

**EFFECT OF USING DIFFERENT KIND OF MINERAL ADMIXTURES TO
PERMEABILITY AND DURABILITY PROPERTIES OF SELF
COMPACTING CONCRETE**

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**FARKLI TÜRDE MİNERAL KATKI KULLANIMININ KENDİLİĞİNDEN
YERLEŞEN BETONUN GEÇİRİMLİLİK VE
DURABİLİTEÖZELLİKLERİNE ETKİSİ**

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ABBREVIATIONS

SCC	: Self Compacting Concrete
SF	: Silica Fume
SCM	: Supplementary Cementitious Material
FA	: Fly Ash
GGBS	: Ground Granulated Blast Furnace Slag
CLSM	: Controlled Low Strength Material
ACAA	: American Coal Ash Association
HVFAC	: High Volume Fly Ash Concrete
OPC	: Ordinary Portland Cement
HAC	: High Alumina Cement
SRC	: Sulfate Resisting Cement
PC	: Portland Cement
PFA	: Pulverized Fly Ash
F Series	: Fly Ash Replaced Self Compacting Concretes
L Series	: Lime Stone Replaced Self Compacting Concretes
S Series	: Sand Stone Replaced Self Compacting Concretes
RMC	: Ready Mix Technical Centre
UPV	: Ultrasonic Pulse Velocity
MK	: Metakaolin
SMF	: Sulphonated Melamine Formaldehyde
SNF	: Sulphonated Napthalene Formaldehyde
AAR	: Alkali Aggregate Reaction
ASR	: Alkali Silica Reaction
PCF	: Poly-carboxylate Ether Super-plasticizer
CEN	: European Committee for Standardization
ASTM	: American Society for Testing And Materials
EFNARC	: European Federation for Specialist Construction Chemicals
JSCE	: Japan Society of Civil Engineers

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EFFECT OF USING DIFFERENT KIND OF MINERAL ADMIXTURES TO PERMEABILITY AND DURABILITY PROPERTIES OF SELF COMPACTING CONCRETE

SUMMARY

According to many researches, which had been published so far, it was observed that the placement and compaction problems influence the concrete's durability properties seriously. At First, the concept of Self Compacting Concrete (SCC) has been developed to solve these problems especially for under-water constructions and some special buildings. Although, SCC provides savings about labor and energy, it was not used so often initially since the cost of chemical admixture, which is utilized for manufacturing a SCC. However, using SCC is spreading also in our country day by day as in all world, due to the innovations of both concrete and chemical technology.

In this study it is investigated that, the effects on the durability properties of SCC by reducing the cement amount gradually, which is one of the high cost parameter of concrete, and using mineral admixtures instead. For this purpose, type and amounts of aggregates, chemical admixtures and water/binder ratios are kept constant for all produced mixes. In order to observe the effects of reducing cement amount, a reference concrete produced by using 500 kg CEM I 42,5 Cement per 1 m³ concrete. Three mixes have prepared with % 20, %30 and % 40 Fly Ash replacement by weight respectively. Besides, three mixes with reducing the cement amount % 20, %30 and % 40 by weight and added Lime-Stone filler instead with % 24, % 36 and % 48 by weight. Finally, three mixes produced with reducing the cement dosage % 20, % 30 and % 40 by weight and used Sand-Stone filler instead with % 24, % 36 and % 48 by weight. In the other word, nine different mixes were prepared except for reference concrete. The different replacement amounts, between Fly ash and Fillers, are sourced by the different unit weights of these materials. Fly Ash's unit weight is less than both Fillers. Therefore, this way was chosen, in order to balance all mixes replacement values by volume.

Before the moulding process; Slump-flow test, V funnel test, L box and U box tests were applied on the samples, among from the fresh concrete experiments. 24 hours later from the moulding process all mixes were moved to water pool. Water cure applied along the 28 days and then air cure was applied to all mixes in the laboratory during 7 days. At the end of 35 th day compressive strength test was applied to mixes in order to figure out both compressive strength and modulus of elasticity values.

For determining to permeability properties of mixes Capillarity test, Water Absorption test and Permeability tests were applied to all mixes. Furthermore, a Sulfate solution was prepared with using % 15 Magnesium sulfate by weight and during the 8 months the Ultrasonic Pulse Velocity and Mass Loss values of all mixes were measured every month periodically. Thus, the changes on the microstructure of concrete were observed. 3 point bending test was applied to all mixes not only before

the sulfate solution process but also after the sulfate solution process. By this way energy absorption capacity and the flexural strength of all mixes were confirmed comparatively both before and after sulfate attack.

When the acquired test results are evaluated, Fly ash and Fillers replacement haven't caused big changes on the placement and compaction properties of SCC.

However, it has seen that, both fly ash and fillers replacement influenced compressive strengths of concrete negatively. When all mixes compared each other, especially sand stone filler replacement led to a significant reduction on the compressive strength values.

Two points are agreed upon on the world's literature for evaluating workability properties of concrete. First of all the excessive viscosity problems which can prevent the self compacting abilities of concrete and the second one is high flowing speed problems which can lead to segregation between concrete components. Segregation was not observed at the end of the tests in this study. However, it should be regarded to segregation risk for L 36 which represents Lime Stone Filler replaced Self Compacting Concrete mixes with the % 36 replacement ratio by weight. Furthermore, excessive viscosity risk might be occurred for S 36 which represents Sand Stone Filler replaced Self Compacting Concrete mixes with the % 36 replacement ratio by weight.

Even if irregular seesaws, was acquired on the Modulus of Elasticity test results, it is clear that Modulus of Elasticity was not influenced significantly from the replacement.

When Fly Ash and Lime Stone filler mixes performed well about permeability especially at the low levels replacement, Sand Stone Filler addition effected to permeability negatively. On the other hand, all permeability values of SCC specimens are still so low when it is compared with conventional concrete.

Sulfate impact on the concrete, was investigated by utilized Ultrasonic Pulse Velocity Test. There are no regular and big variations, were observed on the UPV test results with mineral material addition to SCC. However, It is observed on Mass Loss test that the mineral addition rates increasement, lead to slight negative changes on the samples weight. Furthermore, Lime Stone Filler and Fly Ash contained samples had closer results each other, and better than Sand Stone fillers added mixes.

Mineral material, have no significant effect on the Energy Absorption capabilities of SCC especially at the low addition amounts, independently from Sulfate attack. Only Sand Stone filler caused some reduction. After sulfate attack, almost all mixes test values went down except for Reference concrete.

Even if flexural strength of all SCC concrete decreased with Mineral materials addition independently from Sulfate attack, these reductions were not linear and regular. Sulfate attack also led to reduction on the Flexural Strength of all SCC samples as expected.

FARKLI TÜRDE MİNERAL KATKI KULLANIMININ KENDİLİĞİNDEN YERLEŞEN BETONUN GEÇİRİMLİLİK VE DURABİLİTE ÖZELLİKLERİNE ETKİSİ

ÖZET

Son yıllarda yayınlanan araştırmalara göre geleneksel betonda karşılaşılan yerleşme ve sıkışma sorunlarının betonun durabilite özelliklerini ciddi oranda etkilediği gözlemlenmiştir. Kendiliğinden Yerleşen Beton ilk olarak su altı yapıları ile yüksek dayanım istenen bazı özel yapılarda betonun yerleşme ve sıkışma problemlerini aşmak için geliştirilmiştir. İşçilik ve enerji kullanımında tasarruf sağlayan Kendiliğinden Yerleşen Beton içerdiği kimyasal katkıların yüksek maliyeti nedeniyle ilk zamanlarda çok sık kullanım imkanı bulamamıştır. Ancak beton teknolojisi ve kimyasal katkı sektöründeki gelişmelere paralel olarak Kendiliğinden Yerleşen Beton kullanımı tüm dünyada olduğu üzere ülkemizde de gün geçtikçe yaygınlaşmaktadır.

