SULFATE RESISTANCE OF BLENDED CEMENTS WITH FLY ASH AND NATURAL POZZOLAN

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ABSTRACT

SULFATE RESISTANCE OF BLENDED CEMENTS WITH FLY ASH AND NATURAL POZZOLAN

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Numerous agents and mechanisms are known to affect the durability of a concrete structure during its service life. Examples include freezing and thawing, corrosion of reinforcing steel, alkali-aggregate reactions, sulfate attack, carbonation, and leaching by neutral or acidic ground waters. Among these, external sulfate attack was first identified in 1908, and led to the discovery of sulfate resistant Portland cement (SRPC). Besides SRPC, another way of coping with the problem of sulfate attack is the use of pozzolans either as an admixture to concrete or in the form of blended cements

This study presents an investigation on the sulfate resistance of blended cements containing different amounts of natural pozzolan and/or low-lime fly ash compared to ordinary Portland cement and sulfate resistant Portland cement. Within the scope of this study, an ordinary Portland cement (OPC) and five different blended cements were produced with different proportions of clinker, natural pozzolan, low-lime fly ash and limestone. For comparison, a sulfate resistant Portland cement (SRPC) with a different clinker was also obtained. For each cement, two different mixtures with the water/cement (w/c) ratios of 0.485 and 0.560 were prepared in order to observe the effect of permeability controlled by water/cement ratio.

The performance of cements was observed by exposing the prepared 25x25x285 mm prismatic mortar specimens to 5% Na_2SO_4 solution for 78 weeks and 50mm cubic specimens for 52 weeks. Relative deterioration of the specimens was determined by length, density and ultrasonic pulse velocity change, and strength examination at different ages. It was concluded that depending on the amount and effectiveness of the mineral additives, blended cements were considered to be effective for moderate or high sulfate environments. Moreover, the cement chemistry and w/c ratio of mortars were the two parameters affecting the performance of mortars against an attack. As a result of this experimental study it was found out that time to failure is decreasing with the increasing w/c ratio and the effect of w/c ratio was more important for low sulfate resistant cements with higher C_3A amounts when compared to high sulfate resistant cements with lower C_3A amounts.

Keywords: Blended Cement, Fly Ash, Natural Pozzolan, Sulfate Attack

ÖZ

UÇUCU KÜL VE DOĞAL PUZOLAN KATKILI ÇIMENTOLARIN SÜLFAT DİRENCİ

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Betonarme bir yapının dayanıklılığını hizmet ömrü süresince bir çok etmen ve mekanizmanın etkilediği bilinmektedir. Örnek olarak; donma-çözünme, donatı paslanması, alkali-agrega reaksiyonları, sülfat etkisi, karbonatlaşma ve kalsiyum hidroksitin nötr veya asidik yeraltı sularından dolayı çözünmesi verilebilir. Bunlar arasında sülfat hücumu ilk olarak 1908 yılında tanımlanmış ve sülfata dayanıklı çimentoların bulunmasını sağlamıştır. Sülfat etkisi ile başa çıkmanın sülfata dayanıklı çimento kullanımından başka diğer bir yolu da puzolanların doğrudan betona katkı maddesi olarak katılması veya katkılı çimento içinde kullanılmasıdır.

Bu çalışma, farklı oranlarda uçucu kül ve doğal puzolan içeren katkılı çimentoların, Portland çimentosu ve sülfata dayanıklı çimentolara kıyasla, sülfata karşı dirençleri üzerindeki bir araştırmayı sunmaktadır. Bu kapsamda, değişik oranlarda klinker, doğal puzolan, uçucu kül ve kalker kullanılarak normal portland çimentosu ve beş değişik katkılı çimento hazırlanmıştır. Karşılaştırma amacıyla ayrıca farklı bir klinkerden sülfata dayanıklı çimento da elde edilmiştir. Geçirimliliğin sülfat direncine etkisini görmek amacıyla her tip çimentodan su/çimento (S/Ç) oranı 0.485 ve 0.560 olan iki farklı karışım hazırlanmıştır.

Çimentoların sülfat hücumuna karşı performansları hazırlanan 25x25x285mm’lik prizmatik harç çubukları 78 hafta, 50mm’lik küp numuneler ise 52 hafta süresince %5’lik Na_2SO_4 çözeltisine maruz bırakılarak gözlenmiştir. Numunelerin farklı yaşlardaki göreceli bozunmaları, boy, yoğunluk, ultrasonik ses hızı değişimleri ve dayanımları ölçülerek belirlenmiştir. Kullanılan katkının miktarı ve etkisine bağlı olmakla birlikte mineral katkılı çimentoların orta ve yüksek sülfatlı ortamlar için etkili sayılabileceği görüşüne varılmıştır. Ayrıca, S/Ç oranı ve çimento kompozisyonunun harçların sülfatlı sulara karşı performanslarını etkileyen faktörler olduğu tespit edilmiştir. Yapılan deneysel çalışma sonucunda, S/Ç oranının artmasıyla, bozunmaya kadar geçen sürenin kısaldığı ve S/Ç oranının yüksek C_3A içeren ve sülfata karşı daha az dayanıklı olan çimentolarda, düşük oranda C_3A içeren çimentolara kıyasla daha önemli olduğu gözlemlenmiştir.

Anahtar Kelimeler: Katkılı Çimento, Uçucu Kül, Doğal Puzolan, Sülfat Hücumu

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INTRODUCTION

1.1 General

Sulfate corrosion of cement and concrete is a very serious problem caused by aggressive influence of sulfate solutions from many different sources. Natural groundwater might contain the sulfate ions as a result of an oxidation of sulfide minerals. Concentration of the sulfate ions is particularly high in an industrial environment. Chemical wastes from industrial processes as well as application of fertilizers contribute to an appearance of the sulfate ions [1]. On the other hand the recent modifications in the cement manufacturing technology and the extensive use of mineral admixtures have introduced changes in the chemical and mineralogical composition of the present day cements. These changes may significantly affect the durability of concrete, particularly the sulfate attack. Due to these modifications the need for understanding the mechanism of sulfate attack becomes more important [2].

The cement sales in Turkey between the years of 1996 and 2005 can be seen in Table 1-1. As can be seen from the table, although the sales of ordinary Portland cement (OPC) has increased, blended cement (BC) sales are still higher than the ordinary Portland cement sales. Moreover, the percentage sales of sulfate resistant Portland cement (SRPC) are very low compared to the blended cements. This extensive use of mineral additives has introduced the necessity for new research about physical and chemical properties of present day cements. Among these properties, durability is the one as important as strength and sulfate attack is one of the major durability problems [3].

Table 1-1 Cement sale in the domestic market between the years 1996 and 2005

Year	SRPC (Ton)	OPC (Ton)	BC (Ton)	Other (Ton)	Total Sale (Ton)	SRPC (%)	OPC (%)	BC (%)
1996	225,494	5,592,260	25,970,942	294,720	32,083,416	0.70	17.43	80.95
1997	158,845	4,862,706	27,310,144	296,216	32,627,911	0.49	14.90	83.70
1998	272,297	6,880,484	26,715,854	269,440	34,138,075	0.80	20.15	78.26
1999	200,450	5,784,843	24,428,113	1,116,470	31,529,876	0.64	18.35	77.48
2000	288,385	8,022,184	22,955,461	249,046	31,515,076	0.92	25.46	72.84
2001	301,552	6,929,546	17,664,715	186,282	25,082,095	1.20	27.63	70.43
2002	280,550	8,507,887	17,702,770	320,012	26,811,219	1.05	31.73	66.03
2003	316,893	9,861,027	17,724,708	203,433	28,106,061	1.13	35.09	63.06
2004	257,431	12,469,727	17,704,354	239,098	30,670,610	0.84	40.66	57.72
2005	266,017	15,947,844	18,525,081	344,256	35,083,198	0.76	45.46	52.80

1.2 Objective

The objective of this study is twofold: first to investigate the performance of blended cements containing various amounts of natural pozzolan and fly ash against sulfate attack, and second to investigate the effect of permeability as controlled by w/c on this performance. For this purpose an ordinary Portland cement and five different blended cements were produced with different proportions of clinker, natural pozzolan, low-lime fly ash and limestone. For comparison a sulfate resistant Portland cement obtained a different clinker was also utilized. All these cements were used to prepare mortar specimens with two w/c ratios.

1.3 Scope

This thesis consists of six chapters. Chapter 2 presents a literature review and gives a general background on sulfate attack.

Chapter 3 presents the experimental program, briefly explains the test procedures, and summarizes the experimental data.

Chapter 4 presents the summary and discussion of the results obtained from the experimental data presented in Chapter 3

Chapter 5 gives a summary of thesis and lists the conclusions of this research.

Finally recommendations for future studies and possible further research areas that will complement this thesis are given in Chapter 6.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

Numerous agents and mechanisms are known to affect the durability of a concrete structure during its service life. Examples include freezing and thawing, corrosion of reinforcing steel, alkali-aggregate reactions, sulfate attack, carbonation, and leaching by neutral or acidic ground waters. Among these, external sulfate attack was first identified in 1908 by the United States Bureau of Reclamations [4] and since then it has been the subject of numerous studies and still not totally understood [5].

2.1 Hydration of Portland Cement

Before looking into background review on sulfate attack, a brief review of Portland cement hydration is presented to aid in the explanation of the reactions of external sulfates with the constituents of hardened Portland cement paste.

The primary compounds that constitute Portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and a sulfate hydrate compound called gypsum ($C\bar{S}H_2$) that is added to Portland cement clinker to control flash setting. Tricalcium silicate and dicalcium silicate each react with water to form calcium silicate hydrate ($C_3S_2H_3$) and calcium hydroxide (CH) as shown in equation (2.1) and (2.2). Among the products that are formed, $C_3S_2H_3$ or also known as the C-S-H gel is the primary binding component of hydrated Portland cement and calcium hydroxide is the water soluble by-product that has no cementitious value.

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH \qquad (2.1)$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH \qquad (2.2)$$

A secondary binding component is formed from the hydration of tricalcium aluminate and gypsum. The C_3A and gypsum together with water combine to form ettringite ($C_6A\overline{S}_3H_{32}$) as shown in equation 2.3. Ettringite formed is only stable at high concentrations of sulfate ions. As hydration progresses, the concentration of sulfate ions drops as gypsum is consumed. The ettringite becomes unstable with this decrease in sulfate ion concentration and reacts with the remaining C_3A to form monosulfoaluminatehydrate ($C_4A\overline{S}\ H_{12}$) as shown in equation 2.4 [6].

$$C_3A + 3C\overline{S}H_2 + 26H \longrightarrow C_6A\overline{S}_3H_{32} \qquad (2.3)$$

$$2C_3A + C_6A\overline{S}_3H_{32} + 4H \leftrightarrow 3C_4A\overline{S}H_{12} \qquad (2.4)$$

2.2 Mechanism of Sulfate Attack

When sulfate containing waters seep into hardened concrete, sulfates react with the calcium hydroxide in the hydrated cement paste and form gypsum ($C\overline{S}H_2$) as shown in equations 2.5 and 2.6. This set of reactions are often called the first phase of sulfate attack.

$$CH + N\overline{S} + 2H \longrightarrow C\overline{S}H_2 + NH \qquad (2.5)$$

$$CH + M\overline{S} + 2H \longrightarrow C\overline{S}H_2 + MH \qquad (2.6)$$

This gypsum can react further with hydrated calcium aluminates (i.e. C_4AH_{13}) [7], hydrated calcium sulfoaluminates (i.e. $C_4A\overline{S}H_{12-18}$), or unhydrated tricalcium aluminate (C_3A) to produce ettringite ($C_6A\overline{S}_3H_{32}$) (equations 2.3, 2.7 and 2.8).

$$C_4A\bar{S}H_{12-18} + 2C\bar{S}H_2 + 16 - 10H \longrightarrow C_6A\bar{S}_3H_{32} \quad (2.7)$$

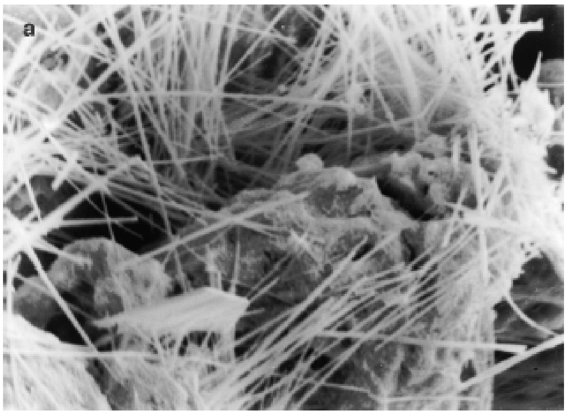
$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \longrightarrow C_6A\bar{S}_3H_{32} + CH \quad (2.8)$$

The critical reaction that defines sulfate attack occurs when the hydrated cement paste is in hardened state. If hardened concrete is exposed to an external source of soluble sulfate ions, the concentration of sulfates in the concrete pore water may increase. As sulfate ion concentration increases, the monosulfoaluminate becomes unstable and reverts back to ettringite as shown in equation 2.7. The formation of ettringite or monosulfoaluminate according to reactions (2.3, 2.4, 2.7 and 2.8) is controlled by the gypsum/tricalcium aluminate molar ratio ($C\bar{S}H_2$/C_3A) [8].

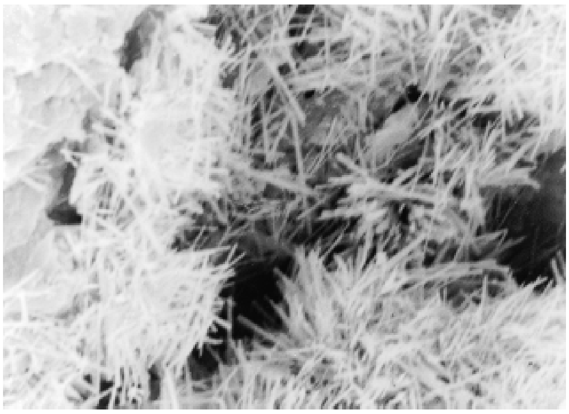
Wee and Suryavanshi [6] claim that sulfate deterioration is significantly controlled by the formation of ettringite and its subsequent expansion due to the moisture absorption. It is hypothesized that the mechanism of sulfate attack comprises a sequence of the following processes: sulfate ions intrude to the concrete dominantly through the aggregate- paste interfaces. Chemical reaction takes place between the sulfate and free portlandite present abundantly near the aggregate-paste interfaces and then with the aluminates, to form ettringite. The ettringite thus formed is poorly crystallized ettringite capable of absorbing a large amount of water on the surface, thereby causing considerable volume change; and expansion of poorly crystallized ettringite results in the cracking and spalling of concrete [6].

It is well known that the formation of ettringite generates excessive expansion in concrete. However, the mechanism by which ettringite formation causes expansion is still a subject of controversy. Exertion of pressure ($\cong$ 240 MPa) by forming ettringite crystals and swelling due to absorption of water in an alkali environment by poorly crystalline ettringite, are two of the several hypotheses that are supported by most researches as explained by Cohen and Bentur [9].

Tasong et al, [10] categorized the ettringite needles into three based on their mode of occurrence and morphology as shown in Figure 2-1.



- Category A: Well formed any randomly oriented rod like crystals of ettringite of high aspect ratio that appeared to grow into pre-existing pores and cracks.



- Category B: Very short ettringite needles that appeared to cover the surfaces of existing particles.

- Category C: Flower-like radiating needles of ettringite at isolated points, scattered all over an entire sample.

Figure 2-1 Ettringite types [10]

Tian and Cohen state that sulfate attack mechanism is indeed complicated. They stated that expansion and cracking of Portland cement concrete under sulfate attack should not exclusively be attributed to ettringite formation. Other factors especially gypsum formation should also be taken into consideration as a possible source of expansion [11]. Sulfate attack through gypsum formation is more generally known to manifest itself through loss of stiffness, strength and adhesion. In literature there are authors either supporting or contradicting the idea that gypsum formation is expansive. According to Hansen [12,13] and Mather [14], the formation of gypsum, according to equation 2.5 or 2.6 would not cause an increase in volume. In other words, the gypsum that forms as a result of this reaction would not occupy a volume larger than that of the cavity in which it is precipitated plus the solid CH that is dissolved to participate in the reaction. Hansen concluded that if a force is exerted by gypsum formation, it is not crystal growth but hydraulic pressure and it is not expansive. On the other hand, a change in the crystal structure from the reactants to product could cause the inclusion of air voids, as is the case when gypsum forms from hemihydrate and the air void inclusions could result in expansion [15]. Bonen and Sarkar [16] also studied the replacement of the CH by gypsum in the interfacial zone (a zone between aggregates and paste) along the boundaries of the aggregate particles. They found that thick deposits of gypsum up to 50 µm wide. The crystallization pressure of gypsum produced tensile stresses and cased disruptive expansion. Their conclusion contradicted Hansen's findings.

In his previous study, Cohen [17] attributed expansion to ettringite formation rather than gypsum formation which has only a softening effect and causes mass and strength loss. However, in his studies with Tian [11,18] he concluded that while the exact mechanism is not clear, sulfate attack mechanism is complicated and cracking of Portland cement concrete should probably not be exclusively attributed to ettringite formation. Tensile stresses during gypsum formation may also play a role in expansion and the subsequent cracking. It was found from their laboratory study that alite (C_3S) paste specimens expanded and cracked significantly in 5% Na_2SO_4 solution after a dormant period of about one year [18]. Finally in their article published in 2003 [19] Cohen and Santhanam declared that there is a possible link between the amount of gypsum and the measured expansion.

Ping and Beaudoin [20,21] suggested a theory based on the principles of chemical thermodynamics. They pointed out the expansive force resulted from the crystallization pressure. There are two conditions for the occurrence of crystallization pressure: i- the solid product should form and grow in a confined space; ii- activity product of reactants in the pore solution should be greater than the solubility product of the solid products under atmospheric pressure. Theoretically, any solid product – not only ettringite– may produce crystallization pressure and cause expansion if the above two conditions are met. They suggested that, in theory, gypsum formation can be one of the principle causes of expansion during sulfate attack.

Nielsen [22], Wang [23], Yang et al. [24], and Gonzales at al. [25] are other authors supporting that the gypsum formation is expansive. Although the number of authors supporting this idea is much more than the contradicting ones, the exact mechanism of expansion is still unknown, therefore more research is needed in this area.

Bellmann [26] agrees with all above authors on that the formation of gypsum can lead to expansion and cracking. However all studies refer to high sulfate concentrations, which are used to accelerate the tests. Sulfate concentration from the environment in most cases is much below than that is used in the laboratories to accelerate the tests. Therefore, the formation of gypsum under field conditions is not fully addressed [26]. He studied the influence of sulfate concentration in the test solutions on the formation of gypsum. The results of his study suggest that at common moderate concentrations the formation of gypsum is either not possible or can not lead to damage, because supersaturation and swelling pressure are very low. At low concentrations instead of gypsum, ettringite and thaumasite had formed [26].

Thaumasite is another compound believed to form during sulfate attack at low temperatures (0-5°C) in the presence of CO_3^{2-} or dissolved atmospheric CO_2 [19]. General reaction for the formation of thaumasite can be summarized by equation 2.9.

$$3CaO.2SiO_2.3H_2O + 2\{CaSO_4.2H_2O\} + CaCO_3 + CO_2 + 23H_2O \longrightarrow 2\{CaCO_3.CaSO_4.CaSiO_3.15H_2O\} \quad (2.9)$$

As C-S-H gels are directly involved in thaumasite formation, it is especially deleterious. While ettringite formation is accompanied by expansion and spalling, thaumasite formation has a more severe damaging effect. Thaumasite is able to transform hardened concrete and mortar into a soft pulpy mass because of a direct attack on the C-S-H [19]. Nevertheless, although there is a controversy about the temperature required [19], the thaumasite formation is not studied in detail as it is not anticipated at normal testing temperatures.

A sodium sulfate attack mechanism is proposed by Santhanam and Cohen [27] in the year 2002 as shown in Figure 2-2. They express that expansion of mortar specimens in sodium sulfate solution follows a two stage process. During the initial stage (Stage 1), the expansion is very low. This period of low expansion is followed by a sudden increase in the expansion. Step 1 depicts the initial state of the process. The mortar specimen is just introduced into the Na_2SO_4 solution that has a pH of 6-8. The pH of the surrounding solution changes to 11-12 just a few minutes after the specimen is introduced. In step 2, gypsum and ettringite start forming in the regions close to the surface. The surface zone of the mortar, where expansive gypsum and ettringite have formed, behaves like a skin that is trying to expand. However, the bulk of the mortar underneath, which is chemically unaltered, tries to resist this expansion. Thus, as described in Step 3, a resultant compressive force is generated in the surface region, while the bulk of the mortar is subjected to tensile forces. This causes cracks to appear in the interior of the mortar, as shown in Step 4. Over time, the surface zone deteriorates due to continued penetration of the solution. When the solution is able to reach the cracked interior zones, it reacts with the hydration products and leads to deposition of attack products inside the cracks, as well as in the paste. Gypsum primarily deposits in the cracks and in voids, because these provide the best sites for nucleation. Hence, as shown in Step 5, a new region inside the mortar becomes the zone of deposition. This region then tries to expand, causing resultant tensile forces in the interior of the mortar. New cracks then appear in the interior zones. At this stage (Step 6), there are three distinct zones within the mortar —the disintegrated surface, the zone of deposition of attack products, and the interior cracked zone that is chemically unaltered.

