,25].

The effect of finer particle size distribution was also observed on the strengths of the mortars produced with the same method of grinding and having the same

amount of perlite and Blaine fineness but containing different perlite types: mortars with P2 produced higher strengths than those with P1. (For example, the strengths of I P2-20/320 were higher than those of I P1-20/320). Moreover, this was an expected conclusion since the strength activity indices of P2 were higher than those of P1 (Table 4.1).

When the strengths of the mortars containing the cements with the same fineness, same perlite and the same grinding method are compared, it is seen from Table 4.7 that 20% replacement produced higher strengths than 30% replacement. The lower strengths of the mortars with the cements containing 30% perlite can be explained by their lower clinker contents (especially for the earlier ages during which pozzolanic reactions were insignificant) and slightly higher w/b.

Table 4.8 shows the effect of the perlite fineness in the separately ground blended cements. In this Table, the strengths of the cements containing perlite with 370 m²/kg Blaine fineness were expressed as percentages of those containing 320 m²/kg Blaine fineness.

As seen from Table 4.8, the relative strength values of the cements containing finer perlites were greater than 100%. This shows that increase in the perlite fineness resulted in higher strengths. Since the pozzolanic reactions are expected not to take place in the very early days, the increase in the early ages could be just due to the filler effect. For the later ages, finer perlites experienced higher amount of pozzolanic reactions as expected.

Table 4.8 Relative Strengths of the Separately Ground Cements
Containing Perlites with Different Finenesses

	Relative Compressive Strengths (%)					
	2-d	3-d	7-d	28-d	56-d	91-d
S P1-20/320	100	100	100	100	100	100
S P1-20/320-370	97	100	112	102	103	104
S P2-20/320	100	100	100	100	100	100
S P2-20/320-370	108	97	106	106	103	103
S P1-30/320	100	100	100	100	100	100
S P1-30/320-370	115	103	100	115	110	111
S P2-30/320	100	100	100	100	100	100
S P2-30/320-370	113	102	101	107	101	103

4.5 Rapid Chloride Permeability

Rapid chloride permeability test (RCPT) results for the specimens containing the cements in Table 3.5 which were cured for 28 days, 3 months and 6 months are shown in Table 4.9. The standard deviations of these results are given in Table A.7 in Appendix.

Table 4.9 Rapid Chloride Permeability Test Results

	Total Charge Passed in 6 hours (coulombs)		
	28 days	3 months	6 months
PC/320	9937	7384	6450
S P1-5/320-370	8254	6633	5098
S P1-20/320-370	6284	3293	1382
S P1-30/320-370	5937	1642	864
S P2-5/320-370	8671	6508	5297
S P2-20/320-370	6493	2881	1392
S P2-30/320-370	6311	1724	936

Table 4.9 shows that the highest values (or highest chloride permeabilities) were recorded for Portland Cement (PC/320). In other words, the use of perlite reduced the chloride permeability.

The benefits of using mineral admixtures in reducing the chloride permeability were noted by several researchers [33,37,39]. Houssam and Toutanji [37] found that the addition of silica fume resulted in a significant decrease in permeability. Byung et al. [33] studied the effects of silica fume, fly ash and blast-furnace slag addition on chloride permeability. It was found that the concretes containing silica fume showed the best performance, and fly ash greatly decreased the permeability even though it did not improve the strength at 28 days. Blast-furnace slag was also found to reduce the chloride

permeability since the secondary chemical reaction of blast-furnace slag contributed to make the microstructure denser.

As it can be seen from Table 4.9, the total charge passed in 6 hours decrease in time. In other words, chloride permeability of the specimens gets lower for the later ages, as expected. The decreased chloride permeability of PC/320 specimens with time can be explained by the higher degree of hydration of portland cement while the improved permeability of the specimens containing perlite was not only due to the PC hydration but also due to the higher amount of pozzolanic reactions of perlite.

Table 4.10 Improvement in Rapid Chloride Permeability Relative to 28 days

	Total Charge Passed as % of the 28-day values		
	28 days	6 months	Improvement (Difference)
PC/320	100	65	35
S P1-5/320-370	100	62	38
S P1-20/320-370	100	22	78
S P1-30/320-370	100	15	85
S P2-5/320-370	100	61	39
S P2-20/320-370	100	21	79
S P2-30/320-370	100	15	85

The lower permeability obtained at later ages can also be observed from Table 4.10. (In this Table, the total charge values of each cement type at 6 months were expressed as percentages of the total charge values of that cement type at 28 days.) However, Table 4.10 was prepared to show that the improvements in the specimens containing perlite were higher than those in PC/320 specimens. Such a result indicates that pozzolanic reactions can decrease the permeability in a greater extent than hydration of PC can. As seen from Table 4.10, the higher benefit provided by the perlite incorporation was more significant as the perlite amount in the specimens increased.

In order to visualize the test results, the values given in Table 4.9 were shown in Figures 4.13-4.15. (In these Figures only the perlite type and perlite amount was given since all of the blended cements were produced by separate grinding method and by blending the materials having same fineness. For example, “P1-5” denotes “S P1-5/320-370”.)

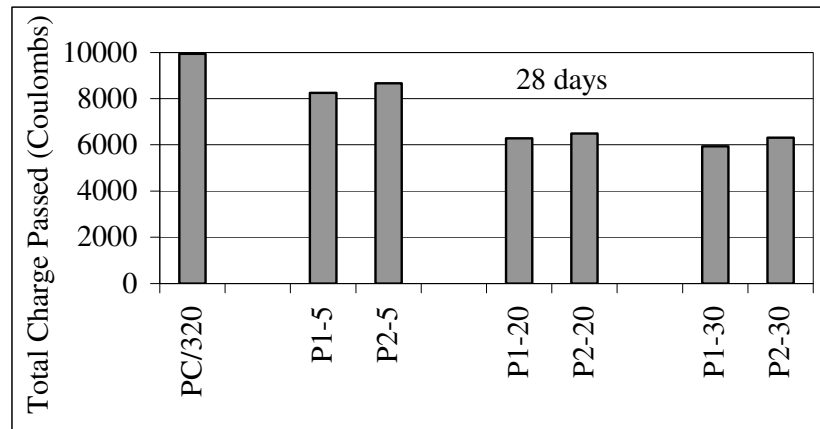


Figure 4.13 Total Charge Passed in 6 Hours for the Specimens with an Age of 28 Days