Bu çalışmada Kendiliğinden Yerleşen Betonun maliyetini arttıran en önemli parametrelerden biri olan çimento miktarının kademeli olarak azaltılarak yerine mineral katkı kullanılmasının betonun durabilite özelliklerine olan etkileri incelenmiştir. Bu amaçla, üretilen betonlarda agrega ile kimyasal katkı tipi ve miktarları ve su/bağlayıcı miktarları sabit tutulmuştur. Çimento miktarındaki azalışın etkilerini gözlemlemek amacıyla 500 kg/m³ CEM I 42.5 çimentosu kullanılarak referans beton üretilmiştir. Bu çimento dozajını kütlece % 20, %30 ve % 40 azaltıp yerine aynı oranlarda uçucu kül eklenerekten üç tip karışım, Ayrıca çimento miktarını kütlece %20, %30 ve % 40 oranlarında azaltıp yerine kütlece % 24, % 36 ve % 48 kireçtaşı filler ilave edilerek 3 tip karışım ve son olarak çimento dozajını kütlece %20, %30 ve % 40 oranlarında azaltıp yerine kütlece % 24, % 36 ve % 48 kumtaşı filler eklenmesiyle de 3 tip beton karışımı üretilmiştir. Başka bir deyişle Referans betondan hariç 9 farklı beton karışımı hazırlanmıştır. Uçucu kül ile kumtaşı ve kireçtaşı fillerin farklı oranlarda kullanılması, bu malzemelerin birim hacim ağırlıklarındaki farklılıktan kaynaklanmaktadır. Uçucu Külün birim hacim ağırlığı her iki Filler den daha düşüktür. Bu yüzden, üretilen betonların yerdeğiştirme değerlerinin hacimce dengelenebilmesi için bu yöntem seçilmiştir.

Üretilen betonlar kalıplara dökülmeden önce taze faz deneylerinden yayılma, V hunisi, L kutusu ve U kutusu deneylerine tabi tutulmuşlardır. Kalıplara dökülen betonlar 24 saat sonra kalıptan çıkarılarak su havuzuna aktarılmışlardır. 28 gün boyunca su kürü uygulanmış daha sonrada 7 gün boyunca laboratuarda hava kürü uygulaması yapılmıştır. 35.günün sonundan itibaren betonlara basınç dayanımı deneyi uygulanarak, basınç dayanımı ve elastisite modülü değerleri bulunmuştur.

Üretilen betonların geçirimsizliğini belirlemek amacıyla kılcallık, ağırlıkça su emme ve basınçlı su geçirimsizlik deneyleri de uygulanmıştır. Ayrıca ağırlıkça % 15 oranında Magnezyum Sülfat kullanılarak sülfat çözeltisi hazırlanmış ve numunelerin 8 ay boyunca her ay periyodik olarak ultrases hızı ve ağırlık değişimi miktarları ölçülmüştür. Böylece sülfat etkisindeki betonun, iç yapısındaki değişimler

gözlemlenmiştir. 3 noktalı eğilme deneyi ise hem sülfat çözeltisi uygulanmadan hem de sülfat çözeltisi deneyleri bittikten sonra yapılarak, üretilen betonların sülfat öncesinde ve sonrasında enerji yutma kapasitesi ile enerji dayanımı değerleri karşılaştırmalı olarak bulunmuştur.

Taze beton özelliklerinin değerlendirilmesinde, bütün dünya literatüründe üzerinde fikir birliğine varılmış iki önemli hususun olduğu söylenilebilir. Bunlardan ilki özellikle de Kendiliğinden Yerleşen Betonda Sıkışma özelliklerini de etkileyebilecek olan Aşırı Viskozite Problemleri, ikincisi ise beton bileşenlerinin ayrışmasına da sebep olabilecek Aşırı Akıcılık Problemleridir. Bu çalışmada yapılan deneyler sonucunda ayrışma hiç bir numunede görülmemiştir. Ancak, L 36 olarak sınıflandırılan ve çimento dozajının ağırlıkça % 36 azaltılarak yerine Kireçtaşı Filler kullanılmasıyla elde edilen karışımda ayrışma riskine, S 36 olarak sınıflandırılan ve çimento dozajının ağırlıkça % 36 azaltılarak yerine Kumtaşı Filler kullanılmasıyla elde edilen karışımda ise, Aşırı viskozite riskine dikkat edilmelidir.

Karışımların elastisite modülü değerleri çok düzensiz değişmiş olsa da kendiliğinden yerleşen betona mineral katkı ilavesinin Elastisite Modülünde çok ciddi değişikliklere sebebiyet vermediği söylenilebilir.

Geçirimlilik açısından Uçucu Kül ve Kireçtaşı Filleri, özellikle düşük oranlarda kullanımı iyi sonuçlar verirken, Kumtaşı Filler kullanımı ise geçirimsizliği olumsuz olarak etkilemiştir. Diğer taraftan geleneksel betonlar ile karşılaştırıldığında Kendiliğinden Yerleşen Betonun geçirimsizlik değerleri iyi seviyelerdedir.

Betondaki sülfat etkisini araştırmak için ultrases hızı testlerinden yararlanılmıştır. Yapılan testlerde, çimento miktarı azaltılarak kullanılan mineral malzemelerin betonun ultrases değerlerinde belirgin ve düzenli bir değişikliğe neden olduğu görülmemiştir.

Kütle kaybı deneyleri ultrases testlerine göre daha belirgin sonuçlar vermiştir. Mineral katkı ilavesi Kendiliğinden Yerleşen Betonda numunelerinin ağırlıklarında az miktarda olumsuz etkiye neden olmuştur. Uçucu Kül ve Kireçtaşı kullanılan karışımlar birbirine yakın ve Kumtaşı fillere göre daha iyi sonuçlar vermiştir.

Sülfat etkisinden önce yapılan testlerde özellikle düşük miktarda mineral katkı kullanımı betonun enerji emme kapasitesini çok etkilememiş yalnız Kumtaşı Filler enerji emme kapasitesinde biraz düşüşe sebep olmuştur. Sülfat saldırısından sonra ise referans beton hariç bütün karışımların enerji Emme kapasitelerinde düşüş görülmüştür.

Sülfat saldırısında önceki Eğilme dayanımı Mineral katkı ilavesiyle düşse de, bu düşüş lineer ve düzenli değildir. Sülfat saldırısı da beklenildiği üzere Eğilme Dayanımında bir düşüşe sebep olmuştur.