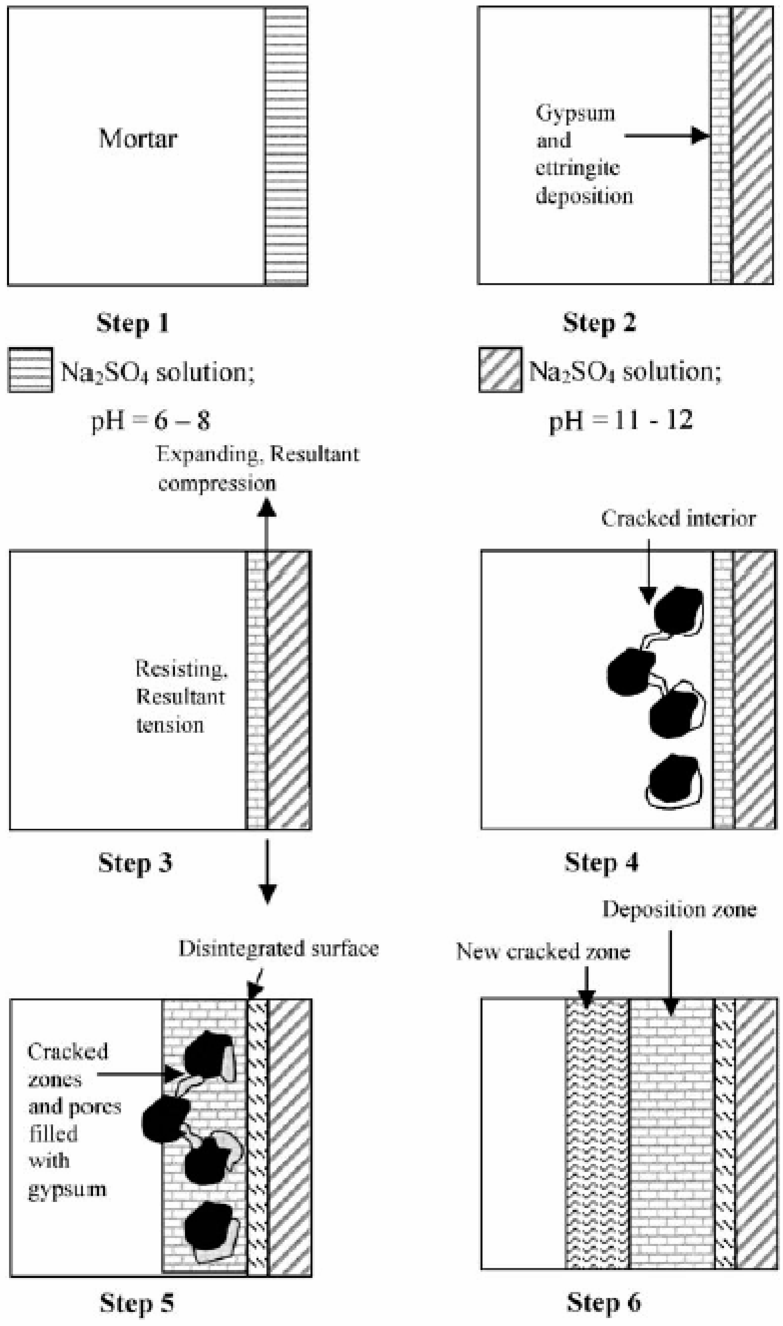


Figure 2-2 Proposed mechanism of sulfate attack [27]

2.3 Types of Sulfate Attack

2.3.1 Internal and External Sulfate Attack

Sulfate attack can be divided into two groups as internal and external sulfate attack depending on the source of sulfate. Internal sulfate attack refers to situations where the source of sulfate is the concrete itself. The source of sulfate can be the cement, supplementary materials such as fly ash or slag, the aggregate, chemical admixtures or the water [28]. Three types of internal sulfate attack have been reported by Scrinever and Skalny [29]. First is internal sulfate attack due to contamination of the aggregates by sulfates –the rise in the recycled building materials as aggregate makes this important issue–. Second is internal sulfate attack due to over sulfation of the cement. In these forms of internal sulfate attack the expansion occurs fairly rapidly, within about 6 months. The amount of sulfate in the cement and aggregates is limited by standards to prevent their occurrence. The third form of internal sulfate attack is Delayed ettringite formation. DEF may be defined as the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete and which have experienced elevated temperatures during curing (above about 70 ºC[30]) either through the external application of heat as in steam curing, or from internal temperature rise due to the heat evolved during hydration [29].

Skalny prefers to talk about the two internal sulfate attack mechanism - excess sulfate-generated expansion and heat treatment-generated expansion – and assigned them different names as *composition-induced internal sulfate attack* and *heat-induced internal sulfate attack*, respectively. Among these only the latter one named as DEF by Skalny [28].

In external sulfate attack, sulfates from an external source enter the hardened concrete, causing its degradation. The deleterious action may include an excessive expansion, crack formation, loss of strength or surface spalling and delamination. The most common external source of sulfates is ground water [28].

2.3.2 Physical and Chemical Sulfate Attack

Some researchers consider sulfate attack to have taken place if sulfates are involved, regardless of the attack mechanism. Skalny believe that to draw a distinction between physical and chemical processes does not serve a useful purpose and will only serve to further confuse engineers [28,31]. On the contrary, most of the authors [5,32,33,34,35,36] limit the concept sulfate attack to the consequences of chemical reactions between sulfate ions and hydrated cement paste, so that chemical changes in the paste take place. Therefore the term “sulfate attack” is used for the same meaning of “chemical sulfate attack”, and it is explained in section 2.2 in detail. However, if sulfates interact with cement and cause damage to it, but the action is physical, and a similar action can occur with salts other than sulfates, than the damage is considered to be “physical attack” or “physical sulfate attack” [5]. A prevalent form of physical attack is the reversible change of anhydrous sodium sulfate (thenardite, Na_2SO_4) into decahydrate (mirabilite, $Na_2SO_4.10H_2O$). If crystallization takes place in the pores at or near the surface of concrete, large pressure may develop, with consequent deleterious action [5]. Slight variations in temperature and relative humidity cause this reversible action as seen in equation. 2.9, and the left to right reaction involves a large expansion [32].

$$Na_2SO_4 + 10H_2O \longleftrightarrow Na_2SO_4.10H_2O \tag{2.9}$$

Hime and Mather state that this is not a classical sulfate attack mechanism since neither gypsum nor ettringite is formed [32].

Corresponding to sodium sulfate, magnesium sulfate can also cause damage, as shown in equation 2.10.

$$\begin{aligned} MgSO_4 + \xleftrightarrow{H_2O} MgSO_4.H_2O + \xleftrightarrow{5H_2O} MgSO_4.6H_2O + \\ \xleftrightarrow{H_2O} MgSO_4.7H_2O \end{aligned} \tag{2.10}$$

However, dehydration of epsomite ($MgSO_4.7H_2O$) occurs only at temperatures above 70°C, so the reverse reaction is unlikely under most conditions.

Another distress mechanism of physical sulfate attack, “salt crystallization”, can be represented by equations 2.11 and 2.12. Salt crystallization involves repeated dissolution of the solid sulfate and recrystallization in concrete pores [32].

$$2Na^{+} + SO_4{}^{-2}(aqueous) \longrightarrow Na_2SO_4(solid) \tag{2.11}$$

$$Mg^{+2} + SO_4^{-2} \longrightarrow MgSO_4\,(or\ hydrates\ of\ it) \tag{2.12}$$

In this study as chemical sulfate attack is investigated, physical sulfate attack is not examined in detail.

2.4 Factors Affecting Sulfate Attack

All cements, including the sulfate-resisting ones are vulnerable to sulfate attack. However, the intensity and the rate of attack depend on some factors that will be discussed in the proceeding sections.

2.4.1 Cement Composition

Tricalcium aluminate and tetracalcium alumino ferrite contents of Portland cement is thought to be particularly important in determining the sulfate resistance [37], because these compounds are directly involved in the formation of ettringite (eq. 2.3 and 2.4). The C_3A content of Portland cement has long been assumed to be the chief contributor to volume change in sulfate attack [38,39]. For this reason ASTM C 150 and TS 10157 limit the C_3A content of sulfate resisting cement to 5%. In one of the largest studies conducted on sulfate resistance, Blaine and Arni [39] showed that C_3A is the dominant factor in sulfate expansion. The relationship between cement with low C_3A contents (0-7%) and expansion is linear, but exponential relationships of the second or third degree seem to best express the relationship between high C_3A (7-

15%) cement and expansion. The results of Blaine and Arni showed that cement characteristics affect the expansions of high C_3A cement and low C_3A cement differently. For high C_3A cement, the principal variables in sulfate expansion other than C_3A, were Fe_2O_3 and the CaO/SiO_2 ratio. Ramyar and İnan [40] state that 5%–8% C_3A-bearing cements contain most of the alumina in the form of monosulfate hydrate ($C_4A\bar{S}H_{12}$ or $C_4A\bar{S}H_{18}$). In cements with more than 8% C_3A, the hydration products may also contain hydrogarnet (C_4AH_{13} or C_4AH_{19}) In the presence of CH, when the cement paste comes in contact with sulfate ions both the alumina containing hydrates are converted to ettringite [2,41] (equations 2.7 and 2.8). In the study of Tikalsky et al. [42] C_3A alone showed no significant correlation with sulfate expansions at any age. In their study Fe_2O_3 was clearly the most predictive variable in sulfate resistance. Their result does not conflict with Blaine and Arni's findings, as they found that for C_3A contents grater than 9%, one of the other principal controlling cement characteristics is Fe_2O_3 content. Odler and Jawed [43] explained that C_4AF also produces ettringite, but at a reaction rate much slower than C_3A, and the resulting ettringite crystals contain iron along with aluminum in lattice. Therefore, to produce sulfate-resistant cement ASTM C 150 and TS 10157 limit the sum of C_4AF plus twice the C_3A content to 20%. Odler and Jawed relate that the iron containing ettringite phases are less expansive than iron-free phases, although the reason is not quite understood. This lower expansion may be either due to the differences in crystal morphology, or the fact that the slower rate of formation of the iron-containing phases allows the cement paste structure to be strong enough to resist the expansive stresses [43,44].

C_3A and C_4AF contents are not the only factors influencing concrete durability in sulfate-bearing environments. Another factor that may determine the sulfate resistance is the silicate ratio (C_3S/ C_2S). Silicate ratio controls the quantity of calcium hydroxide in hydrated cement paste, as well as the rate of early age hydration and strength development when the content of the two aluminates (C_3A and C_4AF) is relatively constant. The chemical reactions for fully hydrated C_3S and C_2S pastes were expressed in equations 2.1 and 2.2. According to Mehta [45] hydration of C_3S would produce 61% $C_3S_2H_3$ and 39% CH, whereas the hydration of

C_2S would produce 82% $C_3S_2H_3$ and 18% CH. It can be also clearly seen from the equations 2.1 and 2.2 that CH production of C_3S is much more than C_2S. CH plays a decisive role in the reactions that produce gypsum and ettringite [46]. As it is shown in equation 2.5 and 2.6, due to continual production of $Ca(OH)_2$, and sufficient supply of SO_4^{2-} ions, large amounts of gypsum may form. This gypsum formation leads to an enhanced sulfate deterioration of hardened cement matrix, and this is called the softening type of deterioration [47]. It is accepted that the gypsum formation with a softening effect on concrete causes spalling, strength loss and mass loss. Irrasar [48] attributed the great expansion of high C_3S cement to gypsum formation located at the paste-aggregate interface at early stage of attack that produces the environmental conditions needed to expansive ettringite formation at advanced attack stages. The assertions related to the contribution of gypsum formation to the sulfate expansion are also explained in the section 2.2. Al-Dulaijan et al. [3] state that the deterioration of hardened Portland cement paste by gypsum formation goes through a process leading to a reduction of stiffness and strength; this is followed by expansion and cracking, and eventual transformation of the material into a mushy or non-cohesive mass. To conclude, in addition to the C_3A and C_4AF content, the C_3S to C_2S ratio has a significant influence on the sulfate resistance [3,47,49].

2.4.2 Mineral Additives

Blended cements are now increasingly being used to improve concrete durability [2]. When pozzolans are added to cement, they react with the calcium hydroxide, in the presence of moisture, to produce secondary calcium silicate hydrate (C-S-H). This pozzolanic reaction has the following beneficial impacts on sulfate attack.

1. The consumption of portlandite (CH) reduces the formation of gypsum: As explained in section 2.2, gypsum formation has a softening effect and causes mass and strength loss. Gypsum may also contribute to expansion. As shown in equation 2.5 and 2.6 portlandite is needed to form gypsum, but when CH

is consumed by the pozzolanic reactions, gypsum formation and therefore its detrimental effects will be reduced [2].

2. As mentioned in section 2.4.1, C_3A is directly involved in the formation of ettringite that causes expansion in hardened concrete. Replacement of part of the cement by a pozzolanic material will reduce the C_3A content of the cement (dilution effect), therefore all the aluminate-bearing phases will accordingly be reduced [2].

3. Even if it is formed, ettringite becomes expansive only at high pH values (pH>12) [2,46]. Mehta categorized ettringite crystals into two types [50]. First are large lath-like crystals, 10-100μm long and several micrometers thick, and formed under conditions of low hydroxyl ions concentration. It is proposed that these types of ettringite crystals are not expansive. Second type of ettringite crystals are small rod-like crystals, 1-2μm long and 0.1-0.2μm thick, and formed under conditions of high hydroxyl ions concentration. These types of ettringite crystals are capable of adsorbing large amounts of water on the surface, thereby causing considerable expansion. Since blended cements consume a significant proportion of the portlandite produced by the cement hydration and reduce the hydroxyl ion concentration, pH is reduced. Since pH is reduced the ettringite becomes less expansive.

4. The formation of secondary C-S-H produce a film or a coating on the alumina-rich and other reactive phases thereby hindering the reaction of secondary ettringite [2,51].

5. By the addition of mineral additives, pore refinement or transformation of larger pores into finer pores occurs [52]. In other words, the formation of secondary C-S-H results in the densification of the hardened cement paste since it is deposited in the pores thereby making blended cements impermeable. Therefore the sulfate ions cannot easily penetrate through the concrete matrix, as in the case of plain Portland cements [2,6,26].

On the other hand mineral additives are also reported to be ineffective in reducing the detrimental effects of sulfate attack.

1. When attacking medium is magnesium sulfate, mineral additives may reduce the performance of concrete in terms of strength reduction and weight loss. The consumption of CH by pozzolanic reaction enhances the attack on C-S-H, (eq. 2.13 and 2.14) transforming the cementitious C-S-H in-to fibrous, non-crystalline M-S-H that possesses no cementing properties [2]. However, the reduction in permeability and refinement of pore structure with use of mineral additives can often overcome this negative effect. Thus, it is essential to determine critical dosage levels of additives to maximize their benefits, and minimize the deleterious effects of magnesium sulfate attack [61].

2. Class-C fly ashes obtained from lignite or subbituminous coals and containing a high ratio of calcium to iron oxides or those with chemically active alumina have been found to exhibit reduced resistance to sulfate attack [53].

3. Irrasar et al., [54] investigated the sulfate resistance of concretes containing mineral additives in a field test in which concrete specimens were half-buried in sulfate soil for five years. Results of their study show that mineral additives improved the sulfate resistance when the concrete is buried in the soil (chemical sulfate attack). Figure 2-3 shows their three half buried specimens made with ordinary Portland cement and 20% and 40% of natural pozzolan exposed to high permeable soil after ten years [55]. The portion of concrete specimens underground for both concrete containing natural pozzolan, while for ordinary Portland cement they were reduced to a putty like mass without strength and easily broken by hand. However, concretes with high content of mineral additives exhibit a greater surface scaling over soil level due to the sulfate salt crystallization (physical sulfate attack). In addition, the damage increases when the percentage of natural pozzolan is

increased. Irrasar state that 20% fly ash provides an integral solution for half buried structures [54].

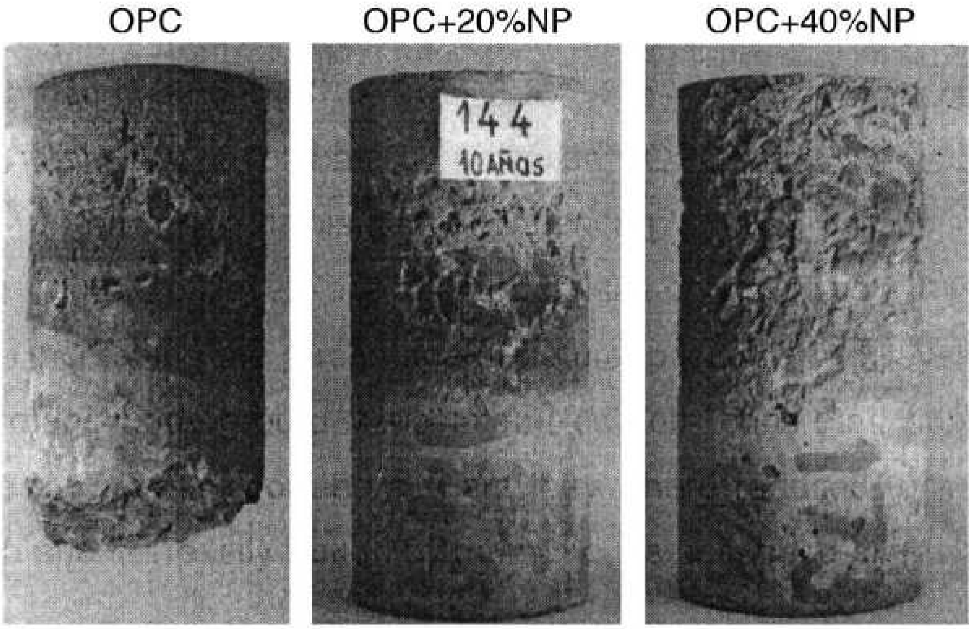


Figure 2-3 Visual aspect of half buried specimens in sulfate soil for 10 years [55]

Consequently, Mineral additives have shown to improve sulfate resistance of cementitious systems. However, the sulfate resistance of blended cement depends on the type, composition and substitution level of the mineral addition, and type of sulfate attack.

2.4.3 Permeability

Permeability is considered to be the key to the durability of concretes in various aggressive environments. Pore structure influences the rate of ingress of sulfate ions into concrete. Therefore, permeable concrete is vulnerable to attack by almost all classes of aggressive agents [56]. Mehta [57] concluded that for the prevention of sulfate attack to concrete, control of the permeability of concrete is more important than the control of the chemistry of the cement. It is well known that low water/cement (w/c) ratio results in a low permeable concrete. Boyd and Mindess [58] also conclude that the use of a lower w/c ratio is more effective than the use of a sulfate-resistant cement in offsetting the detrimental effects of sulfate attack on concrete. However, the answer to the question “which is more important w/c ratio or the type of cement” depends on the cation in the sulfate [5]. For instance, in the case of $M\bar{S}$ solutions, reducing the w/c ratio tends to aggravate the sulfate attack [2]. Al Amoudi et al. [59] attributed the inferior performance of specimens with low w/c ratio, to the dense microstructure and limited pore space for the expansive reaction products to occupy.

On the other hand, when the attack is physical rather than chemical, lower w/c ratio is reported to increase the deterioration due to higher capillarity suction. Nehdi and Hayek [60] found out that lower w/c ratio (0.3) increases the capillarity suction, due to finer pores but the total volume of the solution transported would be lower due to lower porosity and lower pore connectivity, whereas a higher w/c ratio (0.6) results in high porosity but low capillary suction. An intermediate w/c ratio (0.45)could provide a worst compromise.

Moreover, a low w/c ratio does not always result in low permeability as the workability decreases with the reduction in w/c ratio. Therefore, it is important to find out the optimum value of w/c ratio for both physical and chemical sulfate attack. Consequently, unless concrete is well compacted and dense, a low w/c ratio is useless [5].

2.4.4 Sulfate Type

In most of the studies the use of the term “sulfate attack” is focused on the effects of the SO_4^{2-} ion alone. In reality, attack by different sulfate solutions, such as the ones containing Ca, Na and Mg as the cation, proceeds differently with respect to the mechanism and the type of distress caused. This confusion may lead to improper selection of materials for situations where there is an evident danger of exposure to aggressive sulfate-bearing solutions. For example, use of low C_3A cements, which is considered to provide resistance to sodium sulfate attack, can not be appropriate when the solution contains magnesium sulfate [61]. The reactions of magnesium sulfate with the cement hydration products are shown below [2]:

$$C_xS_yH_z + xM\overline{S} + (3x + 0.5y - z)H \longrightarrow xC\overline{S}H_2 + xMH + 0.5yS_2H \tag{2.13}$$

$$4MH + SH_n \longrightarrow M_4SH_{8.5} + (n - 4.5)H \tag{2.14}$$

Unlike NH the magnesium hydroxide (MH) is insoluble and its saturated solution has a pH value of 10.5 compared to CH and NH with the pH of 12.4 and 13.5 respectively. Such a low pH destabilizes both ettringite and C-S-H [62]. Since the magnesium and calcium ions associate well with each other due to their similar radii, $M\overline{S}$ will readily react with C-S-H, thereby producing gypsum, brucite (MH) and silica gel (S_xH). This gel is less cementitious than the original C-S-H. C-S-H tends to liberate lime to raise the pH (decalcification), however the liberated lime instead of re-establishing the pH, reacts further with $M\overline{S}$ and therefore produces more gypsum and brucite. With the increase in brucite a further deleterious action of MH is taken place by reacting with S_xH, thereby producing magnesium silicate hydrate (M-S-H) which is non-cementitious [62,41,59].