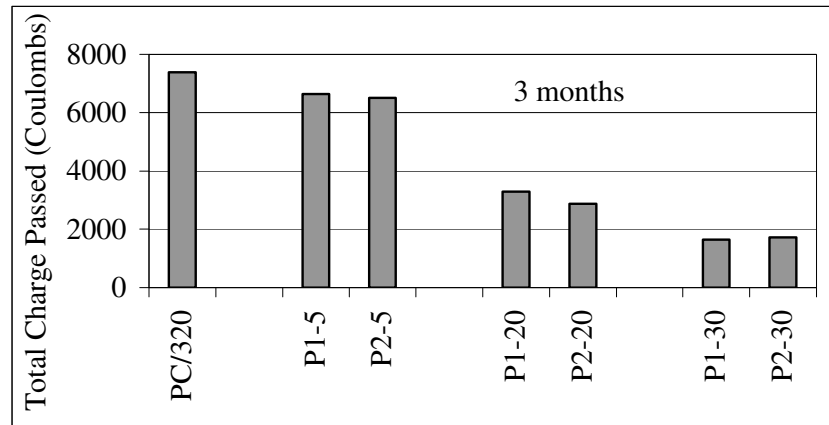


Figure 4.14 Total Charge Passed in 6 Hours for the Specimens with an Age of 3 Months

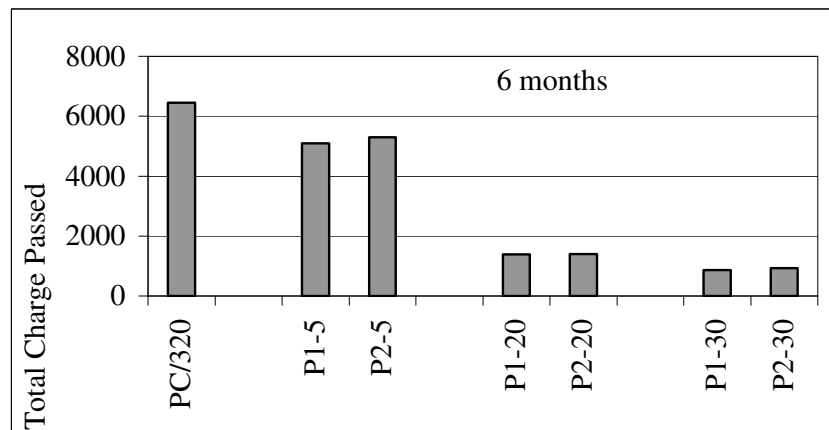


Figure 4.15 Total Charge Passed in 6 Hours for the Specimens with an Age of 6 Months

In the discussions above, it was stated that the increase in the perlite amount increases the difference between the permeability at 28 days and 6 months. Figures 4.13 - 4.15 show that as the perlite amount increases permeability decreases at a given age, too.

It can also be observed from Figures 4.13 - 4.15 that for the same replacement levels, while the values for P1 are slightly lower than those for P2, they are generally close to each other. In other words, P1 and P2 display similar behaviors in improving the permeability.

4.6 Alkali-Silica Reactions

As already mentioned in Section 2.4.1, alkali-silica reaction in concrete starts with the attack on the siliceous minerals in the aggregate by the alkalis in the cement. As a result of the reactions, an alkali-silica gel which has unlimited swelling capacity is formed and such a gel leads to the expansion and cracking of the hardened concrete. Of course, the main source of alkalis in concrete comes from the cement type used. In case that mineral admixtures are used in making concrete or they take place in the blended cements, these minerals may also have an important effect on the amount of alkalis of the concrete. Almost all of the alkalis present in the minerals are released over a long time period. However, only a fraction remains effectively available for ASR, since most of the alkalis have already participated in cement hydration and pozzolanic reactions [88].

Duchesne and Berube [88] investigated the amount of alkalis released by various supplementary cementing materials (fly ash, silica fume and ground granulated blast furnace slag) available for ASR. They found that more alkalis were incorporated into hydrates than released in. Moreover, these materials reduced the alkali concentration in the pore solution when compared to a control, even for those containing much more alkalis than the cement.

Hobbs [89] suggested that 17% of the total Na_2O_e (alkali equivalent = $\text{Na}_2\text{O} + 0.66\text{K}_2\text{O}$) content in the tested fly ash was available for ASR. According to Duchesne and Berube [88], fly ashes with a total alkali content exceeding 5%

Na_2O_e are ineffective, and should not be considered for use with potentially reactive aggregate.

At the beginning of this study, the tests performed to determine the effectiveness of the perlite addition to reduce the expansions induced by ASR was found to be very important since the Na_2O_e contents of the perlites (3.68% and 3.18% for P1 and P2, respectively) caused suspicions on the issue.

The effectiveness of the perlite in preventing the expansions due to alkali-silica reactions were tested by using the mortar bar specimens containing the cements listed in Table 3.5. In these cements, the replacement amounts of perlites were 5%, 20% and 30%. The tests were performed according to ASTM C 1260 [56]. The mortars used in these tests were prepared with 440 g of cement and 990 g of chert satisfying the grading requirements given in the standard. Water/binder ratio of the mortars was 0.47. For each cement type, 3 mortar bar specimens (25 mm x 25 mm x 285 mm) were cast.

ASTM C 1260 test method lasts in 14 days and requires taking 3 length measurements in this period. In this study, mortar bar expansions were determined at 3, 7, 10, 14, 17 and 22 days. The results are given in Table 4.11. Standard deviations are given in Table A.8 in Appendix.

In order to observe the change of expansions with respect to time and compare the blended cements better, the data given in Table 4.11 were also plotted in Figures 4.16 and 4.17. (Similar to the Figures 4.13 - 4.15, only the perlite type and replacement level was shown in the Figures 4.16 and 4.17 instead of giving the complete notation used for naming the blended cements.)

Table 4.11 Mortar Bar Expansions due to Alkali-Silica Reactions

	Expansion (%)					
	3-d	7-d	10-d	14-d*	17-d	22-d
PC/320	0.017	0.039	0.059	0.067	0.069	0.077
S P1-5/320-370	0.032	0.051	0.059	0.073	0.076	0.083
S P1-20/320-370	0.024	0.031	0.034	0.038	0.039	0.048
S P1-30/320-370	0.013	0.019	0.020	0.025	0.025	0.027
S P2-5/320-370	0.025	0.045	0.059	0.072	0.072	0.079
S P2-20/320-370	0.015	0.030	0.033	0.039	0.041	0.047
S P2-30/320-370	0.013	0.020	0.020	0.027	0.028	0.029

* The duration of the test method given in ASTM C 1260 is 14 days.

As can be seen from Figures 4.16 and 4.17, the expansions in the mortar bars containing 20% or 30% perlite were considerably lower when compared to the expansions induced by PC. At the end of 14 days, for example, the reductions for 20% and 30% replacement with P1 were 43% and 63%, respectively. When 20% and 30% replacement levels are considered, it is clear from these Figures that 30% replacement displayed better results at all ages.