1. INTRODUCTION

Concrete is an inorganic composite material formed, in its simplest form from a simple reactive binder, an inert filler and water. In reality, modern concrete is a complex material typically made of a form of hydraulic cement, fine and coarse aggregate, mineral and chemical admixtures, and mix water. The structural properties of plain concrete depend primarily on the chemical reactions between the cement, water and other mix constituents, as well as on the spatial distribution and homogeneity of the concrete components. The chemistry, structure and mechanical performance of the products of the hydration reactions in concrete are, in turn, influenced by the production process and environmental conditions prevailing during the production of concrete. Thus in designing concrete for service in a specific environment, not only the concrete materials per se, but also the processing techniques and environments of use have to be taken into account.[1]

Self-Compacting Concrete (SCC) was first developed in 1990 in order to reach durable concrete structures. Since then, several investigations have been carried out to achieve a rational mix design for a standard concrete, which is comparable to normal concrete. Self-compacting concrete is defined so that no additional inner or outer vibration is necessary for the compaction. SCC is compacting itself alone due to its self-weight and is deaerated almost completely while flowing in the formwork. In structural members with high percentage of reinforcement it fills also completely all voids and gaps. SCC flows like “honey” and has nearly a horizontal concrete level after placing. With regard to its composition, self-compacting concrete consists of the same components as conventionally vibrated normal concrete, which are cement, aggregates, water, additives and admixtures. However, the high amount of super-plasticizer for reduction of the liquid limit and for better workability, the high powder content as “lubricant” for the coarse aggregates, as well as the use of viscosity-agents to increase the viscosity of the concrete have to be taken into account. In principle, the properties of the fresh and hardened SCC, which depend on the mix design, should not be different from NC. One exception is only the

consistency. Self-compacting concrete should have a slump flow S_f of approx. $S_f > 65$ cm after pulling the flow cone [9].

The usefulness and versatility of concrete as a construction material are due in great part to the many field and laboratory investigations made over the past century into its performance when exposed to aggressive conditions. The results of the studies have led to the development of cements having increased chemical resistance and have also shown that the quality of the concrete is of primary importance in resisting damaging chemical or physical actions. Quality is not necessarily related to the mechanical strength of the material, and it does not follow that, because a concrete has ample strength to fulfill the purpose for which it was designed, it will resist attack and disintegration in any environment in which it is placed. There are conditions under which a strong concrete will suffer attack, while a weaker one, made from materials which are chemically more resistant to the destructive elements concerned will prove more durable. Nevertheless it is true that when using any given cement, the less permeable the concrete produced, the greater will be its resistance to attack. Since many factors which influence favorably the density and water tightness of a concrete also have a beneficial effect on the strength, it is also generally true that the stronger a concrete made from any one cement, the more durable it will prove [57].

The mixture design of SCC usually incorporates an efficient super-plasticizer, possibly a viscosity-modifying admixture, relatively high amounts of fine materials, relatively low water-to-powder ratio, and controlled proportions of coarse aggregates with adequate particle size and gradation. Due to the difference in mixture design, placement and consolidation techniques, the durability of SCC may be different than that of normal concrete, and thus needs thorough investigation. In a recent publication, Boel emphasized that essential knowledge on the durability of SCC is still needed before its safe use in various applications. The mixture design of SCC involves many variables such as limiting the coarse aggregate volume fraction, and the use of composite cements with a considerably larger volume fraction of supplementary cementitious materials (SCMs) and/or micro-fillers. In particular, the larger powder content ($400\text{--}600\text{ kg/m}^3$) and volume of cementitious paste (34–40%) of SCC and can make it particularly vulnerable to chemical attack, for example by sulfate solutions. Since the last decade, SCC has been widely used in areas

vulnerable to sulfate attack such as substructures, industrial floors, infrastructure, etc [5].

All sulfate attack mechanisms to be discussed are treated as physicochemical processes that lead to certain physico-mechanical consequences. Such consequences include changes in porosity and permeability, volumetric stability, compressive and flexural strengths, modulus of elasticity, hardness, etc. – all these changes ultimately resulting in loss of durability and shortening of service life.

The beneficial effect of pozzolanic materials on sulfate resistance results from the reduced amount of calcium hydroxide among the hydration products and the formation of additional amounts of the C-S-H phase. This brings about a lower porosity and reduced permeability of the hardened cement paste, thus limiting the capacity of the sulfate solution to penetrate into deeper regions of the concrete structure. A reduced C_3A content in the cement also contributes to the improved sulfate resistance. To obtain a proper performance, however, a sufficient curing time prior to exposure to sulfate solutions is essential. Just as Portland cement, also cements with added pozzolanic additives are more vulnerable to magnesium sulfate than to other sulfate forms, but at very high ash contents (70%) the cement may perform still acceptably well [58].

2.LITERATURE

2.1 Pozzolans

ASTM C125 defines pozzolan as “a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.” Pozzolans can be added to cement during the production process or mixed directly into concrete [2].

Most of the pozzolans consist of the waste industrial materials, which are used widely, contributes to improve of concretes stability properties. Besides natural pozzolans, Fly ash, Silica Fume and Grand Granulated Blast Furnace Slag are used not only concrete technology but also cement manufacturing. Using of pozzolans in concrete and cement technology ensure some utilization of these materials properties. Furthermore they decrease the emission of the CO₂ consequently they can provide the sustainability of development [3].

Table 2.1: Classification of Pozzolans

Natural Pozzolans	Artificial Pozzolans
Volcanic Tuffs	Fly Ash
Volcanic Ashes	Silica Fume
Pumice Stone	Blast Furnace Slag
Trass	Burnt Clay

2.1.1 History of Using Pozzolans in the Concrete

The examination of a concrete slab un- covered in southern Galilee indicated that the invention of lime and lime-pozzolans concrete dates back to the neolithic period (7000 BC) instead of Greek and Roman times [4].

In North America, a natural pozzolan was first used for the Los Angeles aqueduct in 1912. In this structure, 50% Portland cement was replaced by deeply altered rhyolite tuff. About \$700 000 was saved due to the use of this pozzolan [6].

2.1.2 Why We Use Pozzolans In Concrete?

The use of pozzolans has the advantage of lower costs and better durability, but the disadvantage of a longer setting time and a slower early strength development [7].

Cement production is an energy intensive process which also has an important effect on the environment. Producing one ton of Portland cement releases about one ton of CO₂ green house gas into atmosphere and as a result of this production 1.6 billion tons of CO₂ is released every year which is estimated at about 7% of the CO₂ production worldwide. The pressure of ecological constraints and environmental regulations are bound to increase in the coming years which will lead to greater use of supplementary cementitious materials such as fly ash or ground granulated blast furnace slag (GGBS). There are two major reasons to use these by-products in concrete:

- (1) Decreasing cement consumption by replacing part of cement with these pozzolanic materials and
- (2) Improving fresh and hardened concrete properties [8].

In case of using Natural admixtures in concrete the hydration heat is declined, Old ages strength is increased, workability is developed (except for Silica Fume), rigidity of concrete is increased and also in order to use of waste materials we can make utilizations both environmental effects and cost effects.

As we know that during the hydration period of the C₂S and C₃S components of cement in addition to C-S-H, which is the main product of hydration, also Ca(OH)₂ makes up the weakest part of concrete, is occurred. Pozzolans make a reaction with this weakest part. At the end of the reaction Pozzolans both ensure their binding properties and provides us to more intensive and more rigid concrete [3].

The harmful materials in cements such as CaO, MgO, and SO₃ can damage volume stability. The ratio of these materials in cement mixtures should be kept under some values. The amount of CaO is less than 2% (by mass) and the ratio of MgO is less than 5% (by mass), and furthermore, it is known that addition of natural pozzolan

materials decreased the amount of “harmful materials” by reaction with them, depending on the fineness, of the natural pozzolan. Portland cement consists of approximately 75% by mass of C_3S and C_2S . The products of hydration of these two minerals are CSH gel and calcium hydroxide (portlandite) crystals. When supplementary cementing materials or pozzolanic active material (e.g. Fly Ash, granulated blast furnace slag or silica fume) are present, the portlandite is consumed in a pozzolanic reaction, which also produces CSH gel.