Sulfate attack on concrete is primarily attributed to sodium magnesium and calcium sulfate salts. Due to the limited solubility of calcium sulfate in water at normal temperatures (approximately 1400 mg/l SO_4^{2-}) sulfate attack is normally ascribable to presence of magnesium sulfate or sodium sulfate [63].

2.4.5 Sulfate Concentration

Sulfate concentration in water is an important factor governing the extent of damage. Concrete deterioration due to sulfate attack tends to increase with the increase in concentration of sulfate solution. Concentration of 0-150ppm, 150-1500ppm, 1500-10000ppm, and above 10000ppm can be classified as mild, moderate, severe and very severe respectively [64]. Most of the work on the effect of sulfate concentration was done before the 1960s [61]. According to Biczok [65] the mechanism of reaction changes when the concentration of the solution changes. For the attack by sodium sulfate solution, at low concentration of sulfates (<1000 ppm SO_4^{2-}), the primary deposited product is ettringite, while at high concentrations (>8000 ppm SO_4^{2-}), gypsum is the main product. In the intermediate range (1000-8000 ppm SO_4^{2-}), both gypsum and ettringite are observed. In magnesium sulfate attack, ettringite production is observed at a low concentration (<4000 ppm SO_4^{2-}), a combined ettringite and gypsum formation is observed at an intermediate concentration (4000-7500 ppm SO_4^{2-}), and magnesium corrosion dominates at high concentrations (>7500 ppm SO_4^{2-}).

2.4.6 Other Factors

Exposure time, air entrainment, temperature, and chloride ions can be listed as the other factors that may affect the sulfate attack.

Aköz et al.[66], define a critical exposure time for the acceleration of deteriorating of mortar structure. Properties change slowly until the critical exposure time, but when it is exceeded properties change very rapidly and the microstructure goes to failure. This critical exposure time is reported to depend on the sulfate concentration.

Santhanam et. al. [67] states that expansion of mortar specimens in sodium sulfate solution follows a two-stage process, where an initial stage (stage 1) of very low expansion is followed by a sudden increase in the expansion (stage 2). They summarized that an increase in the temperature of the solution led to a decrease in the length of the initial period (stage 1) for the mortars stored in sodium sulfate solution. During stage 2, the rate of expansion was similar at all the temperatures. In the case of the magnesium sulfate solution, the increase in temperature led to an increase of the rate of the expansion of the mortars.

In the same study, [67] Santhanam et. al indicate that the overall expansion and the duration of stage 1 was similar for the air-entrained mortars and nonair-entrained mortars. However, the visual deterioration of the air-entrained specimens was less pronounced. The analyses of their latter test results [27] indicate that the disintegration of air entrained mortars was delayed compared to the nonair-entrained (PC) mortars. The entrained air voids provide sites for nucleation for the attack products, which leads to a reduced distress in the paste. Air voids can also help in arresting the growth of cracks due to their spherical shape. In other words, although the air-entrained mortar undergoes expansion similar to that of the PC mortar, it is able to withstand the expansive stresses better than the PC mortar.

According to Al-Amoudi [2] the concomitant presence of chlorides with the sulfate ions tends to mitigate the sodium sulfate attack due to the enhance solubility of gypsum and ettringite thereby inhibiting their expansive characteristics.

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Materials

3.1.1 Cements

An ordinary Portland cement (OPC) and five different blended cements were produced with different proportions of clinker, natural pozzolan, low-lime fly ash and limestone. The chemical analysis of the raw materials, i.e. clinker, natural pozzolan, fly ash, and limestone is given in Table 3-1. The natural pozzolan was obtained from Bilecik and Yenişehir, the low-lime fly ash was obtained from the Seyitömer power-plant, and the limestone ($CaCO_3$) was obtained from Bursa. The pozzolanic activity of the natural pozzolan was determined following the TS 25 standards as 110 kgf/cm^2 at seven days. The pozzolanic activity of the fly ash was determined following the TS EN 450 standards and computed as %78 and %86 for 28 and 90 days, respectively. Labeling of all cements and their ingredients are provided in Table 3-2. For comparison, a sulfate resistant Portland cement (SRPC) obtained a different clinker was also obtained. The chemical composition and the major compounds of all Portland cements together with their physical properties are presented in Table 3-3.

Table 3-1 Chemical composition of the materials used in blended cement production

Chemical Analysis (%)	Materials used in OPC and Blended Cement Production			
	Clinker	Natural Pozzolan	Fly Ash	Limestone
SiO_2	20.63	66.44	57.10	1.36
Al_2O_3	6.09	12.11	18.67	1.05
Fe_2O_3	3.74	1.78	9.75	0.61
CaO	65.28	5.13	4.71	52.84
SO_3	0.94	1.76	0.67	0.23
MgO	0.44	0.95	4.43	0.28
Na_2O	0.53	0.63	0.38	0.04
K_2O	0.48	2.71	2.05	0.13
LOI	0.36	7.15	2.13	41.93

Table 3-2 Material Proportions of OPC and Blended Cements

Cement		Material (%)			
Label	**Name**	**Clinker**	**NP**	**FA**	**Limestone**
OPC	CEM I 42.5 R	96.5	0.0	0.0	3.5
BC	CEM II/B-M(P-V) 42.5 N	70.8	10.8	14.9	3.5
BC_{FA}	CEM IV/A-V 32.5R	64.7	0.0	31.8	3.5
BC_{NP}	CEM IV/A-P 32.5R	66.3	30.2	0.0	3.5
BC_{NP-FA}	CEM IV/B(P-V)32.5R	61.2	22.2	13.1	3.5
BC_{FA-NP}	CEM IV/B(P-V)32.5 R	60.3	15.3	20.9	3.5

Table 3-3 Chemical Composition, Major Compounds, and Physical Properties of Cements

	OPC[a]	BC[b]	BC_{NP}[b]	BC_{FA}[b]	$BC_{NP\text{-}FA}$[b]	$BC_{FA\text{-}NP}$[b]	SRPC[a]
Chemical Analysis (%)							
SiO_2	20.12	29.17	34.57	29.43	34.38	33.58	19.65
Al_2O_3	5.75	8.73	8.48	9.84	8.96	10.02	4.27
Fe_2O_3	3.26	4.56	3.49	5.44	4.18	5.05	4.55
CaO	63.44	47.47	42.89	45.84	41.08	41.07	63.10
SO_3	2.71	2.51	2.49	2.50	2.47	2.49	0.95
MgO	0.98	1.54	1.15	1.78	1.38	1.70	2.48
Na_2O	0.43	0.62	0.56	0.55	0.59	0.62	0.63
K_2O	0.49	0.95	1.07	0.95	1.09	1.08	0.45
LOI	2.13	3.17	5.12	2.38	4.13	4.08	3.54
Compound Composition (%)							
C_3S	57.9	42.5	39.8	38.8	36.7	36.2	69.6
C_2S	13.4	9.8	9.2	9.0	8.5	8.4	3.8
C_3A	9.5	6.9	6.5	6.3	6.0	5.9	3.6
C_4AF	11.0	8.1	7.5	7.4	7.0	6.9	13.8
C_3S/C_2S	4.3	4.3	4.3	4.3	4.3	4.3	18.3
Physical Properties							
Sp. Gravity	3.18	2.87	2.89	2.75	2.78	2.75	3.21
Blaine (cm^2/gr)	3629	4062	4432	4772	5000	4676	3090
Comp. Strength (MPa)							
2 d	22.0	16.7	16.0	17.9	14.6	12.9	22.8
7 d	45.1	32.5	32.9	31.1	29.3	24.2	39.8
28 d	55.8	49.0	49.0	50.8	46.8	42.6	53.7
180 d	60.9	55.3	55.2	61.6	56.0	53.8	67.6

[a] *Compound compositions were calculated using Bogue's Equations*

[b] *Compound compositions were calculated using compound composition of OPC and mineral addition content of the cement*

3.1.2 Mixtures

Mortar mixtures were prepared using the cements mentioned previously and the Rilem Cembureau Sand meeting the requirements of ASTM C 778. In all mortar mixtures cement: sand ratio was kept constant at 1: 2.75 by weight (Figure 3-1). The flow characteristics as determined by ASTM C 1437 (Figure 3-2) and the w/c ratio of all 14 mixtures are presented in Table 3-4. As seen in Table 3-3, the mixtures can be roughly grouped into w/c of 0.485 and 0.560. OPC and SRPC mixtures were first prepared with a w/c ratio of 0.485 and the flow and consistency characteristics of these mixtures were determined. Later, the blended cement mixtures were prepared by changing the w/c ratio to obtain similar consistency of the blended cements with the previously determined consistency of the OPC and SRPC. Then the groups were completed with the same or similar w/c ratios.

Figure 3-1 Preparing mortar mixtures

Table 3-4 Flow Properties of Mortar Mixtures

Label	Group 1 (w/c = 0.485)		Group 2 (w/c ≈ 0.560)	
	w/c	Flow (%)	w/c	Flow (%)
SRPC	0.485	81	0.570	Overflow
OPC	0.485	83	0.570	Overflow
BC	0.485	26	0.540	80
BC_{FA}	0.485	32	0.550	79
BC_{NP}	0.485	20	0.550	76
BC_{NP-FA}	0.485	21	0.570	80
BC_{FA-NP}	0.485	17	0.570	79

Figure 3-2 Determining flow of mortars

From each mixture, 25x25x285 mm prismatic mortar bars and 50 mm cubes were cast (Figure 3-3). The prismatic mortar bars were used for length measurements and the cubes were used to determine the ultrasonic pulse velocity and density change, and compressive strength. After casting and finishing, the molds were covered with plastic sheets and stored for 24 hours in a moist room (relative humidity: above 95% and temperature: 35±3 ^{0}C). After the initial curing period, the specimens were demolded and cured in lime saturated water (23±1.7 ^{0}C) until the mortar cube specimens gained a compressive strength of 20 MPa as described by ASTM C 1012 (Figure 3-4).

Figure 3-3 Preparing mortar specimens

Figure 3-4 Initial curing of molds

Upon reaching a compressive strength of 20 MPa, all of mortar bar specimens and half of the cubic specimens were stored in a 5% sodium sulfate (Na_2SO_4) solution. The remaining cubic specimens were stored in lime saturated water at 23±1.7 ^{0}C as control specimens (Figure 3-5).

Figure 3-5 Storage of cubic specimens in 5% Na_2SO_4 solution and lime saturated water

3.2 Experimental Procedures and Data

3.2.1 Expansion

Expansion is measured by monitoring the length change of prismatic specimens according to ASTM C 1012 (Figure 3-6). For each mix, six bars were cast and when calculating the length change, average of them is used (Figure 3-7).

After the cubic specimens reached the compressive strength of 20 MPa or higher, initial lengths were determined and the prismatic specimens were placed into containers filled with 4 liter of a 5% (50 g/L) sodium sulfate solution (Figure 3-7).

Figure 3-6 Measuring the length change of prismatic specimens

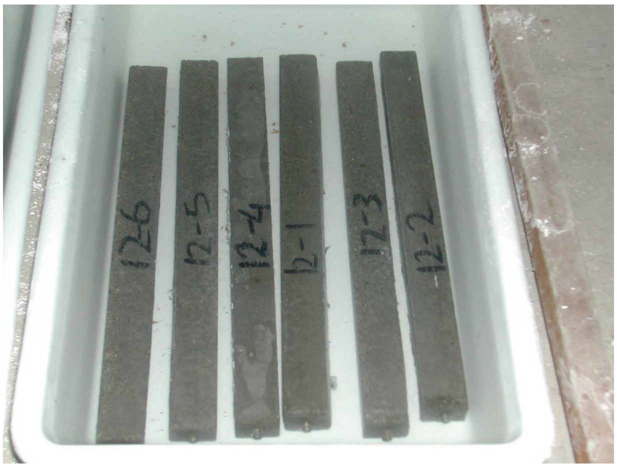
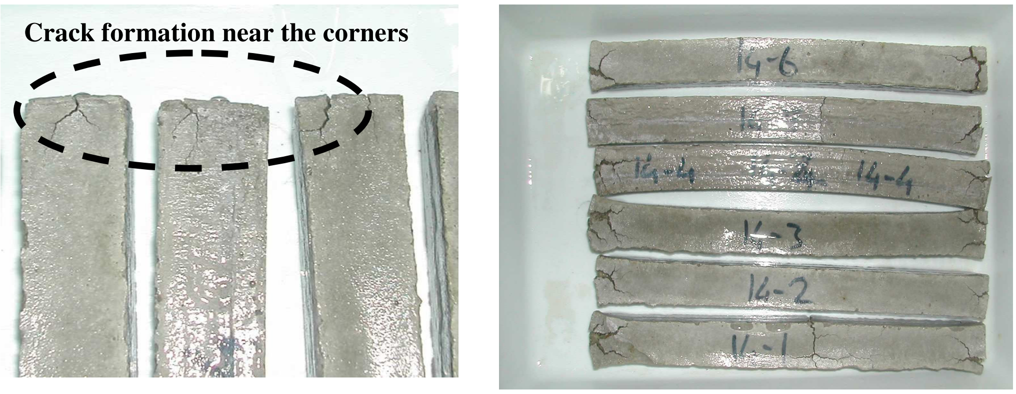


Figure 3-7 Prismatic Specimens

Length measurements of the prismatic specimens were performed at 1, 2, 3, 4, 8, 13, 15, 17, 26, 39, 52, 64 and 78 weeks after immersing the specimens into the sulfate solution. After each measurement, the sulfate solution for the bars was replaced with a fresh solution and the containers were cleaned. Containers were wrapped with stretch film and lips so that the solution would not evaporate. Mean and coefficient of variation of expansions are shown in Table 3-5 and Table 3-6 respectively. As shown in Figure 3-8 measuring the length of OPC mortar bars with a w/c ratio of 0.57 was not possible at the end of 21 weeks as the bars were detrimentally cracked. On the other hand, for the bars prepared with the cement and with a w/c of 0.485, there was visible cracking near the corners of the bars after 26 weeks as shown in Figure 3-9.



after 17 weeks **after 21 weeks**

Figure 3-8 Mortar bars prepared with OPC at w/c =0.570

after 26 weeks **after 38 weeks**

Figure 3-9 Mortar bars prepared with OPC at w/c =0.485

Table 3-5 Expansion of mortars subjected to a 5% Na_2SO_4 solution

Test Age (Weeks)	Expansion (%)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**BC_{NP-FA}**	**BC_{FA-NP}**	**SRPC**
w/c = 0.485							
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.013	0.007	0.016	0.011	0.018	0.019	0.007
2	0.023	0.011	0.021	0.019	0.022	0.020	0.010
3	0.034	0.009	0.023	0.020	0.028	0.023	0.017
4	0.040	0.007	0.025	0.020	0.027	0.022	0.018
8	0.058	0.011	0.036	0.023	0.036	0.022	0.026
13	0.088	0.021	0.049	0.025	0.044	0.029	0.039
15	0.107	0.017	0.050	0.031	0.045	0.033	0.048
17	0.140	0.022	0.054	0.035	0.049	0.032	0.057
26	0.328	0.025	0.076	0.035	0.057	0.037	0.075
39	*	0.040	0.108	0.046	0.069	0.037	0.096
52	*	0.052	0.149	0.048	0.089	0.052	0.113
64	*	0.056	0.185	0.055	0.100	0.051	0.137
78	*	0.056	0.210	0.055	0.110	0.053	0.168
w/c ≈ 0.560							
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.017	0.013	0.014	0.009	0.017	0.015	0.009
2	0.027	0.015	0.020	0.015	0.024	0.020	0.015
3	0.045	0.020	0.025	0.019	0.029	0.025	0.018
4	0.060	0.020	0.030	0.019	0.030	0.024	0.022
8	0.123	0.028	0.038	0.017	0.040	0.032	0.026
13	0.326	0.038	0.049	0.023	0.048	0.040	0.037
15	0.463	0.046	0.054	0.030	0.056	0.046	0.049
17	0.643	0.049	0.056	0.032	0.060	0.049	0.046
26	*	0.060	0.089	0.038	0.074	0.055	0.069
39	*	0.070	0.132	0.045	0.080	0.059	0.108
52	*	0.080	0.188	0.047	0.098	0.065	0.164
64	*	0.092	0.228	0.051	0.111	0.072	0.204
78	*	0.099	0.260	0.052	0.122	0.074	0.230

** Measurements could not be conducted as the specimens disintegrated*

Table 3-6 COVs of Expansion of mortars subjected to a 5% Na_2SO_4 solution

Test Age (Weeks)	Coefficient of variations of Expansions (%)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**$BC_{NP\text{-}FA}$**	**$BC_{FA\text{-}NP}$**	**SRPC**
w/c = 0.485							
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	16.7	17.2	15.2	16.0	7.4	4.5	40.5
2	7.9	4.1	14.6	7.9	6.8	4.0	24.5
3	8.0	13.6	15.3	5.7	2.8	9.8	8.7
4	2.6	18.0	18.1	5.7	2.6	13.2	13.7
8	5.4	18.1	13.9	7.8	5.6	13.2	7.3
13	7.6	10.1	9.5	7.0	2.4	5.1	5.1
15	10.3	13.5	9.6	9.0	2.3	6.8	3.9
17	13.2	10.1	9.1	10.0	3.4	7.7	4.5
26	17.6	12.2	11.7	7.8	4.8	2.8	3.5
39	*	6.4	9.9	6.0	6.4	4.7	6.4
52	*	7.8	7.8	6.9	6.0	5.4	2.6
64	*	7.8	8.7	7.1	5.9	2.8	5.6
78	*	13.9	8.8	9.2	7.1	10.7	8.2
w/c ≈ 0.560							
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	7.6	18.2	16.3	8.6	14.1	9.9	10.5
2	16.3	14.3	3.8	6.2	8.4	4.1	10.5
3	12.6	15.5	4.8	8.3	7.7	5.2	11.8
4	8.3	13.7	5.9	8.9	5.3	8.5	9.8
8	10.7	13.1	8.3	10.7	5.2	1.4	8.4
13	12.4	11.2	5.4	4.2	3.6	5.7	8.4
15	11.6	9.2	7.5	12.1	2.4	5.6	5.7
17	10.7	9.2	5.1	8.5	6.7	4.3	6.7
26	*	6.5	9.3	6.7	2.5	4.8	6.5
39	*	6.4	6.6	5.8	3.4	4.7	7.3
52	*	6.1	5.6	5.6	3.4	4.8	9.2
64	*	6.4	5.5	5.6	3.5	3.5	8.9
78	*	8.2	6.1	7.6	4.3	2.8	9.5

** Measurements could not be conducted as the specimens disintegrated*

3.2.2 Compressive Strength

Cubic specimens were used for determining the compressive strength. In order to determine the time needed for the cement mortars to reach the 20MPa compressive strength, trial mixtures with 12 specimens were prepared. Three specimens were then tested each day to determine the number of days needed to reach the strength of 20MPa. Later on, for each mix minimum 51 cubic specimens were prepared. After the number of days that were previously determined, three of them were tested first to find out the strength. Then specimens numbered from 4 to 27 were soaked into 5 percent sodium sulfate solution and the ones from 28 to 51 were remained in lime saturated water as control specimens (Figure 3-10, Figure 3-5).

Figure 3-10 Cubic specimens

Compressive strength measurements of the cubic specimens were performed at 1, 4, 26 and 52 weeks after immersing the specimens into the sulfate solution. The test was conducted in accordance with ASTM C 109/C 109M-01 using a universal testing machine (Figure 3-11).

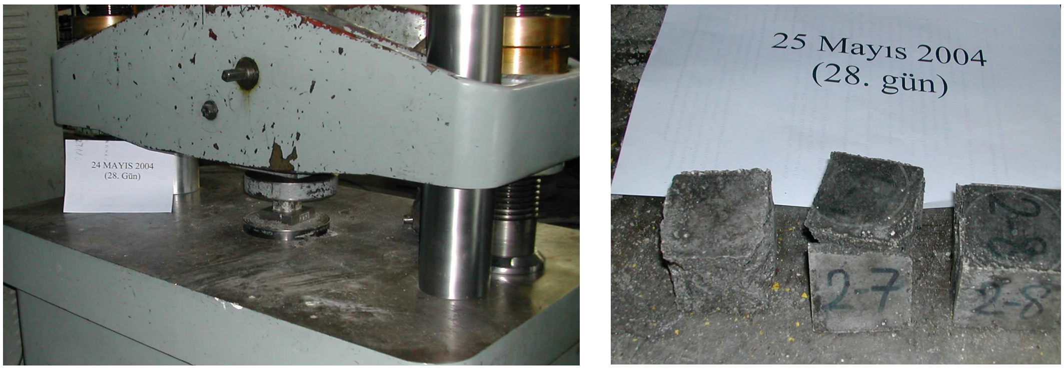


Figure 3-11 Determination of compressive strength

The mean compressive strengths of cubic specimens subjected to 5% sodium sulfate solution and lime saturated water are given below in Table 3-7 and Table 3-8. Coefficients of variations are also given in Table 3-9 and Table 3-10.