These results show that the suspicions on the harmful effect of perlites on ASR expansions were not true. In fact, the Na_2O_e contents of both perlites were lower than the 5% limit suggested by Duchesne [88].

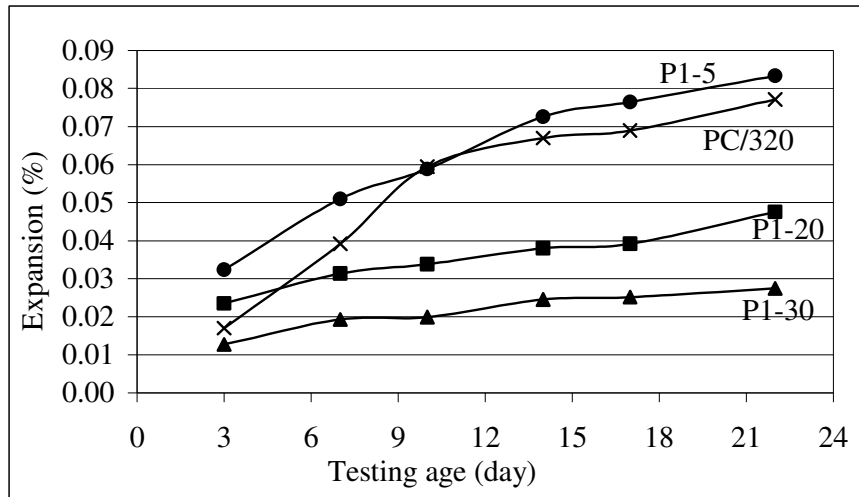


Figure 4.16 Expansions of Mortar Bars Containing PC and Blended Cements with P1 due to ASR

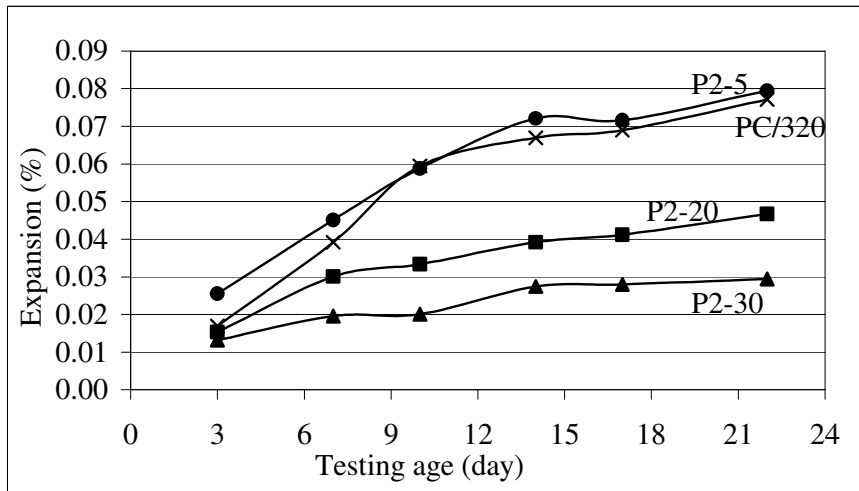


Figure 4.17 Expansions of Mortar Bars Containing PC and Blended Cements with P2 due to ASR

Figures 4.16 and 4.17 show that although replacement levels above 20% reduced the expansions, after 10 days, the mortar bars with 5% P1 or P2 did

not reduce the expansions observed in PC mortar bars; in fact, 5% replacement caused a detrimental effect. According to the pertinent literature, there have been reported cases in which low replacement amounts with mineral admixtures resulted in higher expansions [54]. It was suggested [89] that at a low replacement level, the alkalis contributed by fly ash is greater than those contributed by the Portland cement. In another study, it was found that the lower the pozzolan content, the higher the percentage of available alkalis originating from the pozzolans [88].

According to the discussions above, it is possible to state that the benefit provided by the perlite replacement increased as the amount of perlite in the mix increased provided that the replacement amount is not low. (Figure 4.18 shows the relation between the replacement amount and expansions of the blended cements at 14 days.)

The situation at low replacement level was further investigated by statistical methods. Statistical analysis was performed on the expansion values of PC/320 and the blended cements with 5% P1 or P2 (S P1 5/320-370 or S P2-5/320-370). The similarity of the expansions was checked by using t-statistics for 14, 17 and 22 days [90]. In this analysis, it was assumed that the expansions have approximately normal distributions and have equal variances. The null hypotheses (H_0) and the alternate hypotheses (H_A) are as follows:

For PC/320 and S P1-5/320-370:

$H_0: \mu_{PC} = \mu_{P1}$ (The mean expansion value of PC is equal to that of S P1-5/320-370)

$H_A: \mu_{PC} \neq \mu_{P1}$ (The mean expansion value of PC is not equal to that of S P1-5/320-370)

For PC/320 and S P2-5/320-370:

$H_0: \mu_{PC} = \mu_{P2}$ (The mean expansion value of PC is equal to that of S P2-5/320-370)

$H_A: \mu_{PC} \neq \mu_{P2}$ (The mean expansion value of PC is not equal to that of S P2-5/320-370)

The results of the two-tailed t-test are shown in Tables 4.12 and 4.13 at $\alpha = 0.05$ level of significance.

Table 4.12 Two-tailed t-test for PC/320 and S P1-5/320-370

Hypotheses	Age (days)	t_0	$t_{\alpha/2, n_{PC}+n_{P1}-2}$
$H_0: \mu_{PC} = \mu_{P1}$	14	1.179	2.776
	17	2.006	2.776
$H_A: \mu_{PC} \neq \mu_{P1}$	22	3.210	2.776

Table 4.13 Two-tailed t-test for PC/320 and S P2-5/320-370

Hypotheses	Age (days)	t_0	$t_{\alpha/2, n_{PC}+n_{P2}-2}$
$H_0: \mu_{PC} = \mu_{P1}$	14	0.697	3.182
	17	0.367	3.182
$H_A: \mu_{PC} \neq \mu_{P1}$	22	0.408	3.182

As seen from Table 4.12, the calculated t-statistic values (t_0) are less than the critical values ($t_{\alpha/2, n_{PC}+n_{P1}-2}$) at 14 and 17 days. However, the reverse is true

at 22 days. This shows that the expansions of PC and S P1-5/320-370 were statistically similar at 14 and 17 days while there is sufficient evidence to indicate that the mean expansion values of these cements differ at 22 days. In other words, the tests results at 22 days are statistically significant at the 5% level of significance. (The null hypothesis is rejected at 22 days.)