The presence of supplementary cementing materials thus has a significant influence on the microstructure of the cement matrix. Cement matrix pores containing gel pores and capillary pores resulting from the intrinsic volume change of Portland cement during hydration;

- Pores in aggregates
- Pores formed in the transition zone between cement matrix and aggregate ;
- Water voids and air voids.
- Cracks formed due to the stresses caused by temperature gradients and humidity changes.

According to the IUPAC recommendation the pores can be classified also based on the width as micro-pores (less than 2 μm), meso-pores (between 2 μm and 50 μm) and macro-pores (larger than 50 μm). These void parts of the material are influencing a lot of important properties of concrete, like mechanical parameters, water permeability, resistance against carbonation and overall durability. Extensive research aimed at the study of the concrete porosity has been done during the past and is still appealing. This is especially valid in case of concrete containing supplementary cementing materials, like granulated blast furnace slag or fly ash. These materials, in contact with alkaline environment which is formed during the concrete hydration mainly due to the formation of calcium hydroxide, contribute to the formation of the binding phases in the matrix and thus are further influencing the resulting pore structure of the concrete [11].

2.1.3 Disadvantages of Pozzolans

Advantageous properties which include cost reduction, reduction in heat evolution, decreased permeability, alkali aggregate expansion control, increased chemical resistance, reduced concrete drying shrinkage, and the improvement of the properties of fresh concrete; however, the use of pozzolans also causes longer setting times and lower early strengths compared with pure Portland cement. Increasing the pozzolanic activity of pozzolans will be very important to overcome the disadvantages of low early strengths of cements containing pozzolans. Highly reactive silica fume and metakaolin are widely used to produce high early strength concrete [7].

2.1.4 Evaluation Of Pozzolanic Reactivity

The performance of a hardened paste depends not only on the reaction rate and degree, but also on the nature of the reaction products. For example, the presence of reactive Al_2O_3 in slag can increase the early strength of slag cement, but decrease the later strength of the cement. Performance standards are becoming more important because more diverse materials and combinations of materials are being used to produce satisfactory products. In practice, people are primarily concerned about the performance of the materials used [8].

2.1.5 Effects of Particle Size Distribution

Chemical composition, particle-size distribution, fineness, and pozzolanic activity, and curing conditions of concrete are important factors affecting the properties of concretes with pozzolanic materials. Particle-size distribution clearly plays a very important role in the rate of chemical reactivity and in the water demand. Pozzolanic reaction takes place on the surface of the particles and increasing surface area has an important effect on pozzolanic activity. Thus, the fineness of the pozzolan is very important for the improvement of cement paste-aggregate interfacial zone, which is the weakest link in concrete.

The particle size is an important factor also for the pozzolanic activity of the granulated blast furnace slag. Similar to the fly ash, the strength of slag concretes also increases with slag fineness. Besides increasing the fineness, another solution to overcome the disadvantages of using high amounts of pozzolan, is to use ternary or quaternary blends of portland cement and pozzolans. By using different pozzolans

together, some of the shortcomings can be compensated and more environmentally friendly concretes with specific properties can be obtained. The fly ash and blast furnace slag were ground in a laboratory ball mill.

The original Blaine fineness of the fly ash was 222 m^2 per 1 kg and was increased to 604 m^2 per 1 kg by grinding [2].

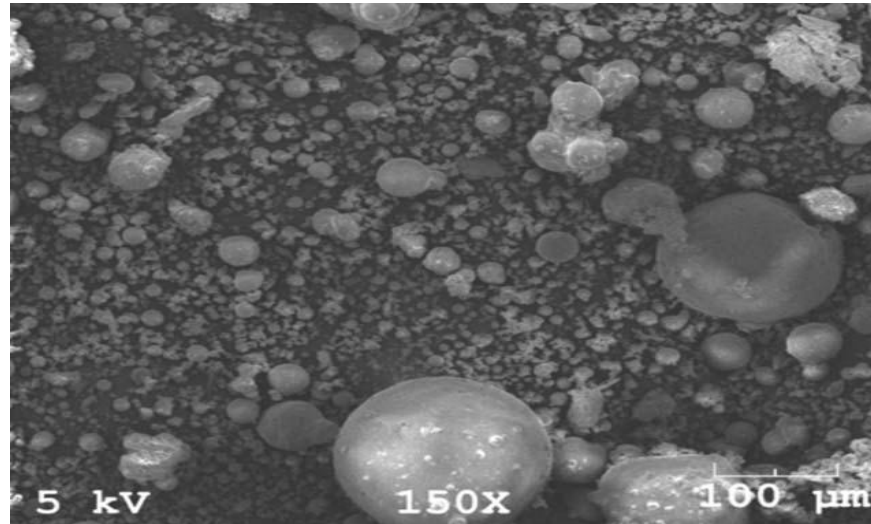


Figure 2.1: Original fly ash particles (before grinding) (Blaine surface area: $222 \text{ m}^2/\text{kg}$)

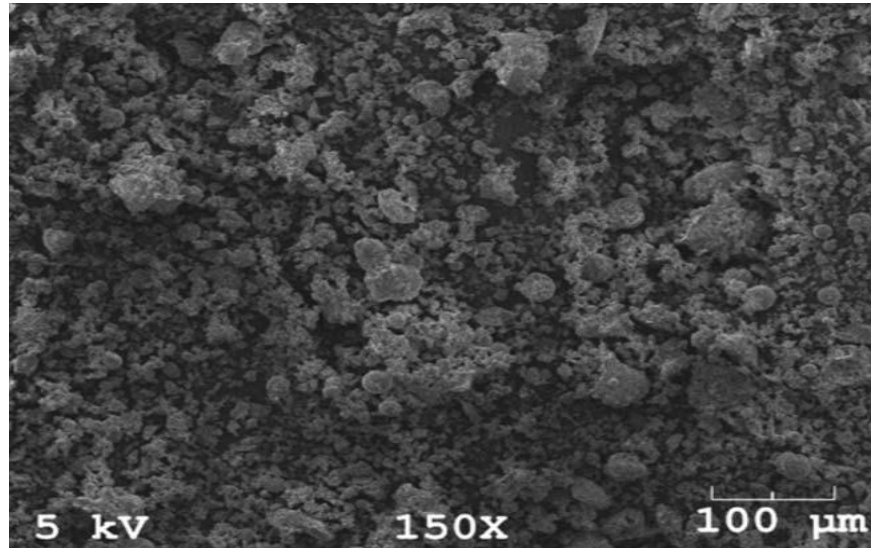


Figure 2.2 Ground fly ash particles (Blaine surface area: $450 \text{ m}^2/\text{kg}$)