Table 3-7 Compressive strength of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Mean Compressive Strength (MPa)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**BC_{NP-FA}**	**BC_{FA-NP}**	**SRPC**
w/c = 0.485							
0	22.3	22.2	19.5	19.4	20.1	18.6	19.1
4	44.8	39.7	43.9	33.2	36.1	39.9	47.7
26	47.3	48.3	47.0	54.4	56.8	50.0	62.1
52	33.4	46.1	48.0	49.8	55.4	51.5	60.8
w/c ≈ 0.560							
0	21.9	21.5	21.1	20.7	19.1	19.3	20.1
4	45.3	45.0	35.0	49.4	39.1	38.8	45.8
26	37.7	45.9	47.1	53.2	39.0	44.3	54.4
52	*	51.6	47.9	54.7	42.7	34.9	63.6

** Measurements could not be conducted as the specimens disintegrated*

Table 3-8 Compressive strength of mortars subjected to lime saturated water

Test Age (Weeks)	Mean Compressive Strength (MPa)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**BC_{NP-FA}**	**BC_{FA-NP}**	**SRPC**
w/c = 0.485							
0	22.3	22.2	19.5	19.4	20.1	18.6	19.1
4	47.8	38.4	35.6	30.5	32.9	37.0	43.9
26	57.5	44.9	41.0	53.0	50.7	45.7	62.0
52	69.9	47.4	50.1	60.2	62.2	46.9	68.4
w/c ≈ 0.560							
0	21.9	21.5	21.1	20.7	19.1	19.3	20.1
4	39.1	46.0	31.1	49.6	30.6	33.9	47.2
26	47.3	49.0	43.6	49.1	42.7	43.7	58.3
52	50.6	58.9	52.7	54.9	48.7	54.7	67.5

Table 3-9 COVs of Compressive strength of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Coefficient of variations (%)						
	OPC	BC	BC_{NP}	BC_{FA}	BC_{NP-FA}	BC_{FA-NP}	SRPC
w/c = 0.485							
0	6.1	1.8	8.8	7.1	19.7	0.1	9.0
4	4.5	8.2	3.9	4.2	5.2	3.8	5.4
26	6.3	0.4	2.7	0.9	4.0	1.9	3.6
52	7.2	8.7	7.0	6.7	7.0	2.4	5.2
w/c ≈ 0.560							
0	4.7	3.2	9.4	10.6	10.4	0.7	0.5
4	1.0	1.6	14.5	2.9	4.6	6.8	2.9
26	*	13.1	1.4	0.4	1.1	14.3	3.7
52	*	4.7	4.8	5.9	0.7	8.6	0.5

** Measurements could not be conducted as the specimens disintegrated*

Table 3-10 COVs of Compressive strength of mortars subjected to lime saturated water

Test Age (Weeks)	Coefficient of variations (%)						
	OPC	BC	BC_{NP}	BC_{FA}	BC_{NP-FA}	BC_{FA-NP}	SRPC
w/c = 0.485							
0	6.1	1.8	8.8	7.1	19.7	0.1	9.0
4	4.9	3.6	13.4	6.0	0.7	3.3	3.7
26	14.6	5.6	24.3	9.0	9.8	0.9	2.8
52	3.2	0.9	9.9	6.0	7.4	2.9	8.1
w/c ≈ 0.560							
0	4.7	3.2	9.4	10.6	10.4	8.1	0.5
4	15.3	3.3	7.8	17.0	12.1	4.6	3.1
26	19.3	15.1	10.9	2.5	1.0	21.9	13.8
52	8.8	15.2	5.2	7.3	5.5	1.3	3.4

3.2.3 Ultrasonic Pulse Velocity

Ultrasonic measurements are used to determine material properties, to detect defects, and to assess deterioration. Velocity of waves in the solids is higher than in the air, therefore, ultrasonic pulse velocities in the specimens give information about the microstructure of the specimens. Therefore an idea about the sulfate resistance of the specimens can be obtained indirectly by this method. As it is a non-destructive test method, a long term monitoring on the same specimens is possible.

This test is conducted on the last six specimens both in the sulfate solution and lime saturated water. Two 150 kHz transducers, one transducer for transmitting the pulse, and the other for capturing the ultrasonic waves were used for direct ultrasonic pulse velocity measurements (UPV) as shown in Figure 3-12. The time between transmission and capturing the waves was recorded and dividing the width of the cube by that time, ultrasonic pulse velocity was calculated. Measurement was done in two dimensions for the smooth surfaces of the cube, and their average is calculated. Ultrasonic pulse velocity measurements of mortars are given in Table 3-11 and Table 3-12. Coefficients of variations are also given in Table 3-13 and Table 3-14.

Figure 3-12 Ultrasonic pulse velocity measurement

Table 3-11 Ultrasonic pulse velocity of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Mean Ultrasonic Pulse Velocity (m/s)						
	OPC	BC	BC$_{NP}$	BC$_{FA}$	BC$_{NP\text{-}FA}$	BC$_{FA\text{-}NP}$	SRPC
w/c = 0.485							
0	3825	4192	4131	4198	4555	4019	4359
1	4096	4549	4463	4559	4864	4468	4319
2	4394	4668	4611	4473	4734	4552	4337
3	4957	4726	4687	4526	4772	4594	4980
4	5022	4741	4705	4491	4772	4619	5047
52	4595	5038	5034	4425	5240	4884	4635
w/c ≈ 0.560							
0	4419	4152	4333	4285	3938	3904	4111
1	4505	4044	4588	4461	3945	3983	4411
2	4573	4150	4523	4571	4076	4066	4551
3	4612	4783	4586	4578	4580	4595	4582
4	4619	4852	4595	4606	4647	4633	4600
52	*	4472	4503	4446	4341	4267	4971

** Measurements could not be conducted as the specimens disintegrated*

Table 3-12 Ultrasonic pulse velocity of mortars subjected to lime saturated water

Test Age (Weeks)	Mean Ultrasonic Pulse Velocity (m/s)						
	OPC	BC	BC$_{NP}$	BC$_{FA}$	BC$_{NP\text{-}FA}$	BC$_{FA\text{-}NP}$	SRPC
w/c = 0.485							
0	3867	4187	4102	4408	4493	3995	3820
1	4329	4559	4428	4793	4790	4427	4247
2	4896	4642	4578	4686	4678	4534	4887
3	4972	4707	4666	4745	4726	4561	4947
4	5068	4725	4713	4748	4756	4603	5046
52	4633	5222	5178	4851	5479	5049	4670
w/c ≈ 0.560							
0	4321	4143	4368	4289	3652	3707	4058
1	4445	4049	4605	4427	3994	4001	4433
2	4553	4148	4532	4563	4510	4534	4566
3	4594	4751	4608	4598	4592	4630	4600
4	4622	4807	4626	4633	4641	4658	4653
52	5085	4448	4673	4734	4368	4349	5144

Table 3-13 COVs of UPV of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Coefficient of Variations (%)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**BC_{NP-FA}**	**BC_{FA-NP}**	**SRPC**
w/c = 0.485							
0	0.32	0.88	0.66	9.95	1.05	1.13	0.56
1	0.29	1.08	0.35	9.82	1.11	0.45	0.64
2	0.48	0.91	0.81	9.45	0.78	0.74	0.88
3	0.72	0.65	0.59	9.53	0.90	0.74	0.28
4	0.28	0.39	0.71	9.60	0.62	0.94	0.25
52	1.09	0.98	0.97	9.95	0.23	0.80	0.76
w/c ≈ 0.560							
0	0.54	1.48	0.45	1.11	1.96	1.12	0.76
1	0.30	0.80	0.51	0.59	1.03	0.78	0.91
2	0.24	1.43	0.38	0.49	0.31	0.53	0.86
3	0.38	0.44	1.70	0.45	0.40	0.73	0.63
4	0.32	0.60	0.83	0.83	0.27	0.35	0.94
52	*	0.62	1.01	1.58	0.50	0.76	0.75

** Measurements could not be conducted as the specimens disintegrated*

Table 3-14 COVs of UPV of mortars subjected to lime saturated water

Test Age (Weeks)	Coefficient of Variations (%)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**BC_{NP-FA}**	**BC_{FA-NP}**	**SRPC**
w/c = 0.485							
0	0.89	1.22	0.53	0.98	1.07	1.53	0.80
1	0.50	1.07	0.21	0.51	0.94	1.21	0.76
2	0.42	0.89	0.39	1.08	0.68	1.16	0.64
3	0.81	0.88	0.29	1.30	0.92	0.99	0.41
4	0.40	1.15	0.44	0.61	0.95	1.48	0.35
52	0.44	0.90	0.21	1.05	0.42	1.05	0.46
w/c ≈ 0.560							
0	0.30	1.05	0.56	0.79	0.55	0.86	1.01
1	0.57	1.43	0.79	1.11	0.13	0.94	0.48
2	0.34	1.03	0.53	0.99	0.48	0.94	0.56
3	0.53	0.43	0.58	0.78	0.27	0.47	0.67
4	0.51	0.65	0.50	0.68	0.67	0.32	0.48
52	0.53	0.43	1.07	1.03	1.65	1.00	0.71

In Table 3-11 and Table 3-12 only 1st, 2nd, 3rd, 4th and 52nd week results are given. Ultrasonic pulse velocity of the mortars between 4th and 52nd weeks, are not given in the tables although they were conducted. The transducers and cables were broken down several times between these weeks. After each repairing process a significant difference was observed between the two measurements carried out before and after the repairing. The results are inconsistent with each other. It is believed that these inconsistencies are resulted from shifting of the device alignment. 52nd week results are also inconsistent with first four week results, however some comments can be inferred from the 52nd week results as they are consistent with each other.

3.2.4 Density

All three dimensions of the cubic specimens were measured using a caliper of 0.01 mm. resolution and they were weighted with a balance of 0.01 gr. at 1, 2, 3, 4, 8, 13, 15, 17, 26, 39 and 52 weeks after immersing the specimens into the sulfate solution (Figure 3-13). The density of the specimens and coefficient of variations are given in Table 3-15, Table 3-16, Table 3-17 and Table 3-18.

Figure 3-13 Weight and dimensional measurements of cubic specimens

Table 3-15 Density of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Density (g/cm^3)						
	OPC	**BC**	**BC$_{NP}$**	**BC$_{FA}$**	**BC$_{NP-FA}$**	**BC$_{FA-NP}$**	**SRPC**
w/c = 0.485							
0	2.237	2.186	2.193	2.173	2.202	2.168	2.251
1	2.248	2.205	2.201	2.184	2.210	2.183	2.261
2	2.250	2.201	2.203	2.187	2.212	2.185	2.263
3	2.252	2.202	2.203	2.187	2.213	2.184	2.262
4	2.251	2.200	2.203	2.188	2.215	2.185	2.264
8	2.255	2.204	2.203	2.189	2.215	2.186	2.267
13	2.260	2.205	2.207	2.187	2.216	2.181	2.271
15	2.260	2.204	2.208	2.190	2.215	2.185	2.269
17	2.260	2.204	2.207	2.189	2.210	2.184	2.269
26	2.268	2.207	2.211	2.192	2.216	2.187	2.271
52	2.289	2.201	2.214	2.191	2.222	2.197	2.274
w/c ≈ 0.560							
0	2.215	2.166	2.179	2.173	2.153	2.146	2.231
1	2.226	2.180	2.187	2.178	2.162	2.154	2.239
2	2.229	2.183	2.190	2.184	2.165	2.156	2.242
3	2.231	2.182	2.190	2.185	2.164	2.156	2.243
4	2.232	2.183	2.192	2.186	2.163	2.155	2.243
8	2.239	2.185	2.193	2.186	2.165	2.156	2.247
13	2.244	2.186	2.197	2.184	2.165	2.158	2.248
15	2.242	2.185	2.202	2.188	2.165	2.157	2.247
17	2.248	2.186	2.192	2.187	2.165	2.155	2.246
26	2.267	2.187	2.197	2.189	2.166	2.158	2.253
52	*	2.187	2.206	2.196	2.166	2.161	2.263

** Measurements could not be conducted as the specimens disintegrated*

Table 3-16 Density of mortars subjected to lime saturated water

Test Age (Weeks)	Density (g/cm^3)						
	OPC	**BC**	**BC$_{NP}$**	**BC$_{FA}$**	**BC$_{NP\text{-}FA}$**	**BC$_{FA\text{-}NP}$**	**SRPC**
w/c = 0.485							
0	2.241	2.185	2.198	2.175	2.204	2.156	2.226
1	2.251	2.195	2.201	2.184	2.208	2.165	2.235
2	2.253	2.196	2.204	2.186	2.211	2.167	2.235
3	2.253	2.196	2.204	2.188	2.212	2.167	2.236
4	2.256	2.196	2.205	2.189	2.213	2.168	2.238
8	2.261	2.201	2.205	2.191	2.216	2.171	2.241
13	2.265	2.202	2.210	2.189	2.217	2.168	2.246
15	2.265	2.202	2.210	2.193	2.217	2.172	2.246
17	2.266	2.196	2.210	2.193	2.213	2.172	2.247
26	2.268	2.204	2.214	2.195	2.220	2.174	2.250
52	2.271	2.211	2.217	2.200	2.225	2.175	2.256
w/c ≈ 0.560							
0	2.203	2.169	2.176	2.170	2.144	2.130	2.240
1	2.212	2.179	2.178	2.176	2.148	2.136	2.246
2	2.213	2.182	2.181	2.178	2.150	2.137	2.246
3	2.216	2.181	2.182	2.180	2.150	2.138	2.248
4	2.216	2.182	2.183	2.181	2.152	2.139	2.248
8	2.221	2.184	2.185	2.183	2.154	2.141	2.252
13	2.223	2.186	2.187	2.181	2.156	2.143	2.254
15	2.219	2.187	2.194	2.185	2.156	2.143	2.254
17	2.223	2.186	2.182	2.186	2.156	2.143	2.253
26	2.227	2.188	2.188	2.187	2.158	2.145	2.256
52	2.233	2.191	2.196	2.190	2.162	2.144	2.261

Table 3-17 COVs of Density of mortars subjected to 5% Na_2SO_4 solution

Test Age (Weeks)	Coefficient of Variations (%)						
	OPC	BC	BC_{NP}	BC_{FA}	BC_{NP-FA}	BC_{FA-NP}	SRPC
w/c = 0.485							
0	0.38	0.71	0.81	0.26	0.67	0.24	0.41
1	0.37	0.73	0.80	0.25	0.67	0.24	0.42
2	0.37	0.72	0.81	0.25	0.66	0.24	0.42
3	0.38	0.73	0.82	0.27	0.66	0.23	0.42
4	0.36	0.71	0.80	0.26	0.65	0.24	0.42
8	0.36	0.69	0.81	0.25	0.65	0.26	0.43
13	0.34	0.70	0.81	0.26	0.66	0.26	0.49
15	0.35	0.72	0.81	0.25	0.66	0.25	0.43
17	0.36	0.72	0.80	0.27	0.69	0.27	0.43
26	0.35	0.71	0.80	0.26	0.68	0.27	0.44
52	0.33	0.78	0.80	0.31	0.71	0.30	0.43
w/c ≈ 0.560							
0	1.00	0.45	0.55	0.74	0.74	0.22	0.60
1	1.00	0.45	0.51	0.74	0.74	0.21	0.57
2	1.01	0.46	0.51	0.75	0.76	0.22	0.62
3	1.01	0.45	0.50	0.74	0.75	0.22	0.63
4	1.01	0.44	0.50	0.75	0.74	0.20	0.63
8	0.99	0.46	0.51	0.75	0.75	0.22	0.64
13	0.97	0.45	0.51	0.75	0.74	0.22	0.65
15	0.96	0.42	0.50	0.75	0.77	0.22	0.65
17	0.97	0.43	0.52	0.75	0.75	0.24	0.66
26	0.94	0.43	0.52	0.74	0.76	0.24	0.70
52	*	0.45	0.50	0.75	0.76	0.22	0.76

** Measurements could not be conducted as the specimens disintegrated*

Table 3-18 COVs Density of mortars subjected to lime saturated water

Test Age (Weeks)	Coefficient of Variations (%)						
	OPC	**BC**	**BC_{NP}**	**BC_{FA}**	**$BC_{NP\text{-}FA}$**	**$BC_{FA\text{-}NP}$**	**SRPC**
w/c = 0.485							
0	0.26	0.68	0.29	0.73	0.42	0.76	0.58
1	0.26	0.69	0.30	0.71	0.40	0.76	0.57
2	0.25	0.68	0.30	0.71	0.41	0.73	0.57
3	0.26	0.70	0.30	0.70	0.41	0.73	0.57
4	0.24	0.70	0.33	0.70	0.41	0.74	0.56
8	0.25	0.69	0.29	0.70	0.41	0.74	0.57
13	0.24	0.69	0.30	0.69	0.40	0.73	0.57
15	0.25	0.70	0.31	0.69	0.40	0.73	0.57
17	0.24	0.71	0.29	0.69	0.40	0.75	0.57
26	0.25	0.71	0.29	0.69	0.43	0.74	0.57
52	0.26	0.71	0.28	0.69	0.40	0.73	0.56
w/c ≈ 0.560							
0	0.98	0.36	0.55	0.59	0.45	0.75	0.74
1	0.99	0.37	0.56	0.59	0.45	0.76	0.72
2	0.99	0.38	0.56	0.60	0.45	0.76	0.74
3	0.98	0.38	0.57	0.59	0.44	0.75	0.73
4	0.98	0.38	0.58	0.59	0.45	0.76	0.73
8	0.99	0.38	0.57	0.59	0.46	0.77	0.71
13	0.97	0.38	0.57	0.60	0.45	0.77	0.70
15	0.97	0.38	0.57	0.60	0.45	0.76	0.71
17	0.96	0.37	0.56	0.60	0.48	0.76	0.70
26	0.97	0.38	0.57	0.61	0.46	0.76	0.69
52	0.97	0.33	0.57	0.61	0.52	0.80	0.69

3.2.5 SEM and XRD Analysis of the Cement Pastes

In order to investigate the products of hydration, scanning electron microscopy analyses (SEM) of cement pastes were performed. The cement pastes were prepared according to ASTM C 305 and subjected to a 5% Na_2SO_4 solution for 52 weeks before the analyses.

To confirm the SEM results and semi-quantitatively identify the products of hydration the cement pastes were examined by XRD (Philips x'pert PW 3040) after 52 weeks of immersion in a 5% Na_2SO_4 solution.

CHAPTER 4

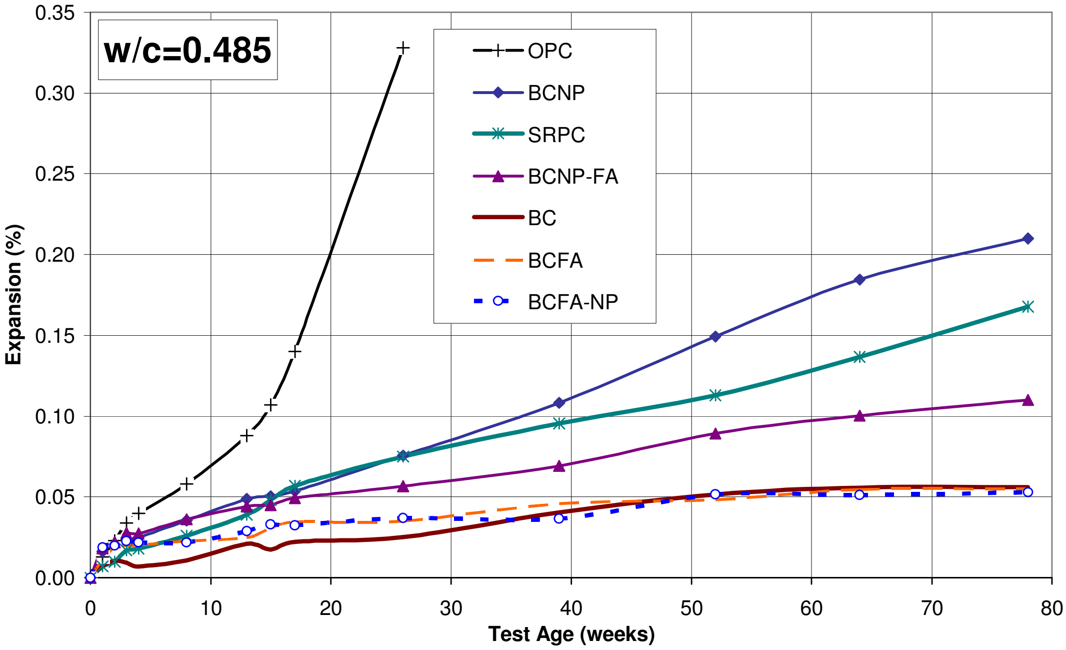
DISCUSSION OF RESULTS

4.1 Expansion

The results of the expansion of the mortar bars subjected to a 5% Na_2SO_4 solution are shown in Figure 4-1 for both w/c ratios. Cements satisfying the expansion limits of 0.10% and 0.05% at 26 weeks are considered as moderate sulfate resistant and high sulfate resistant, respectively by ASTM Subcommittee C01-29 [68]. Based on these limits and Figure 4-1;

- OPC is not suitable for sulfate environments at both w/c.
- For a w/c ratio of 0.485, SRPC, BC_{NP} and BC_{NP-FA} can be classified as moderate sulfate resistant cements and BC, BC_{FA-NP}, and BC_{FA} can be classified as high sulfate resistant cements.
- For a w/c ratio of 0.560, moderate sulfate resistant cements are SRPC, BC_{NP}, BC_{NP-FA}, BC_{FA-NP} and BC, and the only high sulfate resistant cement is BC_{FA}

Therefore, it can be claimed that all blended cements showed nearly the same or some even better performance when compared to the SRPC used in this study. As discussed earlier, one of the most important properties affecting the sulfate resistance of cements is its composition. C_3A, one of the compounds of cement which causes the formation of ettringite thus leading to harmful expansions in hardened cement pastes, is one of the most important parameters affecting the performance of cements.