Table 4.13 shows that the calculated t_0 values are less than the critical values for all ages. Or, it can be stated that the null hypothesis cannot be rejected. Therefore, the expansions of portland cement (PC/320) and the blended cement with 5% P2 (S P2-5/320-370) are statistically similar.

When the two types of perlites are compared for the same replacement amounts, it is seen from Table 4.11 that the effects of P1 and P2 on the expansions caused by ASR were similar to each other. The expansions of the mortar bars with P1 and P2 at 14 days were also illustrated in Figure 4.18. The similar behavior of the perlites was not a very surprising result since both perlites had similar chemical compositions (Table 3.1).

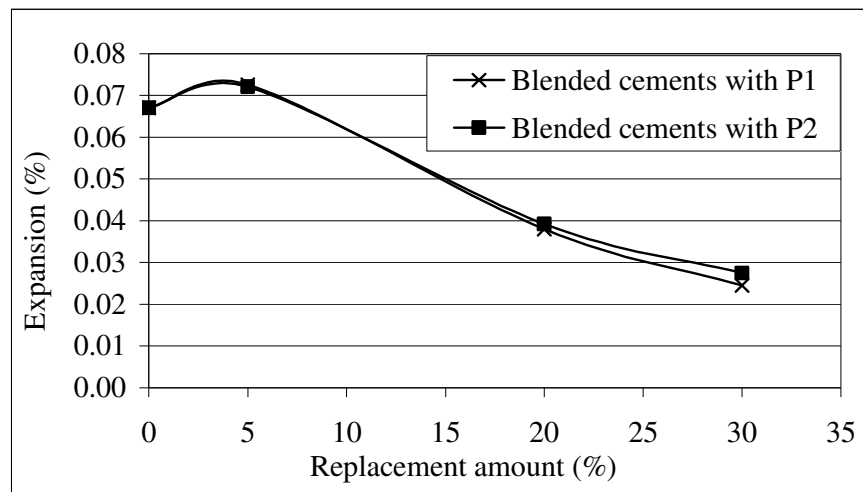


Figure 4.18 Change of expansions at 14 days with replacement amount

4.7 Sulfate Attack

The cements used for the tests to determine the resistance of perlite mortars to sulfate attack were the cements given in Table 3.5. The results of the tests performed up to 39 weeks (or 9 months) are given in Table 4.14 and also in Figures 4.19 and 4.20. (Only the perlite type and replacement level was shown in these Figures instead of giving the complete notation used for naming the blended cements.). The standard deviations of the results are given in Table A.9 in Appendix.

The standard specification ASTM C 1157 [87] does not suggest any value for the sulfate resistance of type GU cements. In ASTM C 595 [86], there is an optional requirement for sulfate resistance of the type IP cements, and according to this requirement, the expansion at 180 days (or 26 weeks) should be less than 0.10%. As seen from Table 4.14, all of the cements satisfied this statement.

As shown in the Figures 4.19 and 4.20, the expansions of different mixes in the first four weeks are very small and very close to each other. Therefore, it is more appropriate to discuss the effects of perlite type and amount starting from 8 weeks.

Figures 4.19 and 4.20 show that PC mortar displayed higher expansions than the perlite mortars. Moreover, the expansions in the mortars with 5% replacement were higher when compared to those with 20% and 30% replacements. There was not so much difference in the expansions of the mortars with 20% and 30% perlite.

Table 4.14 Mortar Bar Expansions due to Sulfate Attack

	Expansions (%)								
	Weeks								
	1	2	3	4	8	13	17	26	39
PC/320	0.003	0.009	0.014	0.020	0.021	0.037	0.047	0.073	0.113
S P1-5/320-370	0.004	0.006	0.014	0.015	0.016	0.027	0.042	0.061	0.111
S P2-5/320-370	0.000	0.004	0.005	0.017	0.014	0.028	0.034	0.059	0.109
S P1-20/320-370	0.002	0.008	0.008	0.010	0.015	0.024	0.027	0.040	0.046
S P2-20/320-370	0.001	0.000	0.004	0.008	0.013	0.019	0.032	0.035	0.047
S P1-30/320-370	-0.001	0.000	0.002	0.009	0.011	0.014	0.028	0.039	0.052
SP2-30/320-370	-0.002	0.005	0.005	0.009	0.011	0.022	0.024	0.038	0.054

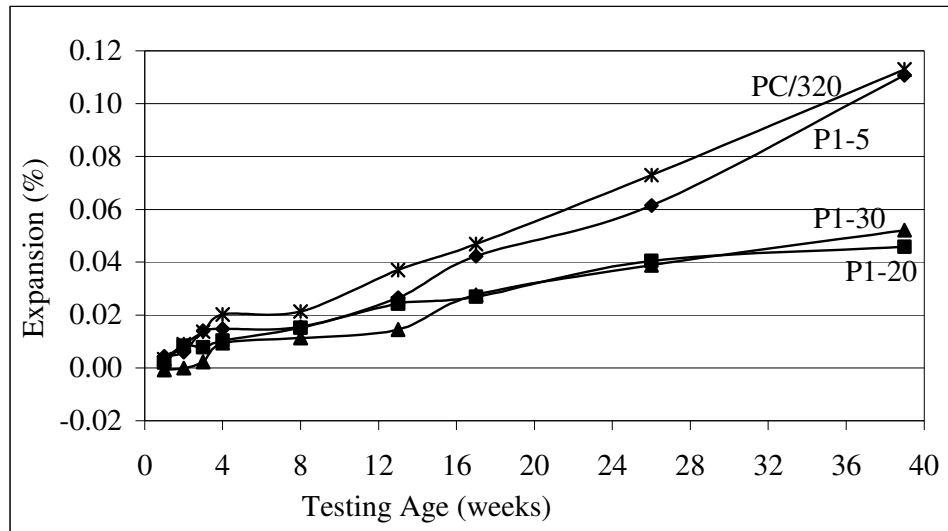


Figure 4.19 Expansions of Mortar Bars Containing PC and Blended Cements with P1 due to Sulfate Attack