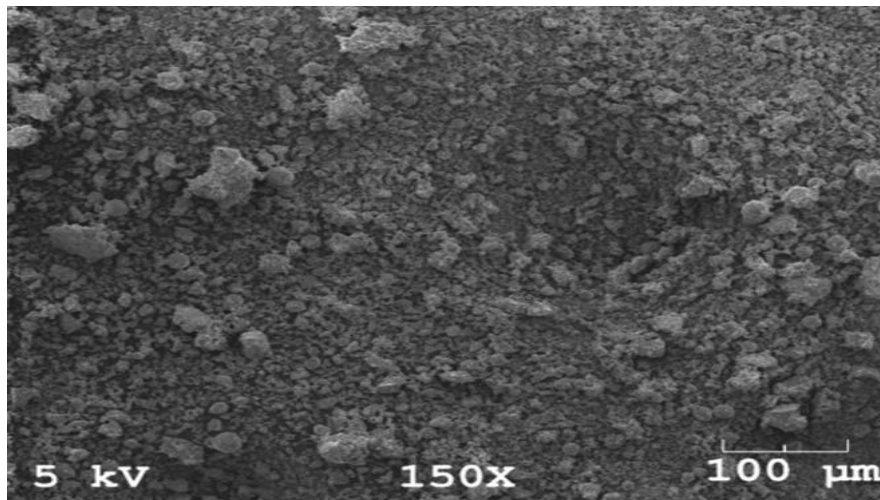


Figure 2.3 Ground fly ash particles (Blaine surface area: $604 \text{ m}^2/\text{kg}$)

2.1.6 Effects On Compressive Strength

Pozzolans react with Ca(OH)_2 , which is one product of hydration of clinker in cement. Therefore, after cement is mixed with water, during the collection time of Ca(OH)_2 it has a diluting effect on portland cement. However, as Ca(OH)_2 is being gathered in the medium, the influences that increase the strength of pozzolan start to emerge, and therefore a fall in the early strength of concrete is expected with pozzolan usage [3].

2.1.7 Effects On Cure Conditions

Curing of concrete affects both the resistance properties and the strength properties of the concrete. According to the Neville's researches if the relative humidity ratio of concrete declines to under % 80, the reaction cement and water finishes. One of the first studies about this issue showed us, the concretes, cured in the water during the 6 months, In case of they cured on the air instead of water the compressive strength of them decreased % 58. Another study indicates that, the concrete samples saved under water during the 5 years makes up a strength increasing constantly. Correspondingly at the end of the 5 years the compressive strengths of the samples without water curing showed the same values with their 28 days strengths. According the one of the Aitcins study the compressive strength of 1 year old samples, cured on the air, gave % 17-22 low values than the same samples, cured under water [2].

2.1.8 Effects on Workability

As the natural pozzolan addition ratio increased, water demand to obtain the same consistency and workability increases by 13% for a 35% natural pozzolan addition. The reason for this is that the rate of increase of water demand is not as high as the natural pozzolan addition ratio can be, so that natural pozzolan is finely divided and has a lubricant effect on concrete.

2.1.9 Effects on Setting Time

Setting properties of cement matrix were affected by the natural pozzolan ratio substituted for cement. Experimental results show a proportional delay in the initial set time, depending on the natural pozzolan addition ratio. However, this proportional delay has occurred more clearly at the final set time, which obviously shows that the samples that the natural pozzolan used decrease the hydration speed with setting delay and by decreasing hydration heat, which also implies that they can be effective against the shrinking danger. However, some studies relate this delay in setting times to the increase in the water/cement ratio [2].

2.1.2 Fly Ash

2.1.2.1 Definition and Some Characteristics

Fly ash is a by-product of coal combustion and has found uses in a wide range of construction applications, including flow-able fill, as shown in Table 2.1 (American Coal Ash Association, 2007). Fly ash is used mostly in Portland cement concrete, but its use in Controlled Low Strength Material (CLSM) has grown considerably in recent years. Though fly ash has established itself as an important construction material, approximately 70–75% of the fly ash generated annually, is land filled [12].

Table 2.2 Fly Ash applications in construction (ACAA, 2007)

Application	Quantity used (Million MetricTons)	% of Total Used
Concrete/concrete products/grout	13,7	43,27
Cement/raw feed for clinker	3,63	11,46
Flow-able fill	0,11	0,34
Structural fills/embankments	7,72	24,38
Road base/sub-base/pavement	0,38	1,2
Soil modification/stabilization	0,86	2,7
Mineral filler in asphalt	0,01	0,03
Aggregate	0,14	0,44
Mining applications	1,36	4,29
Waste stabilization	2,68	8,46
Agriculture	0,05	0,15
Others	1,02	3,22
Total	31,66	100

In commercial practice, the dosage of fly ash is limited to 15–20% by mass of the total cementitious material. Usually, this amount has a beneficial effect on the workability and cost economy of concrete but it may not be enough to sufficiently improve the durability to sulfate attack, alkali–silica expansion, and thermal cracking. For this purpose, larger amounts of fly ash, on the order of 25–35% are being used. Concrete mixtures containing more than 40–50% fly ash by mass of the cementitious material can be defined as high-volume fly ash (HVFA) concrete.

Bayat and Turker, made an extensive research on the characterization of Turkish fly ashes from the view point of mineralogical, morphological, physical and chemical properties. It is not possible to make a generalization for all fly ashes due to differences between their characteristics. The chemical composition (reactive silica, free lime, unburned carbon and sulfur content), physical properties (shape morphology, surface texture, particle size distribution, fineness), and pozzolanic activity of fly ashes are responsible for the good or bad performance in HVFA concrete production [13].

According to Turkish Cement Producers Unions 2003 report, the amount of Fly ash which are occurred all over the world are approximately 600 million tones. There are 11 thermal power plant is given below are still working in Turkey. Afşin-Elbistan, Çatalağzı, Çayırhan, Kangal, Kemerköy, Orhaneli, Seyitömer, Soma, Tunçbilek,

Yatağan ve Yeniköy. And the annual production of fly ash in 11 power plants in Turkey is more than 20 million tones [14].

2.1.2.2 High Volume Fly Ash Concrete (HVFA)

Concrete mixtures containing more than 40–50% fly ash by mass of the cementitious material can be defined as high-volume fly ash (HVFA) concrete. The properties of HVFA concretes, when compared to conventional Portland cement concrete, are summarized by Mehta as follows;

- A high-grade fly ash can act as a water reducer in concrete production depending on the particle size distribution, surface characteristics and morphology. According to Mehta, the fly ashes with small size and glassy texture make it possible to reduce the amount of water required to a given consistency. However, the fineness of cement substituted with fly ash should also be taken into consideration. Another factor affecting the workability improvement capacity of fly ash is the unburned carbon content. Large amounts of carbon in fly ash are harmful for concrete production because the cellular particles of carbon tend to increase the water requirement and the admixture requirement for a specified consistency and/or air content. High-grade fly ashes at high-volumes in concrete usually improve flowability, pumpability, compactability and finishability. High-volume fly ash concrete does not required any special efforts in terms of mixing and placing and can be mixed, transported and placed using conventional means. The improvements in cohesiveness and finishability are particularly valuable in lean concretes or those made with aggregates deficient in fines especially at long distance pumping.
- Early-strength up to 7 days, which can be accelerated with suitable changes in the mix design when earlier removal of formwork or early structural loading is desired. HVFA concrete requires minimum of 50 % of Fly ash by mass of the cementitious materials. Such high proportions of fly ash are not readily accepted by the construction industry due to a slower rate of strength development at early age. The high volume fly ash concrete system overcomes the problems of low early strength to a great extent through a drastic reduction in the water–cementitious materials ratio by using a

combination of methods, such as taking advantage of the superplasticizing effect of fly ash when used in a large volume, the use of a chemical superplasticizer, and a judicious aggregate grading.