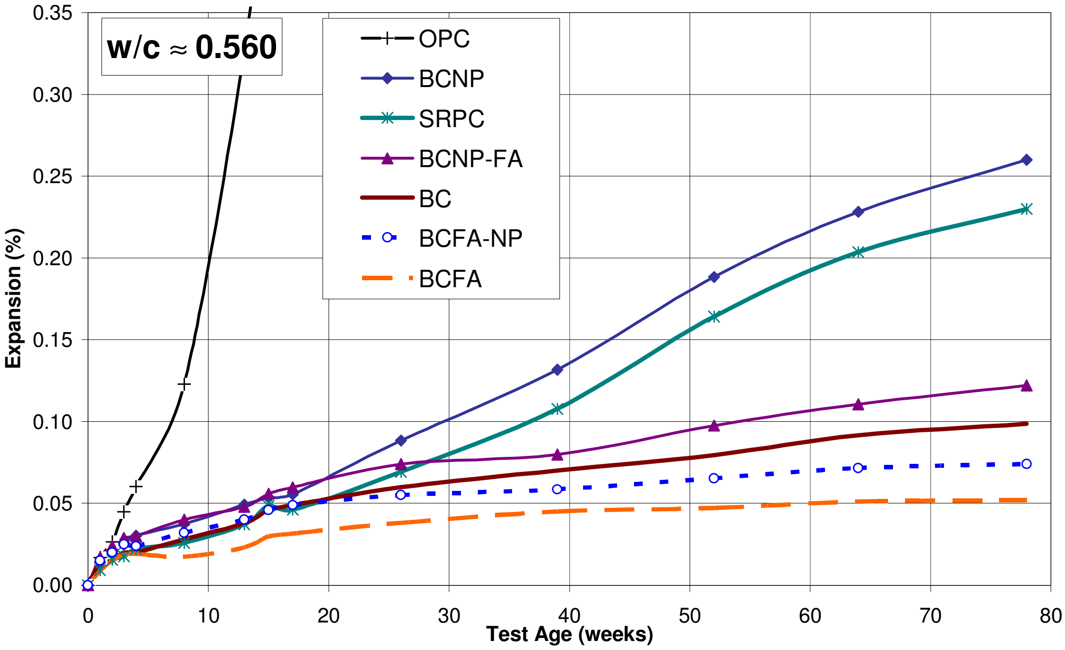


Figure 4-1 Expansion of mortar bars

Using Bogue's equations the amount of C_3A present in SRPC and OPC can be calculated as 3.6% and 9.5% respectively. As a result of the expansions observed after one and a half year, the SRPC expansions were much lower when compared to OPC. The compound composition of blended cements could not be directly calculated by Bogue's equations. However, using the clinker and mineral admixture additions, the amount of C_3A was approximately calculated and seemed to change between 5.9% and 6.9%. The blended cements performed quite satisfactorily even better than SRPC. Therefore it can be concluded that for blended cements consideration of C_3A only, will not be the pinpointing parameter. The beneficial effects like the consumption of CH by pozzolanic reaction or pore refinement must also be considered.

The amount of C_3S and C_2S will also affect the sulfate resistance of cements. Usually as the amount of C_3A reduces, C_3S/C_2S ratio increases and as this ratio increases the amount of CH produced by hydrolysis of these two compounds increases. As explained earlier, CH reacts with the sulfates attacking concrete producing gypsum. The produced gypsum will cause expansion and strength reduction by time in the already hardened concrete. As can be calculated from the data provided in Table 3-3, the SRPC had the highest C_3S/C_2S (18.3) ratio. This high value can be considered as a cause for the relatively poor performance of the SRPC. The results of this study were also inline with the findings of Stephens and Carrasquillo [69], where they recommended testing the sulfate resistant Portland cements with a C_3A content of 4 to 5 percent before suggesting them to a high sulfate environment.

In order to better observe the effect of w/c ratio on the expansions of different cement types, Figure 4-2, which shows the expansions of mortars for different w/c ratios in the same graphs, is provided. When the solid and dashed lines corresponding to the w/c ratios of 0.560 and 0.485 respectively are compared, it can be seen that sulfate resistance of cements are increased with lowering the w/c from 0.560 to 0.485. It is obvious that change in w/c ratio is a factor that affects the expansion of mortar bars. However, this effect is not the same for all cements. The sulfate resistance of OPC is highly sensitive to w/c ratio, compared with other types of cements where changing the w/c ratio does not affect the expansion of BC_{FA} mortars.

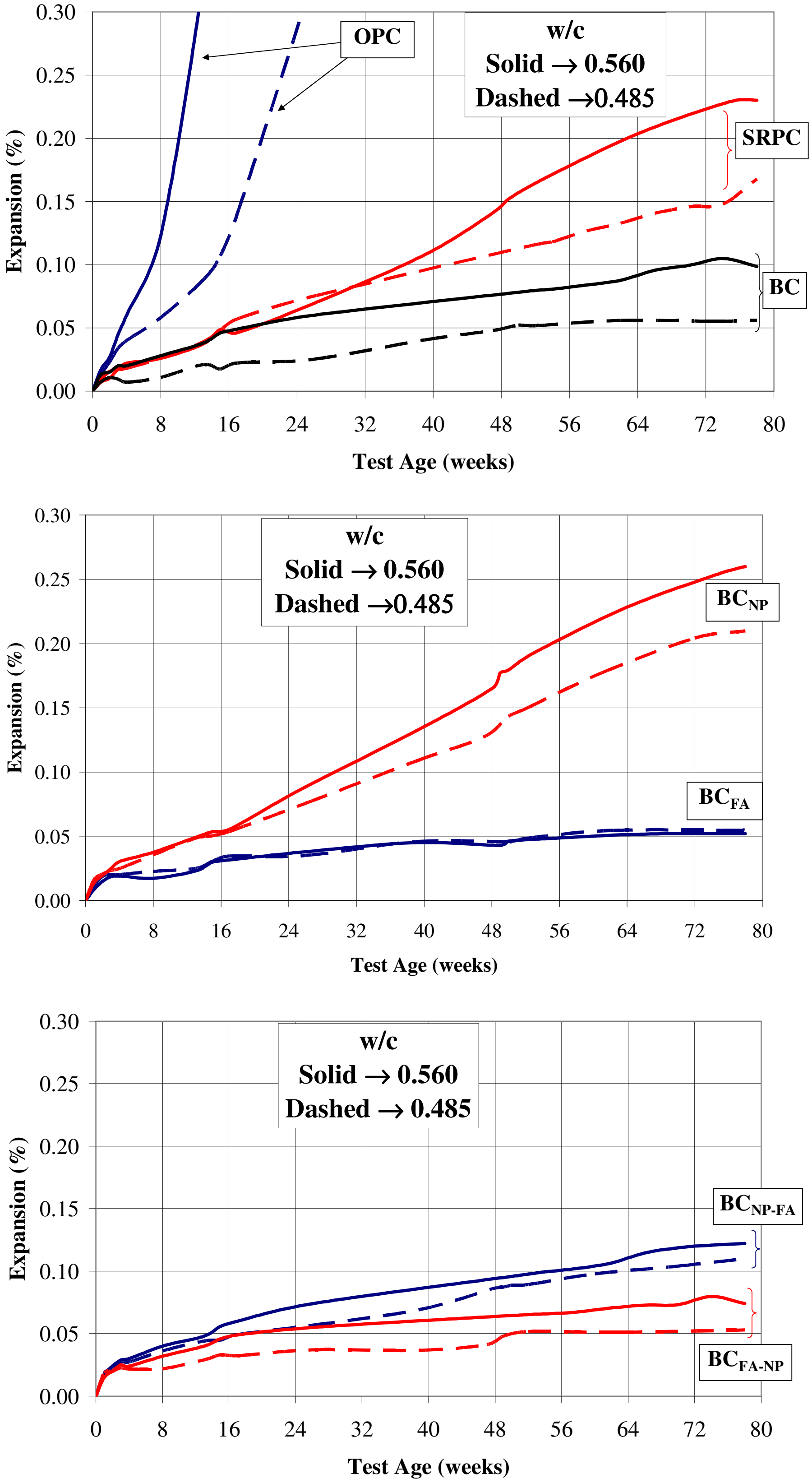


Figure 4-2 Effect of w/c on the expansion of mortar bars

Cement type is another factor in determining the performance of cement in a sulfate environment. In order to quantify the importance of w/c ratio and cement composition, amounts of C_3A and $2C_3A + C_4AF$ are plotted against the 26th week expansions as shown in Figure 4-3. As seen from these two graphs, effects of chemical composition and w/c on the sulfate resistance can now be differentiated. For lower C_3A and $2C_3A + C_4AF$ amounts, the effect of w/c or in general permeability is lower. As the amounts of these compounds are increased the effect of w/c or permeability becomes more pronounced.

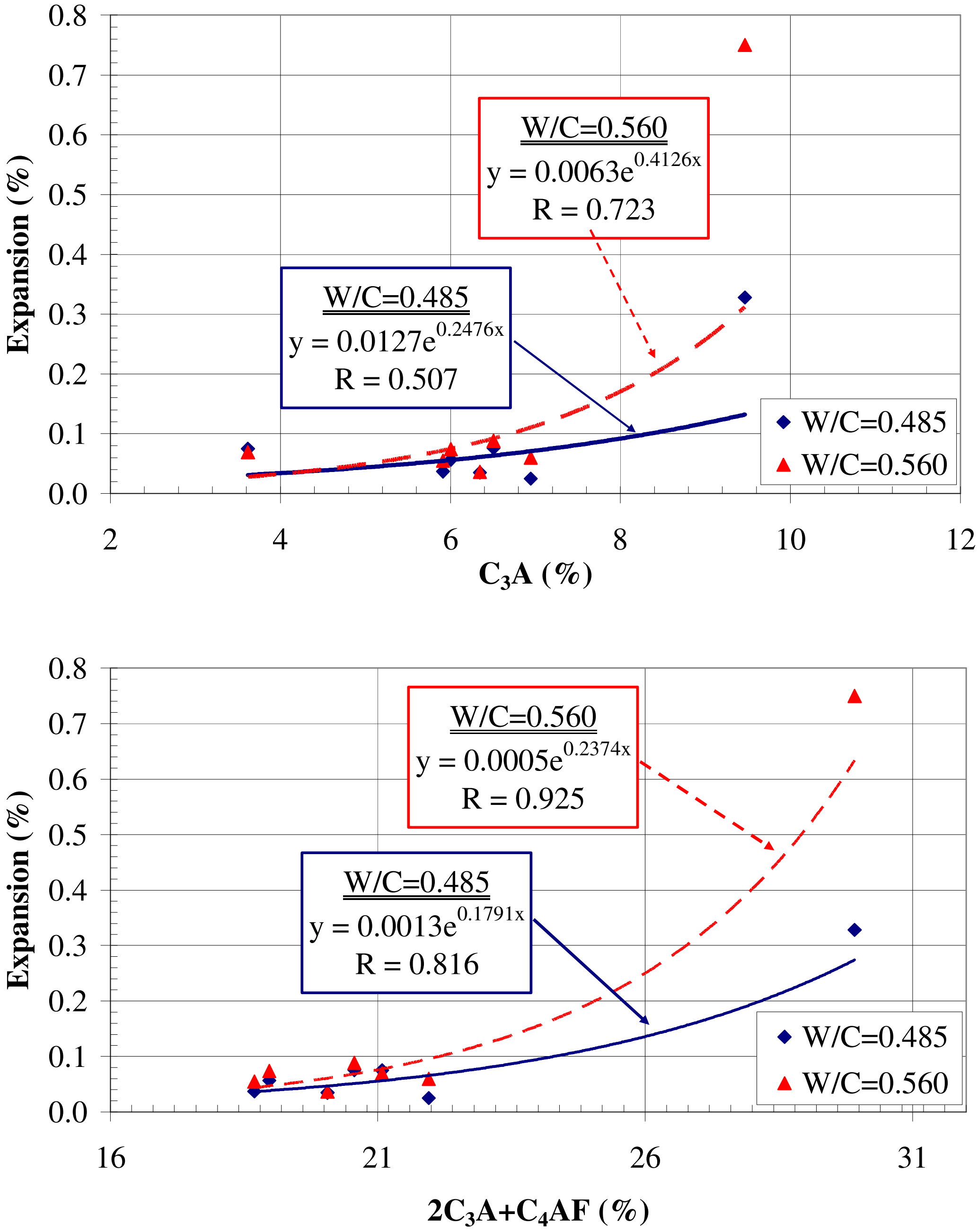


Figure 4-3 Effect of chemical composition and w/c on sulfate resistance

In order to quantify the effect of w/c ratio on the increase in expansion at a given age, when the w/c ratio is increased from 0.485 to 0.560 was calculated for all cement mortars as shown in Figure 4-4. (Note that in this figure for OPC cement mortars extrapolation of the data towards 26 weeks were conducted as the OPC cement mortars cracked before 26 weeks). As seen from this figure the effect of w/c ratio is relatively lower for all blended cements. However, expansion measurements did not dictate any trend as the age of exposure changed from 26 to 78-weeks.

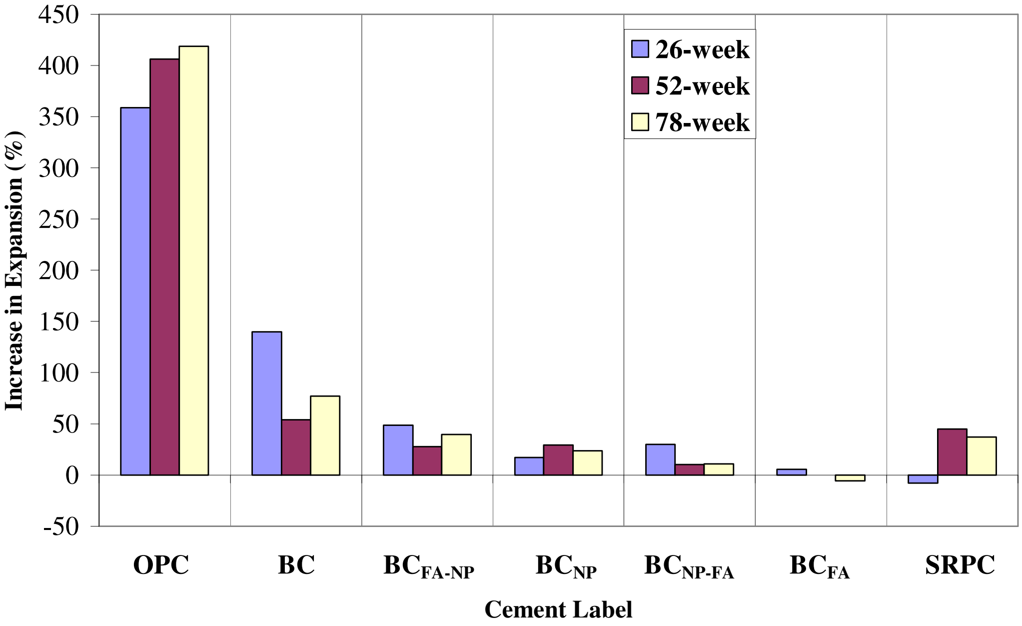


Figure 4-4 Change in the expansion of mortar bars when w/c ratio is increased from 0.485 to 0.560

Ramyar and Inan [40], carried out a multiple regression analyses and found out a relationship between 15-week-expansion and C_3A content, C_3S/C_2S ratio, mineral admixture substitution level and concentration of sodium sulfate solution as follows:

$$E = \frac{A^{-0.1227} S^{0.3995} C^{0.5698}}{(100+K)^{1.0631}} \tag{4.1}$$

where E is the 15-week-expansion upon exposure the sulfate solution (%), A is the C_3A content of the cementitious system (%), S the C_3S/C_2S ratio of the cement (%), C the concentration of sodium sulfate solution (%), and K the mineral admixture substitution level (%).Experimental and calculated 15-week-expansion values using the abovementioned equation of our study are given in Table 4-1.

Table 4-1 Experimental and calculated 15-week-expansion values

	C_3A	C_3S/C_2S	NP+FA	15 week exp (%) (experimental ♠)	15 week exp (%) (calculated)
OPC	9.5	4.3	0.0	0.107	0.051
BC	6.9	4.3	25.7	0.046	0.041
BC_{NP}	6.5	4.3	30.2	0.054	0.040
BC_{FA}	6.3	4.3	31.8	0.030	0.040
BC_{NP-FA}	6.0	4.3	35.3	0.056	0.039
BC_{FA-NP}	5.9	4.3	36.2	0.046	0.039
SRPC	3.6	18.3	0.0	0.048	0.102

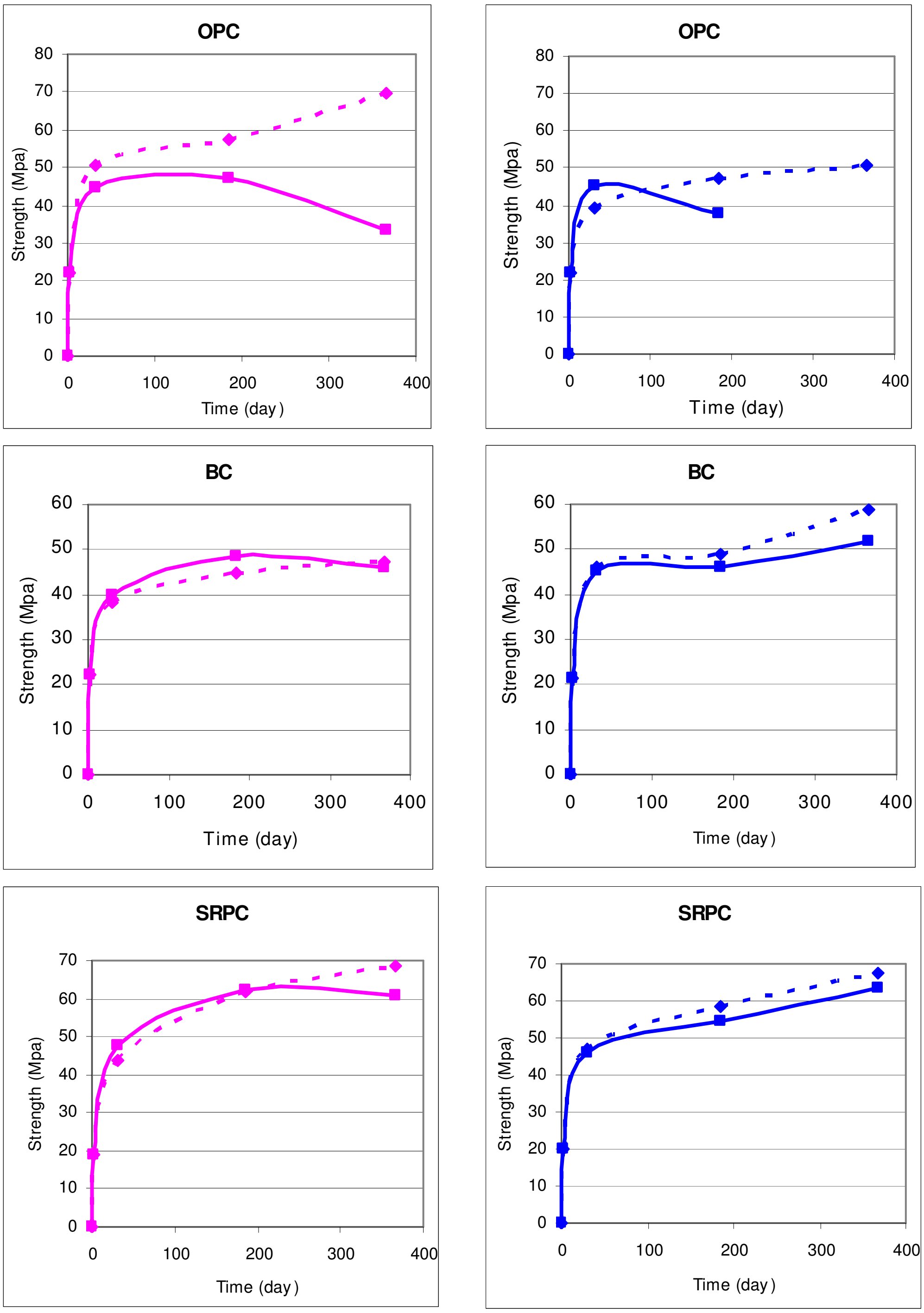
♠ *Experiments were conducted according to ASTM C 1012*

As can be seen from Table 4-1, the estimated expansion values for blended cements are relatively in good agreement with the experimental counterparts. On the other hand for cements without any mineral additives, the estimation of the expansion is relatively poor. The calculated expansion of OPC is very low whereas the calculated expansion of SRPC is very high compared to the experimental results. Therefore, it can be concluded that the abovementioned equation could be used with care only to estimate the expansion of blended cements subjected to sulfate attack.

4.2 Compressive Strength

In Figure 4-5, Figure 4-6, and Figure 4-7 all compressive strengths of mortars subjected to sulfates and lime saturated water are provided. The graphs at left and right of the figures belong to the mortars which have a w/c ratio of 0.485 and 0.560, respectively. In those graphs, the solid lines show the strength of mortars stored in 5% sulfate solution and the dashed lines show the ones stored in lime saturated water.