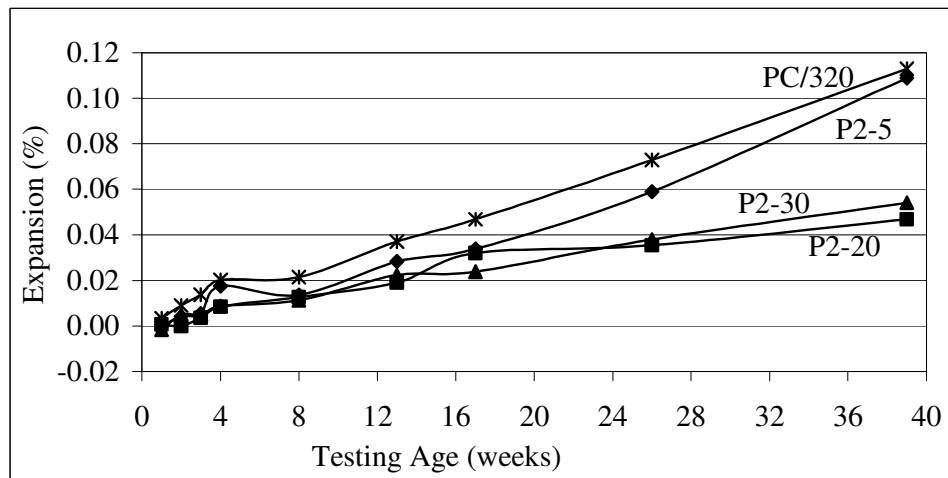


Figure 4.20 Expansions of Mortar Bars Containing PC and Blended Cements with P2 due to Sulfate Attack

The sulfate resistance of portland pozzolan cements containing 10, 20 or 30% Santorin Earth was investigated by Mehta [55]. Similar to the results of this study, the cements with 20 or 30% pozzolan showed the least permeability and the best sulfate resistance. It was concluded that the enhanced strength and durability of portland pozzolan cements were due to the process of pore refinement associated with pozzolanic reactions.

There are also other studies in which the use of mineral admixtures was found to improve the sulfate resistance [65-70]. According to the results of Cao et. al. [54], fly ash, silica fume and blast furnace slag improved the performance. A good overall sulfate resistance was achieved by 40% fly ash blend and 5% silica fume blend. For slag blended cement, this was obtained when the replacement percentage was higher than 60%. Monterio and Kurtis [68] found that samples containing 25% and 45% fly ash showed significantly less expansion when compared to the mixtures containing no pozzolans.

The benefit of perlite incorporation instead of using only portland cement can be explained as follows: When a portion of PC is replaced with a mineral admixture (perlite, in this case), the total C_3A content in the mix will be reduced and the reduction will be higher for higher replacement amounts. As known, the expansions due to ettringite formation will be lower with the mixes having a lower C_3A content. Moreover, due to the replacement of portland cement, calcium hydroxide (CH) production resulting from the hydration of Portland Cement will be reduced. CH amount is further reduced by the pozzolanic reactions. Lower amounts of CH result in an improvement in sulfate resistance since CH takes place in the reactions of ettringite formation.

If the RCPT results are accepted to be an indication of the permeability, Table 4.10 can also be used to explain the results of the sulfate attack tests. As discussed in Section 4.15, the chloride permeability of the PC mixes was higher than that of the blended cement mixes and it was decreased as the perlite

amount increased. Therefore, the lower permeability provided by the use of perlite prevented the ingress of sulfate ions into the mortar bars and reduced the deleterious effects of sulfate exposure.

According to the explanations stated above, 30% replacement should have resulted in lower expansions than 20% replacement, but this was not the case. Why these two replacement amounts displayed similar expansion values could not be explained in this text and require further investigation.

CHAPTER 5

CONCLUSIONS

Since perlite has an amorphous structure and high content of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, the first objective of this study was to investigate whether it possesses sufficient pozzolanic property in a finely divided form. In case that it would exhibit the required degree of pozzolanicity it could provide a great potential to the cement production industry because two-thirds of the world's perlite reserves are located in Turkey.

The following conclusions were derived from this investigation:

1. The tests conducted on the Turkish perlites obtained from two different sources showed that these perlites possess sufficient pozzolanic characteristics to be used in cement and concrete industry. They satisfy the requirements given in ASTM C 618.
2. After finding out that perlites possess sufficient pozzolanic characteristics, the second objective of this study was to produce blended cements with perlite and investigate the properties of these cements. For this purpose, using separate grinding and intergrinding methods, blended cements were produced by

replacing 5%, 20% and 30% perlite at Blaine finenesses of 320 and 370 m²/kg.

Tests on these cements showed that all blended cements with perlite satisfy the requirements stated in ASTM C 595 and C 1157 for setting time, autoclave expansion, compressive strength and sulfate resistance.

The blended cements produced by intergrinding the perlite and clinker resulted in finer particle size distribution and slightly higher compressive strength values when compared to those produced by separately grinding.

3. Perlites are more easily grindable than the portland cement clinker. This means that the energy requirement and cost of grinding for manufacturing blended cements with perlite might be lower than that of portland cement.
4. The increase in the perlite amount increases the durability of the mortars (chloride impermeability, resistance to expansions due to alkali-silica reactions and sulfate attack) but decreases the compressive strength values slightly.

CHAPTER 6

RECOMMENDATIONS

Following items can be recommended for further research:

- In this study, after the pozzolanic properties of the perlites were confirmed, tests were performed for investigation of the use of perlites to produce blended cements. Therefore, the tests were made on blended cements and mortars prepared with them. Since cements are generally consumed in concrete making, the performance of the perlites in fresh and hardened concrete should also be investigated by further studies.
- The cost of manufacturing blended cements with perlite was out of the scope of this study. In further studies, it is suggested to make cost-benefit analyses, considering the perlite sources and locations of the cement factories.
- In the tests conducted to investigate the resistance of the mortars to alkali-silica reactions, it was found that the expansions of the mortars made by blended cements with 5% perlite might be higher when compared to those made by using portland cement only. Although the detrimental effect at low replacement levels was noted by other researchers, further investigation is necessary to explain the causes of this effect.

- In determining the grindability of the materials, the measurements were made on a time basis. Although the duration of the mill operation indicates the energy consumed, further studies should investigate the energy consumption directly.

APPENDIX A

Table A.1 Grinding Time, Specific Gravity, and Fineness Relationships for
PC, P1 and P2

	Grinding time (min.)	Specific gravity	Amount of material retained on 45 μ m sieve (%)	Blaine fineness (m ² /kg)
PC	60	3.11	41.30	252
	90	3.12	31.50	317
	95	3.12	30.45	321
	120	3.13	25.17	371
	150	3.13	22.48	435
	180	3.13	21.48	455
P1	60	2.35	40.96	303
	70	2.35	35.87	320
	80	2.35	30.77	372
	90	2.35	29.88	408
	120	2.35	18.37	483
	150	2.35	14.20	564
	180	2.35	12.45	638
P2	45	2.36	34.65	323
	60	2.36	30.54	367
	90	2.37	22.33	455
	120	2.37	13.92	534
	150	2.38	12.24	612
	180	2.38	11.53	676

Table A.2 Grinding Time, Specific Gravity, and Fineness Relationships for the Intergrind Cements