- Much later strength gain between 28 and 90 days or more. (With HVFA concrete mixtures, the strength enhancement between 7 and 90 days often exceeds 100%, therefore, it is unnecessary to overdesign them with respect to a given specified strength).
- Superior dimensional stability and resistance to cracking from thermal shrinkage, autogenous shrinkage, and drying shrinkage. In unprotected concrete, a higher tendency for plastic shrinkage cracking should be expected.
- After 3–6 months of curing, much higher electrical resistivity, and resistance to chloride ion penetration.
- Better cost economy due to lower material cost and highly favorable lifecycle cost.
- Superior environmental friendliness due to ecological disposal of large quantities of fly ash, reduced carbondioxide emissions, and enhancement of resource productivity of the concrete construction.
- If properly cured high volume concrete products are very homogenous in microstructure, virtually crack-free, and highly durable. Very high durability to the reinforcement corrosion, alkali–silica expansion, and sulfate attack can be obtained [15-16].

2.1.2.3 Effects on the Concrete Durability

It is known that not only the strength of concrete, but also its durability, is important to increase the service life of the construction. The use of certain pozzolans such as some fly ashes increases the durability through the pore refinement and the reduction in the calcium hydroxide of the cement paste matrix. One of the most important aspects of durability of concrete is the resistance to sulfate attack. Both sulfate solution and sulfuric acid solution are harmful to concrete. The other property which also influences the performance of structural concrete is the shrinkage especially the drying shrinkage which could induce cracking and thus reduces the ability of

concrete to resist chemical attack. The effect of fly ash fineness on the strength, drying shrinkage and the resistance to sulfate solution attack is therefore of considerable interest.

Lee tested fly ash with three fineness values and reported that the reacted calcium hydroxide of the fine fly ash cement paste was greater than that of the coarser fly ash cement paste indicating a larger degree of pozzolanic reaction of the fine fly ash. The glass content of the fly ash also contributes to the development of the strength. Chindaprasirt found that the glass content of the fine fly ash portion is higher than that of the coarser fly ash portion from the same batch, and that the use of fine fly ash reduces the water requirement of the mortar mix. The fine fly ash particles underwent a complete burning and are more spherical in shape and smoother surface as compared to the coarser fly ash particles. This reduction in water requirement together with the higher reactivity of the fine fly ash contributes to a higher strength of mortar as compared to a coarser fly ash [17].

2.1.2.4 Properties of Fly Ash

The resultant physical properties of the ash, such as moisture content, particle mass, glass composition and the portion of unburned carbon, will depend on the combustion temperature at which the coal was fired, the air : fuel ratio, coal pulverization size and rate of combustion.

Physical Properties

Fly ash consists of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in the fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt (less than a 0.075 mm or No. 200 sieve). Although sub-bituminous coal fly ash is also silt-sized, it is generally slightly coarser than bituminous coal fly ash. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m²/kg. The colour of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash.

Chemical Properties

The chemical properties of fly ash are influenced to a great extent by the properties of the coal being burned and the techniques used for handling and storage. There are

basically four types, or ranks, of coal, each vary in heating value, chemical composition, ash content, and geological origin. The four types (ranks) of coal are anthracite, bituminous, sub-bituminous, and lignite. In addition to being handled in a dry, conditioned, or wet form, fly ash is also sometimes classified according to the type of coal from which the ash was derived.

The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium, with varying amounts of carbon. Lignite and sub-bituminous coal fly ash is characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash [18].

2.1.2.5 Utilization of Fly Ash In Concrete

Utilization of fly ash appears to be technically feasible in the cement industry. There are essentially three applications for fly ash in cement including,

- replacement of cement in Portland cement concrete,
- pozzolanic material in the production of pozzolanic cements,
- set retardant ingredient with cement as a replacement of gypsum.

Cement is the most cost and energy intensive component of concrete. The unit cost of concrete is reduced by partial replacement of cement with fly ash. The utilization of fly ash is partly based on economic grounds as pozzolana for partial replacement of cement, and partly because of its beneficial effects, such as, lower water demand for similar workability, reduced bleeding, and lower evolution of heat. It has been used particularly in mass concrete applications and large volume placement to control expansion due to heat of hydration and also helps in reducing cracking at early ages. This also reduces the cost of construction. Fly ash concrete provides much strong and stable protective cover to the steel against natural weathering action.

Because of the presence of cementitious compounds of calcium and a reactive glass, the high-calcium fly ash is quite suitable in Portland cement products. Several studies are being conducted to better understand the complexities of alkali aggregate reactivity and sulphate resistance with respect to fly ash in concrete. The availability

of high-lime fly ash containing compounds found in cement has led to high strength concretes produced by the addition of fly ash and plasticizers. High-strength and high performance concrete can also be made with Class F fly ash. The utilization of fly ash in concrete produces less permeability because of the spherical particles, and therefore improved packing, i.e. more dense paste and pozzolanic reaction. In mass concrete, with high percentage replacement of cement with fly ash, there is a lower heat of hydration compared to straight Portland cement concrete, particularly when Class F fly ash is used. Class C fly ash may not lower the heat of hydration.

Mehta has discussed the factors that contribute to attack of sulphates on fly ash concrete. As noted in his review paper on this subject, the agents responsible for concrete expansion and cracking are alumina bearing hydrates, such as calcium monosulfo-aluminate and calcium aluminate hydrate, which are attacked by the sulphate ion to form ettringite and calcium trisulfoaluminate. Acidic type interactions between sulphate ions and calcium hydroxide also lead to strength and mass loss.

Exhaustive research has been conducted on fly ash admixture concrete and its properties. Research showed that fly ash used as an additive to Portland cement has a number of positive effects on the resulting concrete. A decrease in water demand, decreasing the water:cement ratio. An improvement of the packing of particle size decreases air entrainment in the concrete.

Fly ash increases resistance to corrosion, and ingress of corrosive liquids by reacting with calcium hydroxide in cement into a stable, cementitious compound of calcium silicate hydrate. The original calcium hydroxide was soluble, whereas the calcium silicate hydrate is less soluble in fly ash concrete, thereby reducing the possibility of leaching of calcium hydroxide from the concrete. In addition to calcium silicate hydrate being less soluble, reaction products tend to the filling of capillary voids in the concrete mixture, thereby reducing permeability of the concrete.

Addition of fly ash as an admixture increased early age compressive strength and long term corrosion resistance characteristics of concrete. Abrasion resistance of concrete made with Class C fly ash was better than both concrete without fly ash and concretes containing Class F fly ash. High volumes of Class C and Class F fly ash can be used to produce high-quality pavements in concrete with excellent performance. Blending of Class C fly ash with Class F fly ash showed either

comparable or better results than either of the control mixture without fly ash or the unblended Class C fly ash.

HVFAC refers to concrete where fly ash comprises more than 30% of the total cementitious materials. HVFAC has a lower cost and is more durable than conventional concrete, and affords improved resistance to alkali-sulfate reaction and sulfate attack [18].

Table 2.3 Benefits of using Fly Ash in concrete [72].