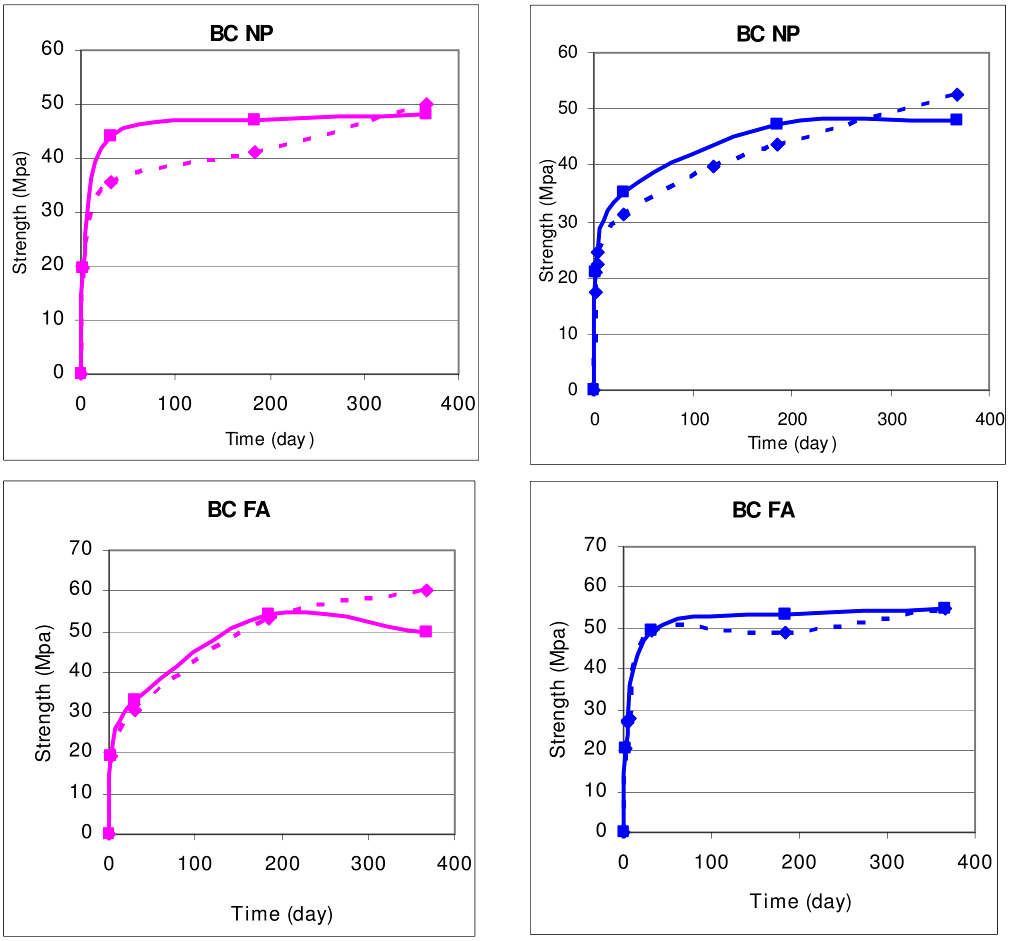
It can be seen from Figure 4-5 that the strength of OPC in sulfate solution is declining much more marginally for both w/c ratios compared to the blended cements and the SRPC. Moreover, for the w/c ratio of 0.560, the 52nd-week-strength of OPC could not be observed as the specimens have deteriorated completely before 52 weeks. This is an expected result because ettringite formation leading to an expansion, cracking and drastic reduction in the strength, and gypsum formation leading to a reduction of stiffness and strength were the major forms of deterioration of mortars containing cements with a high C_3A content [3,59]. Consequently, OPC is not suitable for sulfate environments at both w/c ratios as it was also concluded from the expansion results.



w/c=0.485
Solid→5% sulfate solution
Dashed→lime saturated water

w/c≈0.560
Solid→ 5% sulfate solution
Dashed→lime saturated water

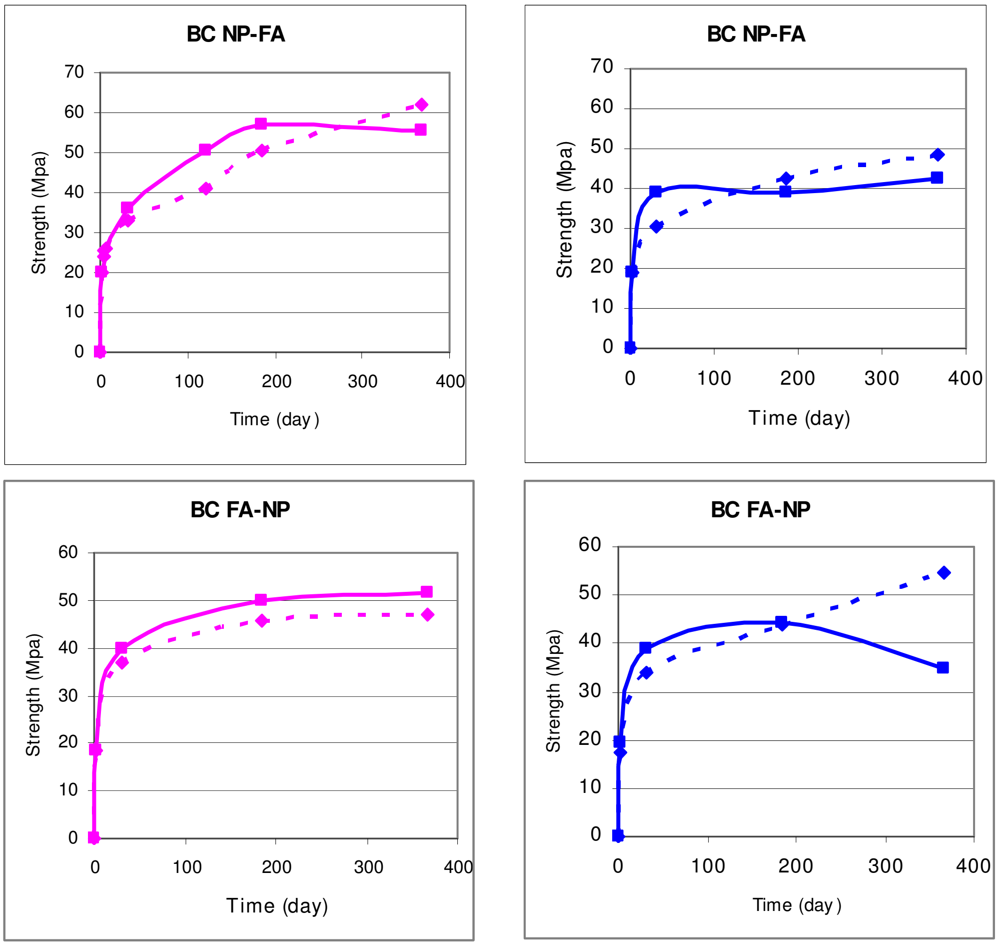
Figure 4-5 Compressive Strengths of OPC, BC and SRPC



w/c=0.485
Solid→5% sulfate solution
Dashed→lime saturated water

w/c≈0.560
Solid→ 5% sulfate solution
Dashed→lime saturated water

Figure 4-6 Compressive Strengths of BC $_{NP}$ and BC $_{FA}$



w/c=0.485
Solid→5% sulfate solution
Dashed→lime saturated water

w/c≈0.560
Solid→ 5% sulfate solution
Dashed→lime saturated water

Figure 4-7 Compressive Strengths of BC $_{\text{NP-FA}}$ and BC $_{\text{FA-NP}}$

The trends in compressive strength indicate a similar performance for blended cements as well as sulfate resistant Portland cement. This is attributed to the formation of secondary C-S-H gels and other beneficial effects of pozzolanic reactions of blended cements as mentioned in section 2.4.2.

According to Aköz et al., reaction products of sulfate with hydrated cement can fill the pores. If the filling is dominant an increase in strength can be observed [66]. Mehta states that rod like ettringite crystals can either be expansive or a source of strength, depending on the environmental conditions such as restraint of the system, stiffness of the cement paste, and the type and concentration of ions in the contact solution [50]. Strength increase in sulfate environment is also observed in our tests as it can be seen in the Figure 4-5, Figure 4-6, and Figure 4-7. All mortars subjected to sulfate solution, have higher strengths than lime saturated water initially. After some period, strength reduction is started to be observed except for the $BC_{FA\text{-}NP}$ mortars with w/c ratio of 0.485. Although this period is not the same for all cements, it seems to be shortening with the increase of w/c ratio from 0.485 to 0.560 at blended cements and SRPC. This is ascribed to increasing permeability that accelerates the penetration of sulfate ions and shortening the time for filling the gaps.

Percentage strength reductions after one year are also illustrated in Figure 4-8. The reductions were calculated as follows:

$$\text{Reduction in compressive strength} = [(A-B)/A]*100 \qquad (4.2)$$

where A is the average compressive strength of three specimens cured under lime saturated water for one year and B is the average compressive strength of three specimens exposed to the 5% sodium sulfate solution for one year.

The reduction in OPC mortars with w/c ratio of 0.560 is 100% as they were deteriorated completely before one year. Although strength reductions in blended cements and SRPC compared to OPC can be seen clearly, they are not consistent with each other. For instance, BC_{FA} with w/c ratio of 0.560 shows the minimum reduction whereas the $BC_{FA\text{-}NP}$ with w/c ratio of 0.560 shows the maximum and also $BC_{FA\text{-}NP}$ with w/c ratio of 0.485 shows increase in strength instead of a reduction. Therefore, any trend can not be observed as the w/c ratio changed from 0.485 to 0.560.

These inconsistencies may have two reasons. First is the insufficient compaction of the mortars. The flows of the blended cement mortars with w/c ratio of 0.485 were very low as it can be seen in Table 3-4. As these mortars were so stiff, a good compaction in the same proportion could not be fulfilled.

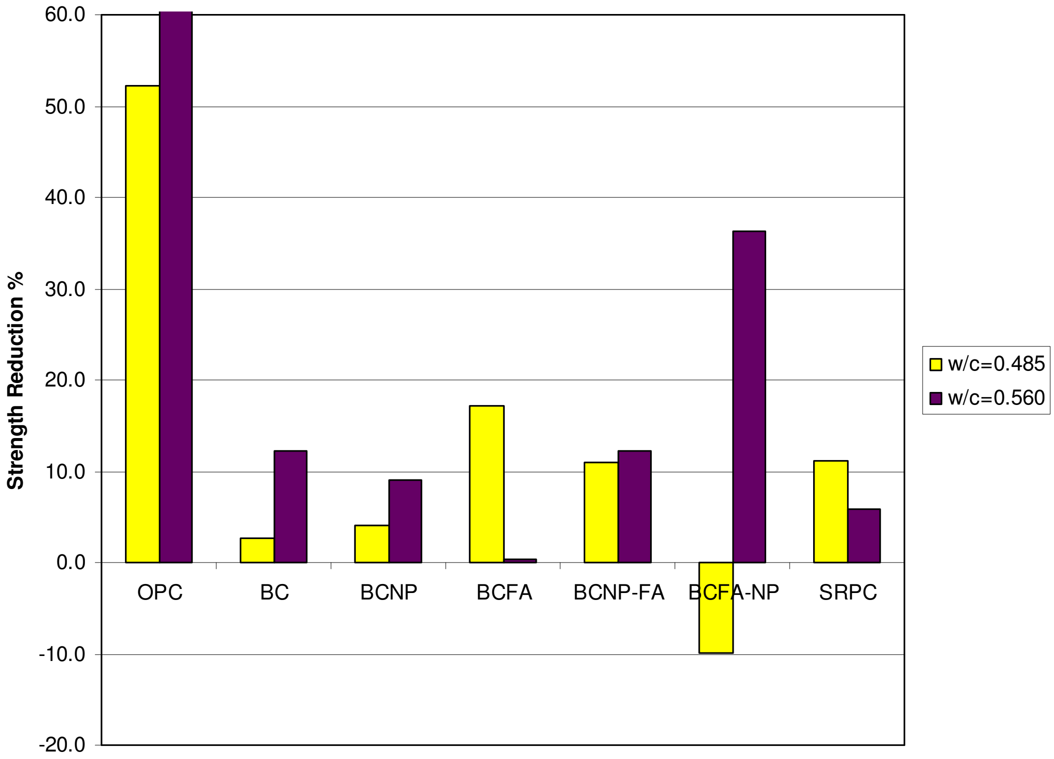


Figure 4-8 Strength reduction after one year

Moreover, the flows of OPC and SRPC mortars with w/c ratio of 0.56 were as high as to overflow from the table. Bleeding was inevitable for these mortars. The water requirement for a good workability was not obtained with these w/c ratios.

The second reason may be the insensitiveness of the compression test itself to be an indicator of sulfate attack.

Harboe reported that the shear resistance and tensile strength of concrete are more sensitive to external sulfate attack than compressive strength [70]. He suggested that the compressive strength is unaffected by sulfate attack, while the splitting tension strength is lowered [70]. Further work on tensile testing was done by Boyd and Mindess, and they [58] claimed that compressive stresses tend to close up cracks; in particular, if cracks are preferentially oriented perpendicular to the direction of loading, compression test will not be a sensitive indicator of internal damage as depicted schematically in Figure 4-9. In this case, tensile tests should provide a much better indicator of internal damage.

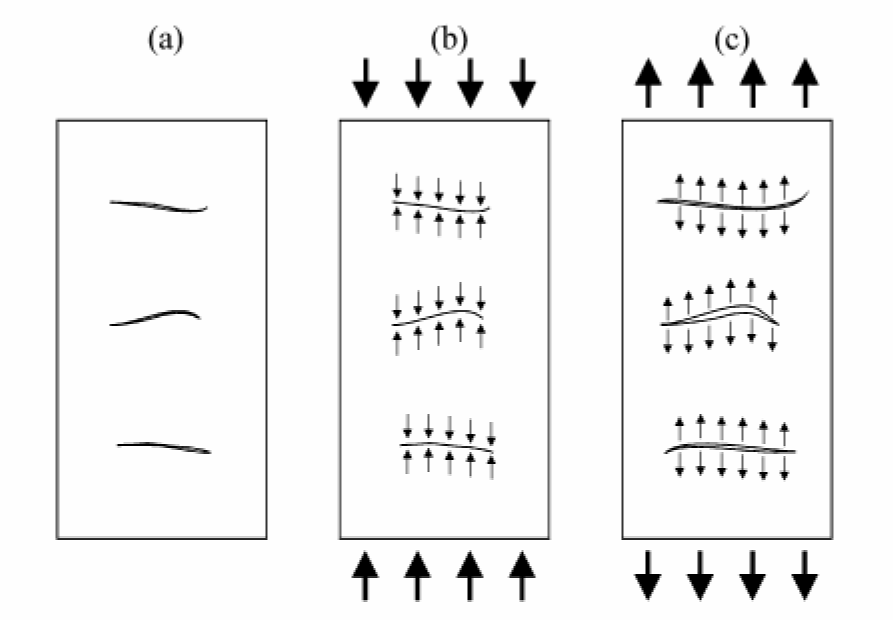


Figure 4-9 Cracked concrete under (a) no stress, (b) compressive stress, and (c) tensile stress. [58]

Skalny [71], also supports the view that the determination of the compressive strength is irrelevant to proving that sulfate attack has or has not taken place. He explains the claim that the tensile strength of concrete is more sensitive to external sulfate attack than compressive strength by “layered damage” [28]. A proof of the existence of layered damage was provided by Malhotra et al. by their measurement of ultrasonic pulse velocity [72]. (The detailed information is given in section 4.3) Taylor is another expert who supports the layered damage theory [73].

The term “layered damage” implies that concrete consists of a number of layers having distinct properties parallel to the exposed surface. Accordingly, if a tensile force is applied at right angles to the layers, failure will occur at a low tensile strength, while a compressive force in the same direction would not be affected by the layered nature of the damaged concrete [5].

On the contrary, Neville declares that both compressive and tensile strengths must be affected by damage in the same manner [5]. He asked if concrete has developed cracks and contains damaged and soft hydrated cement paste, how its compressive strength can remain unimpaired. In his studies, the ratio of the splitting tensile strength to the compressive strength of concretes subjected to sulfate attack is the same as for concrete stored under normal conditions. He emphasized that he used splitting tensile strength as direct tensile strength is not standardized by ASTM or by a British Standard, and a reliable test method is not available. For that matter, testing concrete in direct tension is very difficult because of the danger of eccentricity and of complex end stresses.

Moreover, Irrasar [74], based on a set of experimental results, came to the conclusion that flexural strength development is a very good parameter to evaluate the phases of sulfate attack.

In Figure 4-10, top and side views of the cubic specimens are given. As can be seen from this figure, cracks occurred at the edges of the specimens and gathered at the top layers. All of the specimens showed the same behavior. At the edges of the specimens the sulfate intrusion will be from two adjacent faces of the prisms also at corners intrusion will be from three faces. Therefore formation of the cracks appears at the corners of the specimens. Further, when deterioration was in the advanced stage, more visible cracks were seen on the two end faces of the prisms. Near the end faces, the sulfate intrusion will also take place through the four side faces in addition to the end face itself and this will contribute to greater deterioration of the prisms [6]. In addition, even though the top portions of the specimens were deteriorated, at the bottom of the specimens no visible cracks were observed. This may be resulted from the higher w/c ratio of the top portion because of bleeding. Besides, penetration of sulfate ions is difficult at the underneath of the specimens as underneath of the specimens were directly in contact with the container. Plastic thin rods may be placed under the specimens in order to obtain a uniformity within the X-section of the specimen.

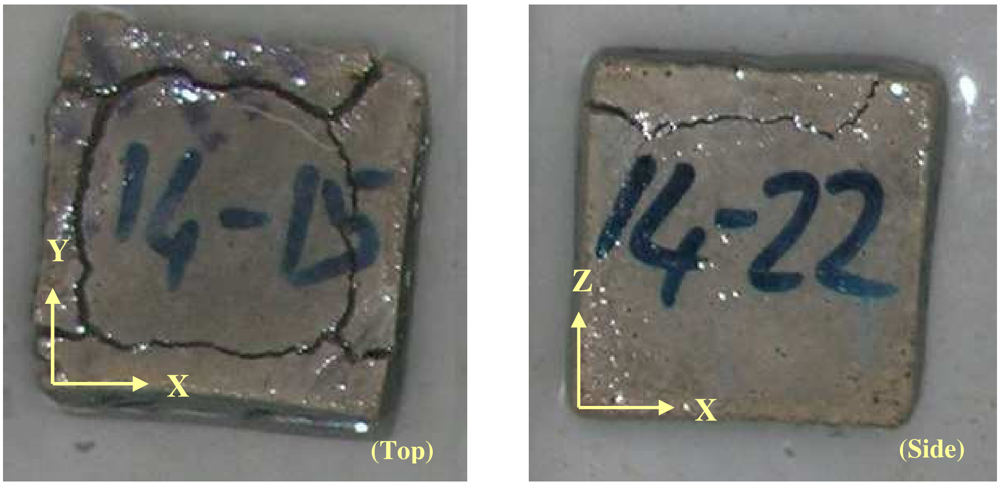


Figure 4-10 Top and side view of deteriorated samples

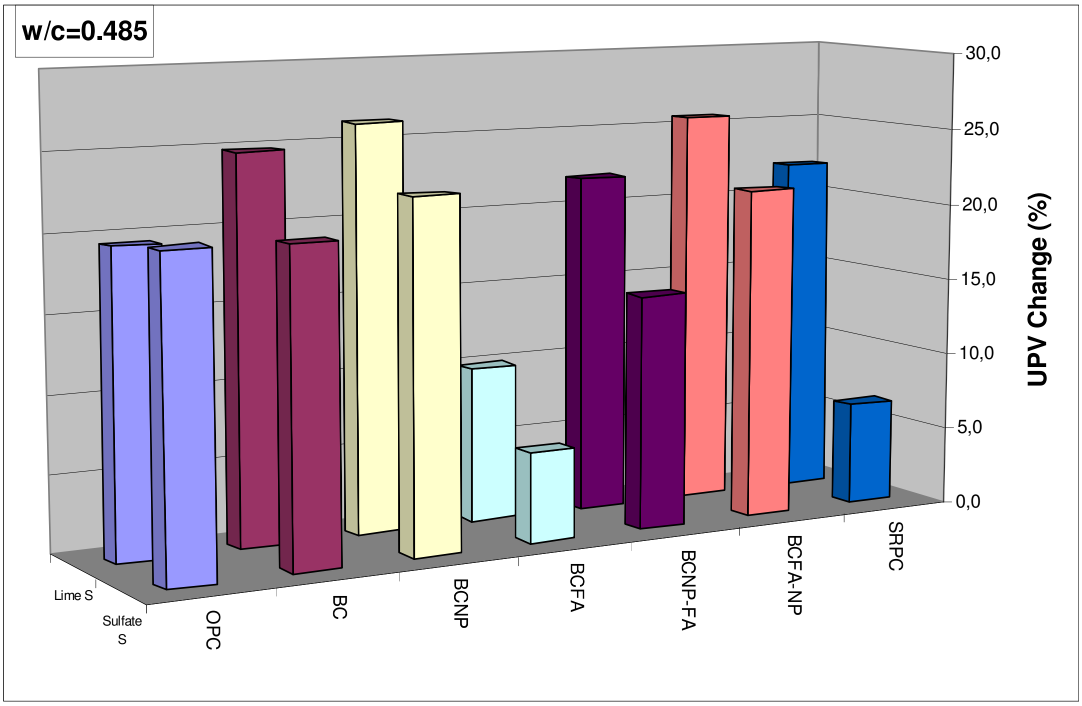
4.3 Ultrasonic Pulse Velocity

Use of ultrasonic pulse velocity in detecting the damage of sulfate attack to concrete is very limited. Çolak [75] used the change in dynamic modulus of elasticity to estimate the effect of durability tests such as freezing-thawing, and sulfate attack. In that study UPV measurements were used to predict the dynamic modulus of elasticity. Ju et al [76], used surface hardness tests and ultrasonic measurements to study deteriorated structures. Core samples were used where access to the structure from two opposite sides was not possible. Malhotra and Carino [72] used one-sided pulse velocity measurements to quantify the depth of degradation that results from the attack by sulfates. In their technique, the transmitting transducer was kept in a fixed position, while the receiving transducer is positioned at various linear distances. A plot was drawn between the time taken by the pulse and the transducer spacing. The point where the slope of the plot changed represented a difference in the layer properties. However, in our study direct transmission was used in determining the UPV and to assess the effects of sulfate attack on the UPV of mortars.