	Grinding time (min.)	Specific gravity	Amount of material retained on 45 μ m sieve (%)	Blaine fineness (m ² /kg)
I P1-20	60	2.92	37.67	249
	90	2.92	29.53	318
	115	2.92	23.83	366
	120	2.92	23.77	377
	150	2.94	19.91	431
	180	2.96	18.15	475
I P2-20	60	2.93	36.70	263
	87	2.94	28.07	322
	90	2.94	27.11	335
	108	2.94	24.58	370
	120	2.94	22.90	389
	150	2.94	20.56	442
	180	2.94	19.20	498
I P1-30	60	2.83	37.75	239
	90	2.84	30.53	310
	97	2.84	28.39	320
	120	2.84	21.35	370
	150	2.84	19.46	422
	180	2.84	15.35	463
I P2-30	60	2.85	36.68	277
	82	2.86	28.79	318
	90	2.86	25.92	343
	101	2.86	25.89	369
	120	2.86	18.24	406
	150	2.86	16.08	453
	180	2.86	15.61	501

Table A.3 Particle Size Distributions for P1, P2, PC and Intergrround
Cements with Blaine Fineness Value of 320 m²/kg

Size (µm)	Materials						
	P1/320	P2/320	PC/320	IP1-20/320	IP1-30/320	IP2-20/320	IP2-30/320
0.533	0.08	0.11	0.15	0.10	0.09	0.10	0.08
0.574	0.18	0.23	0.32	0.21	0.18	0.21	0.17
0.618	0.32	0.40	0.56	0.37	0.33	0.37	0.30
0.666	0.50	0.63	0.87	0.58	0.53	0.58	0.47
0.718	0.72	0.88	1.22	0.82	0.75	0.82	0.68
0.774	0.96	1.13	1.58	1.08	1.00	1.09	0.90
0.834	1.2	1.38	1.92	1.35	1.26	1.36	1.15
0.899	1.46	1.62	2.26	1.63	1.54	1.64	1.41
0.969	1.73	1.86	2.58	1.92	1.83	1.94	1.70
1.04	2.01	2.10	2.91	2.22	2.14	2.25	2.00
1.13	2.29	2.33	3.22	2.53	2.47	2.58	2.33
1.21	2.59	2.56	3.53	2.85	2.82	2.92	2.68
1.31	2.89	2.79	3.83	3.19	3.18	3.27	3.05
1.41	3.19	3.02	4.14	3.55	3.57	3.65	3.44
1.52	3.50	3.27	4.45	3.93	3.97	4.04	3.86
1.64	3.83	3.53	4.78	4.34	4.41	4.46	4.32
1.76	4.16	3.82	5.13	4.77	4.87	4.91	4.80
1.90	4.50	4.13	5.50	5.25	5.37	5.39	5.32
2.05	4.87	4.48	5.92	5.77	5.90	5.92	5.88
2.21	5.25	4.88	6.38	6.33	6.47	6.48	6.49
2.38	5.66	5.32	6.89	6.95	7.09	7.10	7.14
2.56	6.10	5.82	7.45	7.63	7.77	7.77	7.83
2.76	6.58	6.39	8.08	8.37	8.49	8.50	8.58
2.98	7.10	7.01	8.77	9.18	9.28	9.29	9.39
3.21	7.66	7.69	9.52	10.15	10.13	10.14	10.25
3.46	8.27	8.44	10.35	11.00	11.04	11.07	11.17
3.73	8.93	9.25	11.25	12.01	12.02	12.07	12.15
4.02	9.64	10.12	12.21	13.09	13.07	13.14	13.20
4.33	10.42	11.04	13.25	14.24	14.20	14.29	14.31
4.66	11.25	12.01	14.37	15.46	15.39	15.52	15.50
5.03	12.14	13.03	15.56	16.73	16.65	16.83	16.75
5.42	13.09	14.1	16.84	18.07	17.98	18.21	18.08
5.84	14.10	15.19	18.19	19.46	19.38	19.67	19.48
6.29	15.16	16.32	19.63	20.90	20.83	21.20	20.95
6.78	16.28	17.48	21.14	22.39	22.34	22.79	22.48
7.31	17.44	18.65	22.73	23.92	23.90	24.43	24.08
7.88	18.66	19.85	24.39	25.49	25.50	26.13	25.74
8.49	19.93	21.07	26.11	27.09	27.13	27.87	27.45
9.15	21.24	22.3	27.89	28.73	28.80	29.64	29.21
9.86	22.59	23.56	29.72	30.40	30.49	31.45	31.02
10.62	23.98	24.85	31.58	32.10	32.22	33.27	32.87
11.45	25.41	26.17	33.47	33.84	33.96	35.12	34.75
12.34	26.88	27.52	35.38	35.63	35.73	36.99	36.66
13.30	28.39	28.93	37.31	37.46	37.53	38.88	38.60
14.33	29.94	30.39	39.25	39.33	39.36	40.79	40.56
15.45	31.52	31.91	41.19	41.26	41.22	42.72	42.55

16.65	33.15	33.50	43.15	43.24	43.13	44.69	44.56
17.94	34.83	35.16	45.12	45.27	45.07	46.69	46.59
19.33	36.54	36.88	47.12	47.36	47.07	48.74	48.64
20.84	38.31	38.69	49.14	49.50	49.11	50.83	50.73
22.46	40.12	40.56	51.22	51.69	51.21	52.98	52.85
24.20	41.99	42.51	53.35	53.92	53.37	55.18	55.00
26.08	43.92	44.53	55.54	56.20	55.59	57.45	57.19
28.11	45.91	46.62	57.82	58.50	57.86	59.78	59.43
30.29	47.97	48.77	60.17	60.84	60.19	62.18	61.71
32.00	49.53	50.39	61.96	62.56	61.94	63.97	63.41
35.18	52.31	53.28	65.16	65.57	65.02	67.15	66.42
37.92	54.59	55.63	67.81	67.96	67.52	69.75	68.85
40.86	56.95	58.06	70.55	70.37	70.05	72.40	71.33
44.04	59.39	60.56	73.33	72.77	72.60	75.04	73.83
48.00	62.30	63.53	76.54	75.50	75.51	78.04	76.70
51.15	64.50	65.78	78.89	77.49	77.64	80.20	78.80
55.12	67.17	68.50	81.59	79.79	80.10	82.67	81.23
59.41	69.93	71.27	84.19	82.04	82.50	85.03	83.58
64.00	72.73	74.07	86.63	84.20	84.80	87.23	85.82
69.00	75.56	76.90	88.93	86.30	87.01	89.29	87.96
74.36	78.34	79.68	91.01	88.30	89.08	91.17	89.95
80.14	81.06	82.41	92.89	90.17	91.00	92.87	91.77
86.36	83.67	85.05	94.55	91.91	92.75	94.39	93.43
93.07	86.15	87.54	96.00	93.50	94.32	95.74	94.90
100.3	88.46	89.87	97.22	94.92	95.69	96.91	96.18
108.1	90.57	91.99	98.22	96.18	96.87	97.89	97.28
116.5	92.47	93.88	99.00	97.25	97.86	98.70	98.19
125.6	94.15	95.52	99.58	98.15	98.67	99.41	98.92
135.3	95.62	96.90	99.93	98.88	99.28	99.90	99.46
145.8	96.88	98.02	100.00	99.46	99.71	100.00	99.81
157.2	97.93	98.90	100.00	99.87	99.95	100.00	99.97
169.4	98.77	99.54	100.00	99.99	100.00	100.00	100.00
182.5	99.39	99.92	100.00	100.00	100.00	100.00	100.00
196.7	99.77	100.00	100.00	100.00	100.00	100.00	100.00
213.0	99.94	100.00	100.00	100.00	100.00	100.00	100.00
228.5	100.00	100.00	100.00	100.00	100.00	100.00	100.00
246.5	100.00	100.00	100.00	100.00	100.00	100.00	100.00
265.4	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table A.4 Particle Size Distributions for P1, P2, PC and Intergrround
Blended Cements with Blaine Fineness Value of 370 m²/kg