Concrete Properties	Impact Of Fly Ash
Water demand of fresh concrete	Reduced
Component segregation of fresh concrete	Reduced
Workability of fresh concrete	Increased
Setting time of fresh concrete	Elongated
Bleeding on fresh concrete	Reduced
Hydration of fresh concrete	Reduced
Early strength of hardened concrete	Reduced
Long term strength of hardened concrete	Reduced
Permeability of hardened concrete	Reduced
Freezing-Thawing of hardened concrete	Reduced
Alkali-Aggregate reaction	Reduced
Sulfate resistance	Increased
Concrete casting in hot weather	Made easy

Influence On Water/Cement Ratio

The use of fly ash as an additive in Portland cement will generally reduce the water demand of the mix. Typical Portland cements require 150-250 L/m³, water, representing 15-25% of the total volume of the mix. As the water content increases, so does the drying shrinkage of the concrete and a less desirable condition is created. By adding ash to the mix, the water content can be reduced, due to the lubricating qualities of the fly ash. The ash acts as tiny 'ball bearings' and improves the workability of the cement, while decreasing the water demand of the mix. Generally, a reduction of 15-20 L/m³ water can be attained by fly ash addition to the cement mix [19].

Influence on Curing Temperature

In order to determine the influence of fly ash on the cement hydration and the compressive strength development, Maltais and Marchand made an investigation, various mortar specimens were prepared with an ordinary portland cement and two different North-American Class F fly ashes (according to ASTM C 618). The mortar mixtures were produced at a constant water/binder ratio of 0,50 and at a binder/sand ratio of 2,5. In order to evaluate the effect of fly ash on cement hydration, fly ash was used at a cement replacement level of 10%, 20% and 30% (by total mass of binder). The mortar specimens were subjected to an isothermal curing temperature of 20°C and 40°C. Test results indicate that the use of fly ash significantly contributes to reduce the early compressive strength of the mixtures cured at 20°C. For instance, when fly ash is used, the compressive strength development is approximately reduced from 15 to 25 % after 7 days of isothermal curing at 20°C. The compressive strength reduction clearly depends upon the cement replacement level (10, 20 or 30 %).

Influence on the Cement Hydration Process

This observation is in good agreement with the previous conclusions of many authors who also found that most Class F fly ash only begin to hydrate after a substantial curing period. If fly ash does not react during the first days of curing, test results clearly indicate that it cannot be considered as a totally “inert” material. Despite very little pozzolanic activity, the presence of fly ash appears to increase the mortar non-evaporable water content at early days. Many authors have attributed this increase to an acceleration of the early cement hydration in presence of fly ash. In many cases, the addition of fly ash tends to increase the number of fine particles in the system. The presence of these fine particles contributes to increase the density of the matrix. The replacement of cement particles by fly ash is also believed to increase the available space in the floe structure created by the cement grains. Finally, the fine particles provide additional nucleation sites for cement hydration products such as C-S-H, portlandite and ettringite.

Test results clearly confirmed that an elevation of the curing temperature contributes to reduce the long-term compressive strength of OPC mixture. On the other hand, data also indicate that an increase of the curing temperature is much less detrimental

for fly ash mixture sand. An elevation of the curing temperature from 20°C to 40°C has contributed to increase the long-term compressive strength of all fly ash mixtures with a replacement level of 20 % and 30 % [20].

2.1.3 Silica Fume

2.1.3.1 Definition and Some Characteristics

Silica fume is a pozzolanic material which is a by-product of the silicon smelting process. It is used to produce silicon metal and ferrosilicon alloys which have a high content of glassy-phase silicon dioxide (SiO_2) and consist of very small spherical particles. Silica fume is known to produce a high-strength concrete, and is used in two different ways: as a cement replacement, in order to reduce the cement content (usually for economic reasons); and as an additive to improve concrete properties (in both fresh and hardened states) [21].

As a pozzolana, SF reacts with calcium hydroxide (CH) liberated by the hydrolysis of C_3S and C_2S of Portland cement. The CH constitutes about 20–25% of the volume of the hydration products and CH crystals grow in solution. Due to their morphology, they are relatively weak, brittle and not cementitious. Cracks can easily propagate through regions populated by CH crystals, especially at the aggregate cement paste matrix interface.

The percentage of CH consumed by SF is represented as an index of the pozzolanic activity of SF. It has been reported that due to high pozzolanic action of SF, about 25% of SF consumes most of the liberated $\text{Ca}(\text{OH})_2$ at about 28 days [22].

2.1.3.2 Effects of Using Silica Fume In Concrete

The addition of silica fume to concrete is effective for increasing the compressive strength, decreasing the drying shrinkage, increasing the abrasion resistance, increasing the bond strength with the reinforcing steel and decreasing the permeability. As a result, silica fume concrete is increasingly used in civil structures. However, silica fume causes workability loss, which is a barrier against proper utilization of silica fume concrete [23].

A scanning electron microscope (SEM) analysis of 16 years old concrete with addition of SF shows that the microstructure of this material is more homogeneous and dense than the concrete without SF. The most important region in the

microstructure of the concrete is around the aggregate. The addition of SF in concrete leads to reduction in porosity of the transition zone between matrix and aggregate in the fresh concrete and provides the microstructure needed for a strong transition zone. Investigation on the aggregate matrix interface concluded that, in concrete with SF, a transgranular fracture is observed, hence, the cracks usually traversed the aggregates, pointing to a lower porosity of the interfacial zone as a result of SF inclusion [24].

Influence on The Air Content of Mortar

The durability of concrete depends upon the permeability of mortar. The amount of air present in the mortar influences the strength of the product. It has been reported that the strength decreases as the air content or permeability increases. As the SF is finer than the cement particles, the finer particles of SF fill the gap between cement particles resulting in impermeable microstructure of the cement paste. The micro filling effect of SF is one of the important factors for the development of dense concretes with very high strength. At 0% SF, the air content was 2%, whereas it decreased to 1% with 30% SF. A small amount of air content significantly decreases the strength of mortar.

Influence on the Workability of Mortar

Workability of mortar slightly decreases as the SF content increases. This has been due to the higher specific surface of SF, which needs more water for complete hydration and for workability. The effect of condensed SF on the rheology of fresh mortar is generally viewed as a “stabilizing effect”. In other words, the addition of very fine particles to a mortar/concrete tends to reduce segregation and bleeding tendencies. Without SF, the finest particles in mortar are those of Portland cement. Since the sand particles are bigger than the cement particles, the latter act as stabilizers by reducing the dimensions of channels through which bleed water rises to the surface of mortar.

Influence on the Setting Times of Concrete

The ability of cement to make fluid concrete to hardened state is represented by the time of setting. The fineness of the cement and its chemical composition influences the setting times of concrete. It has been observed that the initial setting time decreases as the SF content increases. At smaller contents, the setting times of

cement paste did not affect much. However, at higher SF contents, the initial setting time significantly decreases. At 30% SF, the initial setting time has been only 30 min. It indicates that if higher contents were added, it would have been produced with cement pastes with false setting. The final setting times seem to be not influenced by the SF. The pozzolanic action of SF seems to be very active at early hours of hydration. Cheng Yi and Feldman reported that SF accelerates the hydration of C_3A and C_3S reaction at the early hours of hydration. According to Swamy, the addition of SF in small amount (about 10% by weight of cement) to cement composites either has no significant effect or alter the time of set very slightly.

Influence on the Soundness of Cement

The resistance against volume changes of cement is measured by the soundness. It has been generally observed that the soundness of cement increases or the expansion decreases with the addition of SF. The pure cement paste exhibited very high expansion than those with SF. The cement paste obtained with SF shows very good resistance against volume changes. It has been observed that drying shrinkage increases as the SF content increases. The data from drying shrinkage tests by many researchers show that the short-term drying shrinkage of cementitious composites increases with the addition of SF. But the test results on long-term drying shrinkage indicate that there has been no significant effect of SF addition. However, the presence of coarse aggregate in concrete could restrain the shrinkage stress produced with the addition of SF [22].