Percentage ultrasonic pulse velocity changes from the first time that the specimens were soaked into sodium sulfate solution to one year are shown in Figure 4-11. The front rows are pertaining to the specimens in 5% Na_2SO_4 solution, and the back rows are in lime saturated water. OPC mortars having w/c ratio of 0.560 in 5% Na_2SO_4 solution cracked before one year and any extrapolation can not be done as the preceding data is inconsistent, therefore the column for OPC mortars having w/c ratio of 0.56 in 5% Na_2SO_4 solution was omitted.

For both w/c ratios and for all cements ultrasonic pulse velocities increased as expected. However the increase in the UPV of the cubes in lime saturated water is higher than the cubes in sulfate solution except OPC with w/c of 0.485. The lesser UPV increase in the sulfate solution may be attributed to the formation of microcracks caused by expansion of the compounds formed by sulfate attack. As mentioned earlier, OPC has the highest C_3A content and therefore, the maximum amount of ettringite formation is expected from OPC. The contrast behavior of OPC can be ascribed to filling of the cracks with newly occurred ettringite in time. This thought is also confirmed by SRPC results. For the w/c of 0.485 the maximum difference between the UPV change of mortars in lime saturated water and sulfate solution is observed in SRPC which had the lowest C_3A content. Moreover SRPC has the highest C_3S/C_2S ratio resulting in higher gypsum formation. As it is explained in section 2.2 in detail, gypsum formation can results in expansion or mass loss.

Nevertheless, it is not possible to come to the above conclusions with a w/c ratio of 0.560 probably due to the workability problems observed in OPC and SRPC cements.



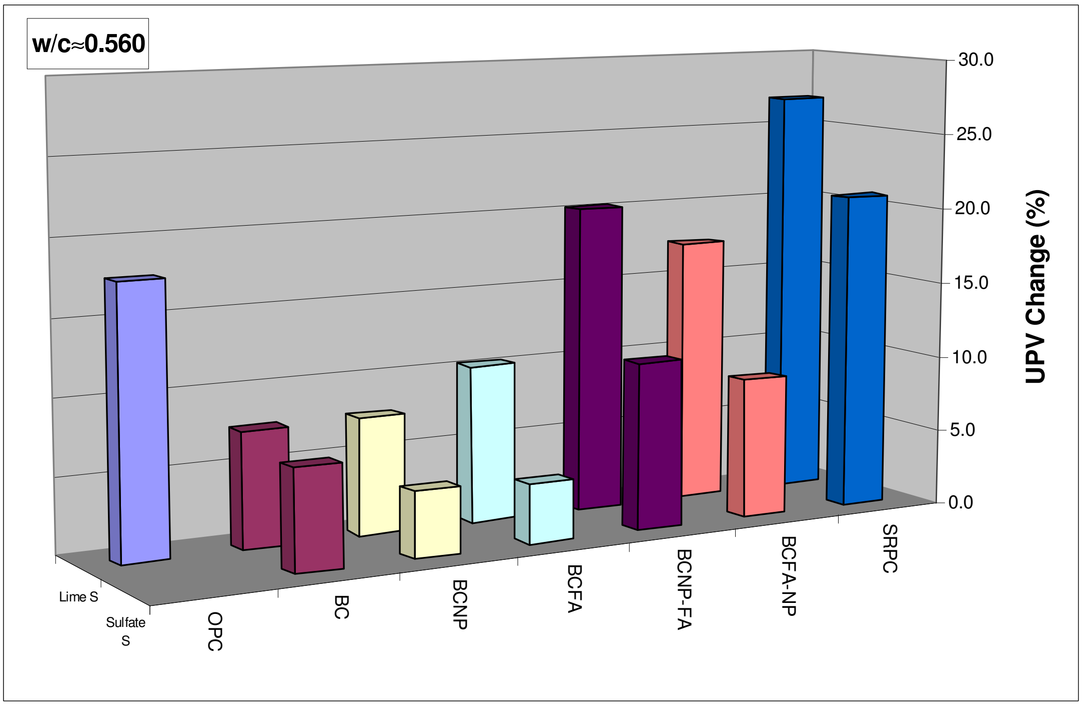


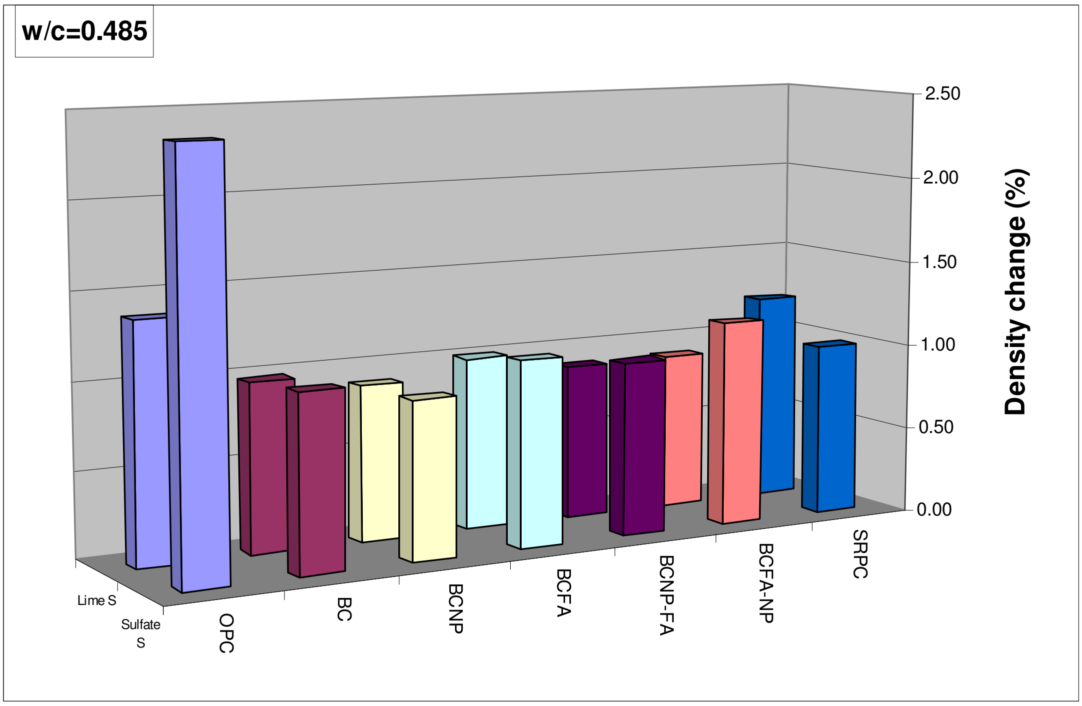
Figure 4-11 One-year-ultrasonic pulse velocity changes

4.4 Density

Percentage density changes from the first time that the specimens were soaked into sodium sulfate solution to one year are shown in Figure 4-12. The front rows belong to the specimens in 5% Na_2SO_4 solution, and the back rows belong to the specimens in lime saturated water as OPC mortars having w/c ratio of 0.56 in 5% Na_2SO_4 solution cracked before one year, 26th week result is shown instead of 52nd week density change.

As can be seen from the Figure 4-12, the density change of the blended cements are very close to each other, and also the numbers showing the density changes are very small. Because of these, to draw a conclusion on the density changes of blended cements may not be true. However, it is noticed that the density changes of the OPC and SRPC mortars with w/c of 0.485 verified the UPV results. The density change of OPC mortars in sulfate solution is very high compared to the ones in lime saturated water. (It can be seen better in Figure 4-13) This can be attributed to the excessive amounts of ettringite formation. On the contrary, density increase of the SRPC mortars in sulfate solution is less than the mortars in the lime saturated water. Like the UPV results, this can be ascribed to limited amount of C_3A in SRPC, and higher C_3S/C_2S ratio which results in gypsum.

However, meaningful conclusions can not be drawn with the density change results of the mortars with w/c ratio of 0.560, like the UPV results.



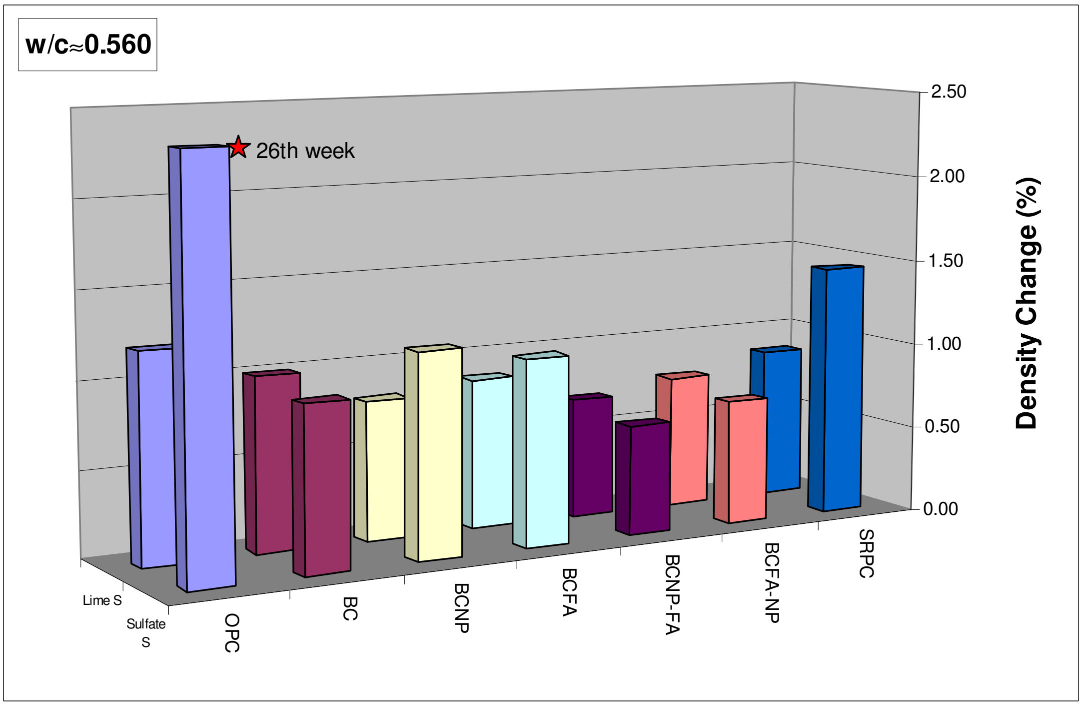


Figure 4-12 One year density changes

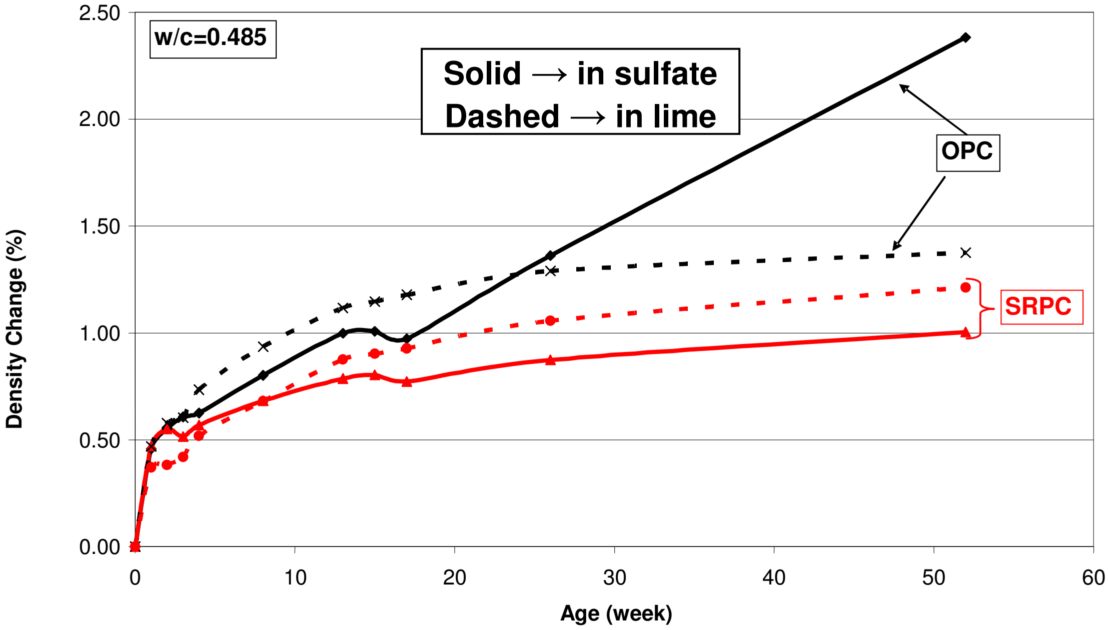
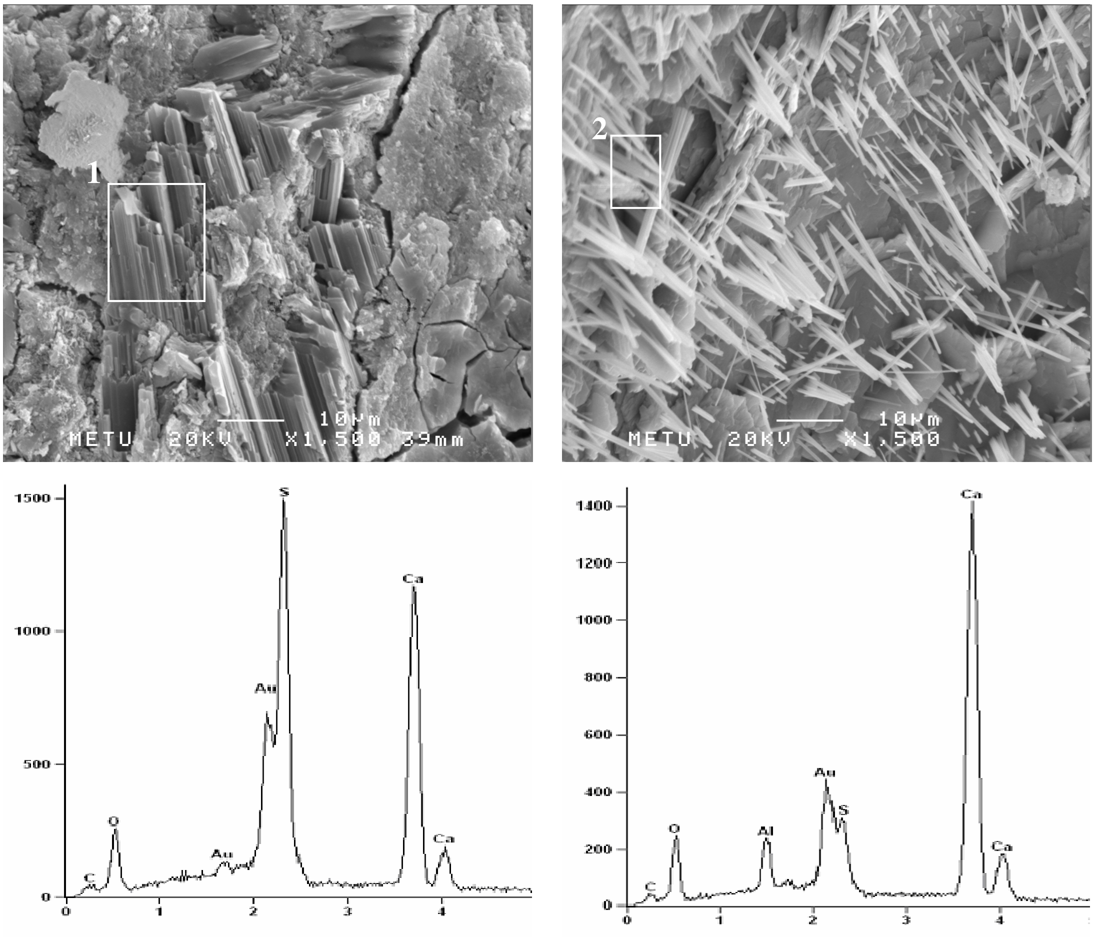


Figure 4-13 Density change of OPC and SRPC

4.5 SEM and XRD Analysis of the Cement Pastes

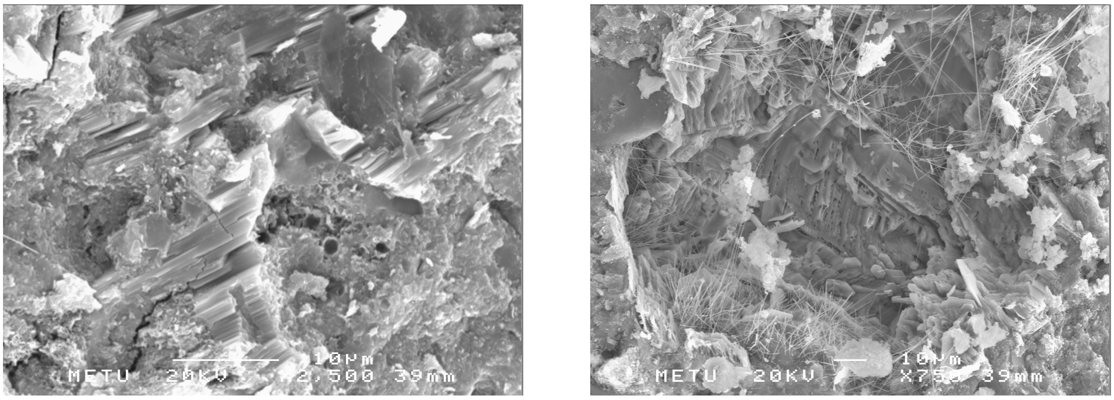
In order to investigate the products of hydration, scanning electron microscopy (SEM) of cement pastes was performed. Cement pastes were first produced together with the mortars and these pastes were subjected to a 5% Na_2SO_4 solution. At the end of one year, there were visible cracking and disintegration of the cement pastes prepared from OPC when subjected to sulfates. SEM examinations of fractured pieces obtained from OPC cement pastes demonstrate the formation of ettringite and gypsum (Figure 4-14). EDX analysis of Section 1 in Figure 4-14 (a) showed only high calcium and sulfur peaks. It was then concluded that the phase was gypsum. EDX analysis of Section 2 in Figure 4-14 (b) showed a high calcium peak and smaller sulfur and aluminum peaks, confirming the identification of ettringite. Well-formed and randomly oriented rod-like crystals were observed in the pre-existing pores at the end of one year. These observations explained the results of expansion measurements.



(a) Section 1 - Gypsum **(b) Section 2 - Ettringite**

Figure 4-14 SEM and EDX analysis of disintegrated OPC paste at 52 weeks

Pastes with blended cements that had been exposed to a sulfate solution for a year were also examined in SEM but significantly lesser amounts of ettringite or gypsum was observed (Figure 4-15). On the other hand, the expansion measurements revealed that the performance of SRPC was relatively poor when compared to the blended cements. This fact was explained by the SEM and EDX analysis of cement paste. Figure 4-16 shows the relatively higher amounts of flower like ettringite needles in SRPC pastes.



(a) BC_F **(b) BC_N**

Figure 4-15 SEM analysis of two blended cement pastes at 52 weeks

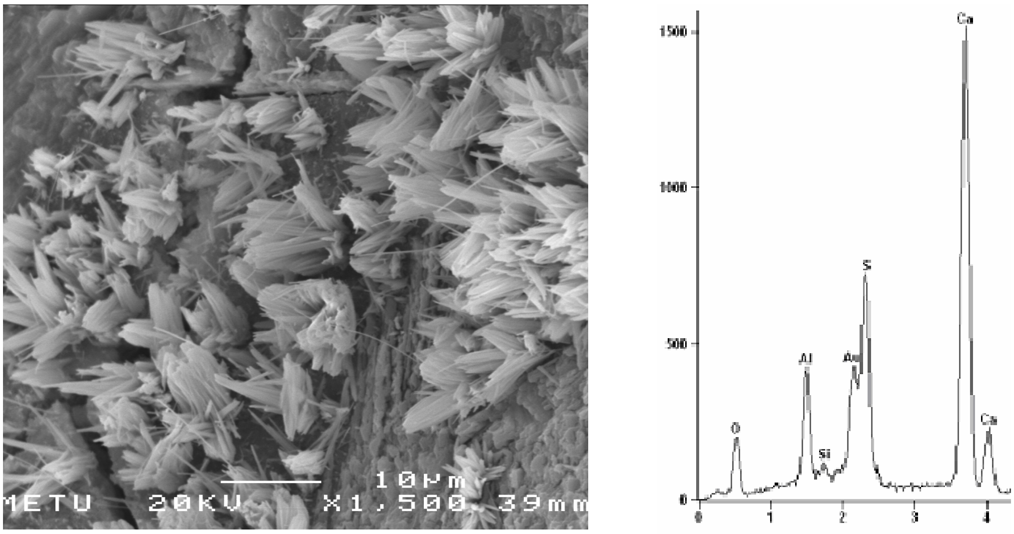


Figure 4-16 SEM and EDX analysis of the SRPC paste at 52 weeks

To confirm the SEM results and semi-quantitatively identify the products of hydration five of the cement pastes were examined by XRD after 52 weeks of immersion in a 5% Na_2SO_4 solution. The analyzed samples were taken from the surface of the cement pastes. According to Figure 4-17 ettringite and gypsum were identified in all cement pastes. After an exposure period of 52 weeks, the peak of calcium hydroxide (CH) was also detected also in all cement pastes. However, the amount of *CH* was comparatively lower in blended cement pastes due to the pozzolanic reaction of fly ash and natural pozzolan with calcium hydroxide.