Size (µm)	Materials						
	P1/370	P2/370	PC/370	I P1-20/370	I P1-30/370	I P2-20/370	I P2-30/370
0.533	0.09	0.10	0.09	0.13	0.13	0.12	0.13
0.574	0.19	0.20	0.18	0.27	0.26	0.25	0.27
0.618	0.35	0.37	0.33	0.48	0.47	0.46	0.49
0.666	0.55	0.59	0.52	0.76	0.75	0.73	0.78
0.718	0.78	0.84	0.75	1.08	1.07	1.04	1.11
0.774	1.02	1.11	1.01	1.43	1.42	1.38	1.47
0.834	1.27	1.41	1.29	1.79	1.78	1.74	1.84
0.899	1.54	1.72	1.59	2.17	2.16	2.12	2.22
0.969	1.81	2.05	1.92	2.56	2.55	2.51	2.62
1.04	2.10	2.4	2.28	2.96	2.96	2.93	3.04
1.13	2.39	2.76	2.66	3.38	3.38	3.36	3.46
1.21	2.70	3.15	3.07	3.81	3.80	3.81	3.89
1.31	3.02	3.55	3.50	4.24	4.24	4.27	4.33
1.41	3.35	3.98	3.97	4.69	4.70	4.75	4.79
1.52	3.71	4.42	4.47	5.16	5.16	5.25	5.25
1.64	4.08	4.90	5.00	5.64	5.64	5.77	5.73
1.76	4.47	5.39	5.57	6.14	6.15	6.31	6.23
1.90	4.89	5.92	6.18	6.67	6.68	6.89	6.75
2.05	5.34	6.49	6.83	7.23	7.24	7.50	7.30
2.21	5.83	7.09	7.53	7.83	7.85	8.16	7.89
2.38	6.35	7.74	8.29	8.48	8.50	8.86	8.52
2.56	6.91	8.43	9.10	9.19	9.20	9.62	9.19
2.76	7.51	9.18	9.97	9.95	9.97	10.44	9.92
2.98	8.15	9.97	10.91	10.79	10.81	11.32	10.71
3.21	8.84	10.83	11.91	11.69	11.72	12.28	11.57
3.46	9.58	11.74	12.99	12.68	12.71	13.31	12.49
3.73	10.36	12.72	14.14	13.75	13.78	14.50	13.48
4.02	11.20	13.77	15.36	14.9	14.95	15.60	14.55
4.33	12.09	14.88	16.67	16.15	16.2	16.87	15.69
4.66	13.04	16.06	18.06	17.48	17.55	18.23	16.9
5.03	14.04	17.32	19.53	18.89	18.99	19.66	18.18
5.42	15.10	18.65	21.08	20.39	20.51	21.18	19.54
5.84	16.23	20.05	22.71	21.96	22.12	22.76	20.96
6.29	17.41	21.53	24.41	23.61	23.80	24.42	22.45
6.78	18.66	23.08	26.17	25.32	25.56	26.15	23.99
7.31	19.97	24.70	28.00	27.09	27.38	27.93	25.60
7.88	21.34	26.39	29.88	28.91	29.25	29.77	27.25
8.49	22.78	28.13	31.81	30.78	31.17	31.65	28.95
9.15	24.27	29.94	33.78	32.67	33.13	33.57	30.7
9.86	25.82	31.8	35.78	34.6	35.11	35.52	32.49
10.62	27.42	33.7	37.8	36.55	37.12	37.49	34.32
11.45	29.07	35.65	39.85	38.52	39.14	39.48	36.19
12.34	30.76	37.63	41.92	40.5	41.18	41.49	38.1
13.30	32.49	39.63	44.00	42.5	43.22	43.51	40.05
14.33	34.26	41.67	46.09	44.52	45.27	45.54	42.05
15.45	36.06	43.72	48.19	46.56	47.32	47.58	44.10
16.65	37.89	45.8	50.31	48.62	49.39	49.64	46.19

17.94	39.75	47.89	52.44	50.71	51.47	51.72	48.34
19.33	41.65	50.01	54.58	52.84	53.57	53.82	50.54
20.84	43.57	52.14	56.75	55.00	55.69	55.95	52.8
22.46	45.54	54.3	58.93	57.3	57.83	58.12	55.12
24.20	47.54	56.48	61.13	59.46	60.01	60.34	57.50
26.08	49.59	58.69	63.36	61.76	62.22	62.6	59.95
28.11	51.70	60.93	65.6	64.11	64.46	64.91	62.44
30.29	53.86	63.19	67.88	66.52	66.74	67.29	65.01
32.00	55.48	64.86	69.57	68.32	68.44	69.07	66.93
35.18	58.37	67.79	72.51	71.50	71.42	72.22	70.32
37.92	60.73	70.12	74.83	74.03	73.81	74.75	73.01
40.86	63.14	72.48	77.13	76.56	76.2	77.3	75.69
44.04	65.62	74.84	79.41	79.05	78.57	79.84	78.34
48.00	68.56	77.55	81.96	81.85	81.24	82.69	81.33
51.15	70.79	79.5	83.79	83.84	83.16	84.71	83.45
55.12	73.46	81.76	85.87	86.08	85.34	86.98	85.86
59.41	76.12	83.93	87.84	88.18	87.41	89.08	88.13
64.00	78.72	85.99	89.7	90.13	89.35	90.99	90.23
69.00	81.28	87.95	91.44	91.92	91.17	92.71	92.16
74.36	83.73	89.75	93.02	93.52	92.83	94.2	93.89
80.14	86.06	91.4	94.45	94.95	94.31	95.48	95.41
86.36	88.22	92.89	95.72	96.20	95.62	96.55	96.72
93.07	90.21	94.22	96.83	97.27	96.76	97.44	97.80
100.3	92.01	95.4	97.78	98.17	97.74	98.15	98.67
108.1	93.62	96.44	98.55	98.88	98.53	98.73	99.37
116.5	95.06	97.32	99.16	99.42	99.16	99.18	99.83
125.6	96.32	98.07	99.64	99.78	99.64	99.53	99.97
135.3	97.39	98.68	99.94	99.97	99.94	99.77	100.00
145.8	98.28	99.16	100.00	100.00	100.00	99.89	100.00
157.2	98.99	99.5	100.00	100.00	100.00	99.97	100.00
169.4	99.55	99.71	100.00	100.00	100.00	100.00	100.00
182.5	99.92	99.83	100.00	100.00	100.00	100.00	100.00
196.7	100.00	99.91	100.00	100.00	100.00	100.00	100.00
213.0	100.00	99.97	100.00	100.00	100.00	100.00	100.00
228.5	100.00	100.00	100.00	100.00	100.00	100.00	100.00
246.5	100.00	100.00	100.00	100.00	100.00	100.00	100.00
265.4	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table A.5 Initial and Final Setting Time Values of the Cements

Cement	Initial Setting Time (min)	Final Setting Time (min)
PC/320	124	168
I P1-20/320	157	194
S P1-20/320	139	190
I P2-20/320	191	223
S P2-20/320	148	190
I P1-30/320	189	221
S P1-30/320	174	209
I P2-30/320	213	248
S P2-30/320	175	216
PC/370	104	139
I P1-20/370	172	201
S P1-20/370	151	183
I P2-20/370	160	191
S P2-20/370	156	185
I P1-30/370	180	217
S P1-30/370	181	211
I P2-30/370	188	228
S P2-30/370	182	224
S P1-20/320-370	142	177
S P2-20/320-370	146	195
SP1-30/320-370	153	179
S P2-30/320-370	150	195

Table A.6 Standard Deviations of the Compressive Strengths of PC and Blended Cements

	Standard Deviation (MPa)					
	2-d	3-d	7-d	28-d	56-d	91-d
PC/320	0.95	1.80	2.44	1.44	4.21	1.01
I P1-20/320	0.50	1.11	0.46	2.40	4.54	0.61
S P1-20/320	1.20	0.92	0.61	1.29	4.61	1.06
I P2-20/320	2.08	1.03	0.61	0.92	2.66	0.40
S P2-20/320	1.11	1.55	0.80	2.60	1.44	0.83
I P1-30/320	0.61	2.34	0.23	0.46	0.83	1.62
S P1-30/320	1.30	0.20	0.23	1.44	1.62	1.74
I P2-30/320	0.46	1.40	0.23	0.61	1.01	0.61
S P2-30/320	2.65	0.70	1.44	1.00	0.40	4.05
S P1-20/320-370	1.29	0.20	0.61	4.60	1.06	3.70
S P2-20/320-370	1.40	0.53	0.83	0.61	0.23	6.25
S P1-30/320-370	0.76	2.66	0.61	2.05	0.80	5.00
S P2-30/320-370	0.35	0.46	0.46	2.12	2.12	5.62
PC/370	2.14	4.04	3.76	1.01	1.03	3.64
I P1-20/370	0.26	0.83	3.61	1.67	3.94	0.46
S P1-20/370	2.91	0.85	1.06	1.29	0.23	4.97
I P2-20/370	1.10	1.51	1.06	0.61	1.51	2.27
S P2-20/370	2.48	0.81	1.67	3.45	0.61	3.40
I P1-30/370	0.85	0.91	1.51	0.46	1.22	1.80
S P1-30/370	0.64	0.67	0.80	1.67	0.83	0.61
I P2-30/370	0.61	1.47	1.01	0.00	3.06	1.16
S P2-30/370	0.38	1.82	1.51	2.60	2.60	1.06

Table A.7 Standard Deviations of Rapid Chloride Permeability Test Results

	Standard Deviation (coulombs)		
	28 days	3 months	6 months
PC/320	417.0	608.2	361.1
S P1-5/320-370	604.0	592.1	271.3
S P1-20/320-370	786.8	197.5	20.6
S P1-30/320-370	211.8	40.7	21.5
S P2-5/320-370	409.3	361.8	281.6
S P2-20/320-370	405.2	230.4	66.1
S P2-30/320-370	468.9	42.5	85.2

Table A.8 Standard Deviations of Mortar Bar Expansions due to Alkali-Silica Reactions

	Standard Deviation (%)					
	3-d	7-d	10-d	14-d	17-d	22-d
PC/320	0.0020	0.0035	0.0147	0.0082	0.0057	0.0030
S P1-5/320-370	0.0015	0.0014	0.0026	0.0010	0.0029	0.0014
S P1-20/320-370	0.0028	0.0069	0.0007	0.0007	0.0000	0.0076
S P1-30/320-370	0.0045	0.0015	0.0025	0.0035	0.0020	0.0010
S P2-5/320-370	0.0042	0.0028	0.0083	0.0076	0.0111	0.0097
S P2-20/320-370	0.0015	0.0020	0.0029	0.0042	0.0035	0.0006
SP2-30/320-370	0.0035	0.0017	0.0007	0.0039	0.0028	0.0043

Table A.9 Standard Deviations of Mortar Bar Expansions due to Sulfate Attack

	Standard Deviation (%)								
	Weeks								
	1	2	3	4	8	13	17	26	39
PC/320	0.0020	0.0013	0.0023	0.0020	0.0023	0.0039	0.0028	0.0047	0.0068
S P1-5/320-370	0.0018	0.0023	0.0024	0.0034	0.0029	0.0038	0.0038	0.0072	0.0128
S P2-5/320-370	0.0027	0.0021	0.0029	0.0026	0.0032	0.0043	0.0033	0.0036	0.0053
S P1-20/320-370	0.0025	0.0013	0.0021	0.0023	0.0026	0.0020	0.0026	0.0020	0.0015
S P2-20/320-370	0.0011	0.0014	0.0026	0.0029	0.0029	0.0033	0.0033	0.0042	0.0048
S P1-30/320-370	0.0040	0.0018	0.0093	0.0028	0.0036	0.0029	0.0040	0.0045	0.0060
SP2-30/320-370	0.0027	0.0028	0.0032	0.0024	0.0042	0.0026	0.0024	0.0048	0.0044

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