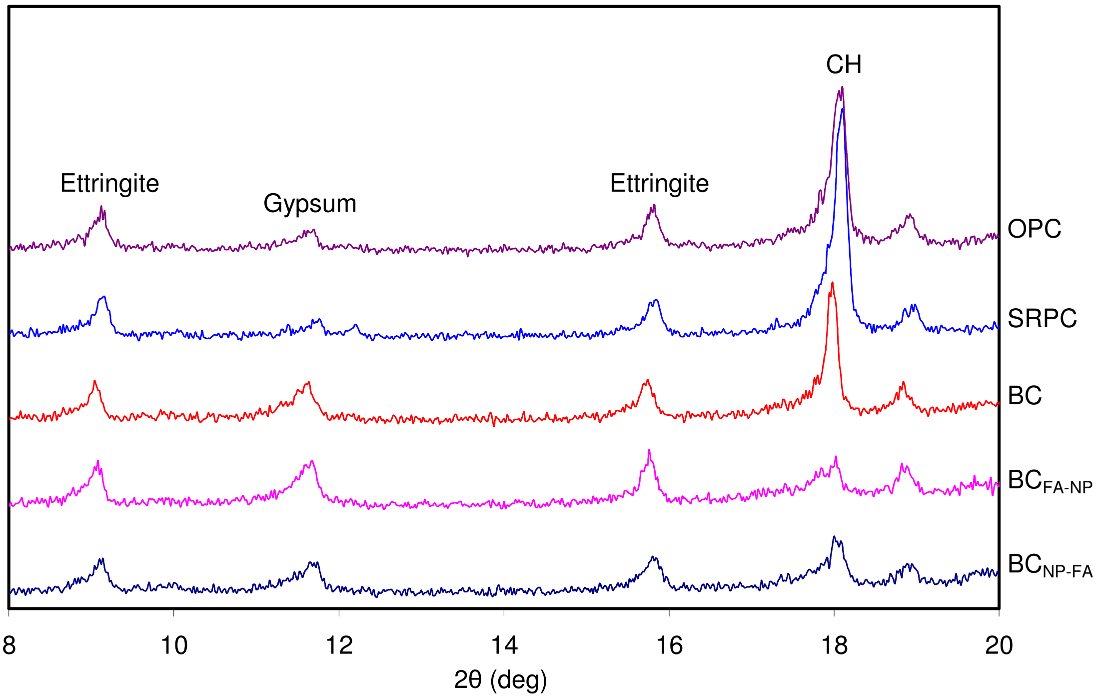


Figure 4-17 XRD patterns of cement pastes at 52 weeks

CHAPTER 5

SUMMARY AND CONCLUSIONS

This thesis discusses the results of an experimental program carried out to investigate the effects of permeability as affected by w/c ratio and different mineral additives: at different proportions on the sulfate resistance of cement mortars. Two different w/c ratios (0.485 and 0.560) and two different mineral additives (Class F fly ash and a natural pozzolan) were used. As a result of this experimental study, the following conclusions could be made:

- Cement chemistry is an important parameter in coping with sulfate attack. Considerable amount of deterioration was observed in the mortar bars prepared with the OPC. For these cements, as the w/c decreased the extent of deterioration drastically decreased. Even though, this was the case, OPC was still not suitable for sulfate environments regardless of the w/c ratio.

- Reducing the amounts of C_3A and C_4AF compounds in a cement may reduce the formation of ettringite. From the experiments performed on the cements that do not contain any mineral additives, i.e., SRPC and OPC, it was determined that the amount of C_3A and C_4AF is the most important compound which is followed by the C_3S/C_2S ratio.

- Blended cements prepared with mineral additives (both fly ash and natural pozzolan) improved the resistance of mortars to sulfate attack due to the reduction in C_3A content. Moreover, the pozzolanic reactions of blended cements also reduced the CH content which was necessary for the formation of gypsum. Therefore, depending on the amount and effectiveness of the mineral additives, blended cements were considered to be effective for moderate or high sulfate environments. In this respect, the low-lime fly ash used in this study performed better than the natural pozzolan.

- The effect of w/c is important especially for low sulfate resistant cements with higher amounts of C_3A. High sulfate resistant cements were not affected by w/c to the same extent. As a result, the chemistry of cement appears to be more effective than the w/c in offsetting the destructive effects of sulfate attack on concrete.

- Increase in compressive strength can be observed instead of a strength reduction at sulfate environments, especially at initial periods. However, increase in w/c ratio accelerates the failure and shortens the time elapsed for the start of strength reduction. Therefore, time to failure is decreasing with increasing w/c ratio.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE STUDIES

As a result of this experimental study, the following recommendations could be made for other researchers:

- Long term monitoring of cement mortars subjected to sulfate attack is possible with using ultrasonic pulse velocity. However UPV is affected by various factors such as temperature. Also the device alignment may shift, as it did in our experiments, and the device may need to be recalibrated. For this reason, it is very important to measure a reference material when using the ultrasonic pulse velocity device.

- When subjecting the specimens to a sulfate environment, the lids of the containers must be closed tightly so that the water can not evaporate. If the water evaporates, crystallization will take place and the reactions will shift towards physical sulfate attack.

- Varying one parameter at a time in a mortar mix is not quite possible. For example, at a given w/c ratio a change in the cement type brings about a change in workability. In our tests, the flows of the blended cement mortars with w/c ratio of 0.485 were very low whereas the flows of the OPC and SRPC mortars with w/c of 0.560 were very high. In order to eliminate the permeability differences resulted from the compaction factor, it is recommended to use superplasticizers.

The following topics could be studied to gain better understanding of the sulfate attack phenomenon on blended cements.

- The additive types of cements which are produced by the cement factories that are members of Turkish Cement Manufacturers Association (TCMA) are given in Table 6-1. As can be seen from that table, in Turkey the most widely used additive type is "Limestone". In future studies, sulfate resistance of blended cements with limestone therefore can be tested.

Table 6-1 Additive types of blended cements under control of TCMA at 23 May 2006

Additives					Number of cement types including at least one additive
Slag					5
Limestone					9
Natural pozzolan					7
Natural pozzolan	+	Slag			8
Natural pozzolan	+	Limestone			32
Natural pozzolan	+	Fly Ash			5
Slag	+	Limestone			1
Fly Ash	+	Limestone			1
Natural pozzolan	+	Fly Ash	+	Slag	1

- As it is explained in the section 2.3.2, physical sulfate attack is different from the classical sulfate attack. Mineral additives and lowering the w/c ratio may have detrimental effects instead of to be beneficial. Using type V cement may also be useless as the distress mechanism is not related to ettringite. Therefore, the term physical attack can be investigated with half buried samples into soil or by applying wetting and drying cycles.

- Kyathi et al. [77], claim that permeability has significantly less important role in mortar samples as the cross sections of mortar samples were significantly smaller than the concrete samples. Thus, the sulfate resistance of mortars could be expected to be derived mainly from the chemical resistance of the binder, whereas in concrete samples the sulfate resistance was due to both physical (permeability) and chemical (binder) resistance. In literature most of the works done about sulfate attack was on the mortars. Taking into consideration the Kyathi's claim, a work with concrete specimens could be done.

- In literature there are authors who oppose using the compressive strength in determining the sulfate resistance of cements. This thought may be investigated. Flexural strength or splitting tensile strength tests may be conducted besides the compressive strength tests.

- In our study, the amounts of C_3A were about 6 for blended cements and it is 3.6 for SRPC whereas 9.5 for OPC. There is a lack between these numbers. In addition, the six of the cements have the same C_3S/C_2S ratio 4.3. In order to understand the effect of chemical composition on sulfate resistance, a study can be conducted with cements having different amounts of C_3A or C_3S/C_2S ratio.

REFERENCES

1. Harrison W.H., Concrete, V.21 (2), pp.18, 1987.

2. Al-Amoudi O.S.B., “Attack on plain and blended cements exposed to aggressive sulfate environments”, Cement&Concrete Composites, V.24, pp.305-316, 2002.

3. Al-Dulaijan S.U., Maslehuddin M., et al., “Sulfate resistance of plain and blended cements exposed to varying concentrations of sodium sulfate”, Cement&Concrete Composites, V.25, pp.429-437, 2003.

4. Bellport B.P., “Combating Sulfate Attack on Concrete on Bureau of Reclamation Projects”, Performance of Concrete: Resistance of Concrete to Sulphate and other Environmental Conditions, ed. E.G. Swenson, University of Toronto Press, Canada, pp. 77-92, 1968.

5. Neville A., “The confused world of sulfate attack on concrete”, Cement and Concrete Research, pp. 1275-1296, (34) 2004.

6. Wee, T. H.; Suryavanshi, A. K.; Wong, S. F. ; and Rahman, A. K. M., “Sulfate resistance of concrete containing mineral admixtures,” ACI Material Journal, V. 97, No. 5, pp. 536-549 Sept-Oct 2000.

7 Al-Amoudi O.S.B., “Sulfate attack and reinforcement corrosion in plain and blended cements exposed sulfate environments”, Building and Environment, V.33, pp.53-61, 1998.

8. Casanova,I., Aguado, A., and Agulló, L., “Aggregate expansivity due to sulfide oxidation – II. Phsico-chemical modeling of sulfate attack”, Cement and Concrete Research, V.27, No.11, pp.1627-1632, 1997.

9. Cohen M. D., Bentur A., Durability of portland cement-silica fume pastes in magnesium sulfate and sodium sulfate solutions", ACI Materials Journal, 85(3), 148-157, 1988.

10. Tasong W.A., Wild S., Tilley R. J. D., "Mechanisms by which ground granulated blastfurnace slag prevents sulfate attack of lime-stabilised kaolinite", Cement and Concrete Research, V.29, pp.975-982, 1999.

11. Tian B., Cohen M. D., "Does gypsum formation during sulfate attack on concrete lead to expansion?", Cement and Concrete Research, V.30, pp. 117-123, 2000.

12. Hansen W. C., "Attack on portland cement concrete by alkali soil and water - a critical review", Highway Research record 113, pp. 1-32, 1966.

13. Hansen W. C., "Crystal growth as a source of expansion in portland cement concrete", Proceedings of American society for Testing and Materials, Vol.63, pp.932-945, 1963.

14. Mather B., Discussion of "The process of sulfate attack on cement mortars", Advanced Cement Based Materials, 5, pp.109-110, 1996.

15. Lea F. M., Nurse R. W., "Problems of Crystal Growth in Building Materials" Cryst. Growth: Discuss. Faraday Soc (5) 109-110, 1949.

16. Bonen D., Sarkar S. L., "Replacement of Portlandite by Gypsum in the interfacial zone and cracking related to crystallization pressure, Ceramics Transtractions, V.37, Cement Based Materials: Present, Future, and environmental aspects, AmCeram Soc , Westerville, OH, pp.49-59, 1993.

17. Cohen M. D., Mather B., "Sulfate attack on concrete –research needs", ACI Materials Journal, V.88, pp.62-69, 1991.

18. Tian B., Cohen M. D., "Expansion of alite paste caused by gypsum formation during sulfate attack", Journal of Materials in Civil Engineering/24, 2000.

19. Santhanam M., Cohen M. D., Olek J., "Effects of gypsum formation on the performance of cement mortars during external sulfate attack", Cement and Concrete Research, V.33, pp. 325-332, 2003.

20. Ping X., Beaudoin J.J., "Mechanism of sulfate expansion I. Thermodynamic principles of crystallization pressure, Cement and Concrete Research, V.22, pp.631-640, 1992.

21. Ping X., Beaudoin J.J., "Mechanism of sulfate expansion II. Validation of thermodynamic theory, Cement and Concrete Research, V.22, pp.845-854, 1992

22. Nielsen J., "Investigation of resistance of cement paste to sulfate attack", Highway Research Record, 113, pp.114-117, 1996.

23. Wang, J. G., "Sulfate attack on hardened cement paste", Cement and Concrete Research, V.24, pp.735-742, 1994.

24. Yang S., Zhongzi Z., Mingsu T., "The process of sulfate attack on cement mortars", Advanced Cement Based Materials, 4, pp.1-5, 1996.

25. Gonzales M. A., Irassar E. F., "Ettringite formation in low C_3A Portland cement exposed to sodium sulfate solution", Cement and Concrete Research, V.27, pp.1061-1072, 1997.

26. Bellmann F., Möser B., Stark J., "Influence of sulfate solution concentration on the formation of gypsum in sulfate resistance specimen", Cement and Concrete Research, V.36, pp.358-363, 2006.

27. Santhanam M., Cohen M. D., Olek J., “Mechanism of sulfate attack: a fresh look Part 2. Proposed mechanisms”, Cement and Concrete Research, V.33, pp.341-346, 2002.

28. Scalny, J., Sulfate Attack on Concrete, London.. GBR: Routledge, 2001.

29. Scrinever K., Skalny J. P., “Conclusions of the International RILEM TC 186-ISA Workshop on internal sulfate attack and delayed ettringite formation (4-6 September 2002, Villars Switzerland)” Materials and Structures, 38, pp.659-663, July 2005.

30. Taylor, H.F.W., Famy, C. and Scrinever, K.L., “Delayed Ettringite Formation”, Cement and Concrete Research, V.31, pp.683-693, 2001.

31. Scalny J., Odler I., Young F., “Discussion of ref 32.”, Cement and Concrete Research, V.30, pp.161-162, 2000.

32. Hime W. G., Mather B., ““Sulfate attack” or is it?”, Cement and Concrete Research, V.29, pp.789-791, 1999.

33. Hime W. G., Mather B., “Reply to the discussion of ref 32.”, Cement and Concrete Research, V.30, pp.163-164, 2000.

34. Concrete Society, Diagnosis of Deterioration in Concrete Structures, Technical Report, No.54, 2000.

35. Mehta P.K., “Sulfate Attack on Concrete: Separating Myths from Reality, Concrete International”, 22 (8), pp.57-61,2000.

36. Collepardi M., “A State-of-the-art review on delayed ettringite attack on concrete”, Cement and Concrete Composites, 25, pp.161-162, 2000

37. Neville A.M., Properties of Concrete, Wiley, New York, 1997.

38. T.J. Reading, “Combating sulfate attack in corps of engineers concrete construction”, Durability Concr. (ACI Publication SP-47)., 343–366, 1975.

39. Blaine R.L., Arni H.T., “Interrelations Between Cement and Concrete Properties: Part 4”, Washington, DC, Building Science Series 15, National Bureau of Standards, Washington, D.C., 1969.

40. Ramyar K., İnan G., “ Sodium sulfate attack on plain and blended cements”, Building and Environment, In Press, Available online 27 December 2005.

41. Rasheeduzzafar, Al-Amoudi O.S.B., et al., “Magnesium-sodium sulfate attack in plain and blended cements”, ASCE J. Mater Civil Eng. pp 201-222. (6)2, 1994.

42. Tikalsky P.J., Roy D., et al., “Redefining cement characteristics for sulfate-resistant portland cement”, Cement and Concrete Research, V.32, pp.1239-1246, 2002.

43. Odler I., Jawed J., Expansive reactions in concrete, in: Skalny J., Mindess S., Materials science of concrete II, American ceramic society, Westerville, OH, 1989

44. Odler I., Gasser M., “Mechanism of sulfate expansion in hydrated Portland cement”, J. Am. Ceram. Soc. 71, pp 1015-1020, 1988.

45. Mehta P.K., Concrete: Structures, Properties and Materials, Prentice-Hall, Inc., New Jersey, 1993.

46. Mehta P.K., “Mechanism of expansion associated with ettringite formation”, Cement and Concrete Research, V.3, pp.1-6, 1973.

47. Moon H.Y., Lee S.T., “Influence of silicate ratio and additives on the sulphate resistance of Portland cement”, Advances in Cement Researches, 15, No.3, July, 91-101, 2003.

48. Irrassar E. F., Gonzales M. A., V. Rahhal, “Sulfate resistance of type V cements with limestone filler and natural pozzolona”, Cement&Concrete Composites, V.22, pp.361-368, 2000.

49. Rasheeduzzafar, Dakhil F.H., et al., “Influence of cement composition on the corrosion of reinforcement and sulfate resistance of concrete”, ACI Materials Journal, 87(2), 114-122, 1990.

50. Mehta P.K., “Mechanism of sulfate attack on portland cement concrete – Another look”, Cement and Concrete Research, V.13, pp.401-406, 1983.

51. Lea F.M., Chemistry of Cement and Concrete, 3rd edition, Edward Arnold, London, 1970.

52. Memon A.H., Radin S.S., et al., “Effect of mineral and chemical admixtures on high-strength concrete in seawater”, Cement and Concrete Research, V.32, pp.373-377, 2002.

53. Dunstan, E.R., “A possible method for identifying fly ashes that will improve the sulfate resistance of concretes”, Cement, Concrete and Aggregates, V.2, No.1, pp.20-30, 1980.

54. Irrasar E.F, Di Maio A., Batic O.R., “Sulfate attack on concrete with mineral admixtures”, Cement and Concrete Research, V.26, pp.113-123, 1996.

55. Irrasar E.F., “A discussion of the paper 75.”, Cement and Concrete Research, V.34, pp.1265-1266, 2004.

56. Mehta P.K., Concrete structure, properties, and materials, International Series in Civil Engineering and Engineering Mechanics, third ed., Prentice-Hall, Englewood Cliffs, NJ, 161–171, 1986.

57. Mehta P.K., Skalny J., Material Science of Concrete II, American Ceramic Society, pp. 102-130,1992.

58. Boyd A.J., Mindess S., "The use of tension testing to investigate the effect of W/C ratio and cement type on the resistance of concrete to sulfate attack", Cement and Concrete Research, V.34, pp.373-377, 2004.

59. Al-Amoudi O.S.B., Maslehuddin M., Saadi MM., "Effect of magnesium sulfate and sodium sulfate on the durability performance of plain and blended cements", ACI Materials Journal, 92 (1), 15-24, 1995.

60. Nehdi M., Hayek M., "Behavior of blended cements mortars exposed to sulfate solutions cycling in relative humidity", Cement and Concrete Research, V.35, pp.731-742, 2005.

61. Santhanam M., Cohen M. D., Olek J., "Sulfate attack research – whither now?", Cement and Concrete Research, V.31, pp.845-851, 2001.

62. Lea FM, "The Chemistry of Cement and Concrete", 3rd ed. London, Edward Arnold, 1970.

63. Al-Amoudi O.S.B., " Performance of fifteen reinforced concretes in magnesium-sodium sulfate environments" Constr Build Mater, pp.25-33, 9(1), 1995

64. Committee Report, ACI Committee 201, ACI Materials Journal, (98), 544, 1991

65. Biczok I., Concrete Corrosion Concrete Protection, Chemical Publishing, New York, 1967.

66. Aköz F., Türker F., et al., "Effects of sodium sulfate concentration on the sulfate resistance of mortars with and without silica fume" Cement and Concrete Research, V.25, pp.1360-1368, 1995.

67. Santhanam M., Cohen M. D., Olek J., "Mechanism of sulfate attack: a fresh look Part 1. Summary of experimental results", Cement and Concrete Research, V.32, pp.915-921, 2001.

68. Patzias, T., "The development of ASTM method C1012 with recommended acceptance limits for sulfate resistance of hydraulic cements", Cement Concrete and Aggregates, pp. 50-57, (13) 1991.

69. Stephens, J.B. and Carrasquilo, R.L., "Evaluating performance based test and specifications for sulfate resistance in concrete", Research Report 1706-3, The University of Texas at Austin, December 2000.

70. Harboe E.M., "Long time studies and field experiences with sulfate attack" George Verbeck Symposium On Sulfate Resistance of Concrete, ACI SP 77, pp. 1-20, 1982.

71. Skalny J., Pierce J.S., "Sulfate attack: an overview, Sulfate attack mechanisms", Materials Science of Concrete, Amer. Ceramic Society, Ohio, pp.49-63, 1999

72. Malhotra V. M., Carino N. J., CRC Handbook of Nondestructive Testing of Concrete, CRC Press, Boca Raton, FL, 1993.

73. Taylor H.F.W., Cement Chemistry, Second edition, Thomas Telford, London, 1997.

74. Irrasar E.F. "Sulfate resistance of blended cement: prediction and relation with flexural strength", Cement and Concrete Research, V.20, pp.209-218, 1990

75. Çolak A., "Characteristics of pastes from a Portland cement containing different amounts of natural pozzolan", Cement and Concrete Research, V.33, pp.585-593, 2003.

76. Ju J.W., Weng L.S., et. al., "Damage assessment of service life prediction of concrete subject to sulfate attack, Sulfate Attack Mechanism" Materials Science of Concrete, Amer. Ceramic Society, Ohio, pp.265-282, 1999.

77. Khatri R.P., Sirivivatnanon V., Yang J.L, Roll of permeability in sulfate attack, "Cement and Concrete Research", V.27, pp.1179-1189, 1997.