2.1.3.3 Effects of Silica Fume on the Concrete Durability

Aggressive attack of sulphate ions is one of the factors responsible for damage to Portland cement concrete. Sulphate ions can react with some constituents of cement pastes producing sulphotoaluminate hydrates (ettringite or monosulphate) and gypsum, which cause expansion and cracking of concrete. Condensed silica fume is a by-product of the manufacture of silicon or silicon alloys which are produced in the submerged arc electric furnaces. Silica fume particles appear to be formed by the oxidation and condensation of the gaseous silicon sub-oxide SiO that is formed in the reaction zone. The silica fume is mainly amorphous and has about 20–25 m^2/g surface area, therefore it has a good pozzolanic activity. These blended cements have a good resistance to sulphate attack due to the fine pore structure and reduction of

lime content. Helmy studied the role of silica fume on the chloride and sulphate attack on the composite of 85% SRC and 15% high alumina cement (HAC). It was found that the substitution of HAC with SF improved the attack of chloride and sulphate ions on cement pastes.

Different blended cement pastes were prepared starting from a mixture of 85% ordinary Portland cement and 15% alumina cement, the latter was substituted by 0, 5, 10 and 15% of silica fume or granulated slag. After 28 days (0 time) curing in tap water, hardened samples were immersed in 4% MgSO_4 solutions for 1, 3, 6, 9 and 12 months. The solution was renewed every month to keep the concentration of SO_4^{2-} as much as possible constant.

The results show that the free lime content of all cement pastes decreases with curing time up to one year. This is mainly due to the reaction of Ca(OH)_2 , which is liberated during the hydration of Portland cement with silica fume and HAC. Also, the decrease of free lime of cement pastes in MgSO_4 solution is mainly due to the reaction of Ca(OH)_2 with MgSO_4 to give gypsum and Mg(OH)_2 , therefore the amounts of free lime content decreases with curing time up to one year. On the other hand as the amount of silica fume increases the free lime decreases due to the reaction of more silica fume with Ca(OH)_2 . Generally the hardened cement pastes containing silica fume give lower values of free lime than those without silica fume.

The total sulphate of the silica fume blended cement pastes shows higher values than those of blended cement pastes without silica fume. As the silica fume increases, the total sulphate increases. This is due to the reaction of free lime with sulphate ions. Also, the mixing water increases with silica fume therefore, the porosity increases. As the porosity increases the sulphate ions are penetrated in the open pores then the sulphate content increases. On the other side, the alumina cement can not react with sulphate ions and Ca(OH)_2 , therefore, the silica fume blended cement pastes show higher values of total sulphates [25].

2.1.4 Ground Granulated Blast Furnace Slag

2.1.4.1 Definition and Some Characteristics

Slag is a mixture of lime, silica and alumina, the same oxides that make up Portland cement, but not in the same proportion. The composition of blast furnace slag is determined by that of the ores, fluxing stone and impurities in the coke charged into

the blast furnace. Typically, silicon, calcium, aluminum, magnesium, and oxygen constitute 95% or more of the blast-furnace slag. To maximize hydraulic (cementitious) properties, the molten slag must be chilled rapidly as it leaves the blast furnace. Rapid quenching or chilling minimizes crystallization and converts the molten slag into fine-aggregate-sized particles generally smaller than a 4.75 mm (No. 4) sieve, composed predominantly of glass. This product is referred to as granulated iron blast-furnace slag. GGBS is obtained by finely grinding of this material. Hydrated cement paste involves approximately 70% C–S–H, 20% Ca(OH)_2 ; 7% sulpho-aluminates and 3% secondary phases. The Ca(OH)_2 which appears as the result of the chemical reactions affect the quality of the concrete adversely by forming cavities as it is partly soluble in water and lacks enough strength. The use of ground granulated blast-furnace slag has a positive effect on binding the Ca(OH)_2 compound, which decreases the quality of the concrete. At the end of the reaction of the slag and Ca(OH)_2 , hydration products, such as C–S–H gel, are formed [26].

Blast furnace slag has been used as a secondary cementing material for more than 100 years and there is a broad knowledge regarding its application. Most commonly it is used for the production of blended cements and slag cements. Currently, there is high interest in the application of this alternative material because the production of Portland cement clinker contributes about 5% to the global man-made CO_2 emissions. Despite the fact that the amount of available slag is limited, there is an increasing demand for slag cement to reduce the CO_2 emissions due to the production of cement and concrete. The hydration of blast furnace slag is slow when compared to Portland cement clinker, resulting in lower early strength and higher strength gain at later ages. The heat release during hydration at room temperature is significantly lower than during hydration of Ordinary Portland Cement (OPC). Due to its slow reaction, slag cement produces a very dense microstructure and is highly resistant to chemical attack. Blast furnace slag contains less lime than Portland cement clinker and calcium hydroxide is not formed during reaction of the slag particles. Instead of this, calcium silicate hydrate (C–S–H) with a low calcium/silicon ratio, hydrotalcite, and ettringite or AFm phases are formed [27].

2.1.4.2 Effects Of The Blast Furnace Slag On The Concrete Durability

The long-term durability of concrete is dependent upon a number of physical and chemical parameters. It is generally recognized that the foremost prerequisite for

durable concrete is that it be dense and impermeable to liquids and gases with a high resistance to the penetration of ionic species such as sulfates and chlorides. For the best performance the mixture proportions must be appropriate to the particular application and the preparation, placing, compaction and curing should be carried out under proper supervision. Low C_3A , sulfate-resisting Portland cement (SRPC) concretes were highly resistant to attack, as were combinations of the medium and high C_3A normal Portland cements with low alumina slags. Sulfate attack was greatest when both the C_3A content of the Portland cement and the alumina level of the slag were high. [28]

Hadj-sadok , Kenai , Courard , Darimont had made some experiments with these materials, are given below, and found those consequences. Ordinary Portland cement (OPC) type CEM I 52.5 with a fineness of $4200 \text{ cm}^2/\text{g}$ was used for mortar mixes. The ground granulated blast furnace slag (GGBFS) used in this research project was produced in the iron steel company of El Hadjar (Algeria). The GGBFS was ground in a laboratory mill to a Blaine fineness of $4150 \text{ cm}^2/\text{g}$. The specimens were a RILEM mortar (three parts of sand, one part of cement and 0.5 part of water) in which cement has been partially substituted in mass with 0% (M0), 30% (M30) and 50% (M50) of slag, respectively. Even after 360 days, the mortars with slag (M30 and M50) have a volume of pore higher than that of the M0 mortar. That could be due to the higher porosity of the CSH resulting from the slag hydration. Indeed, the increase of the pores volume for mortars with slag (particularly M50) compared to M0 mortar is mainly induced in the fraction of small radius pores (pore radius less than $35 \text{ }\mu\text{m}$ and particularly between: 20 and $40\mu\text{m}$) this class of small pores is usually attributed to the porosity of the CSH gel, which is more present in the matrices containing slag cement.

Observation of M0 (Mortar without slag)mortar sample in SEM reveals a structure of hydrates (crystals and gel) combined to the ettringite needles (Fig.2.4a).In M50(Mortar with 50 % slag) mortar (Fig 2.4.b), hydrates structure appears relatively denser and ettringite needles are not detected: this could explain the porosity refinement observed in pore distribution of M50 mortar (MIP results) and thus reflects good hydration of slag after 360 days curing in wet conditions [29].

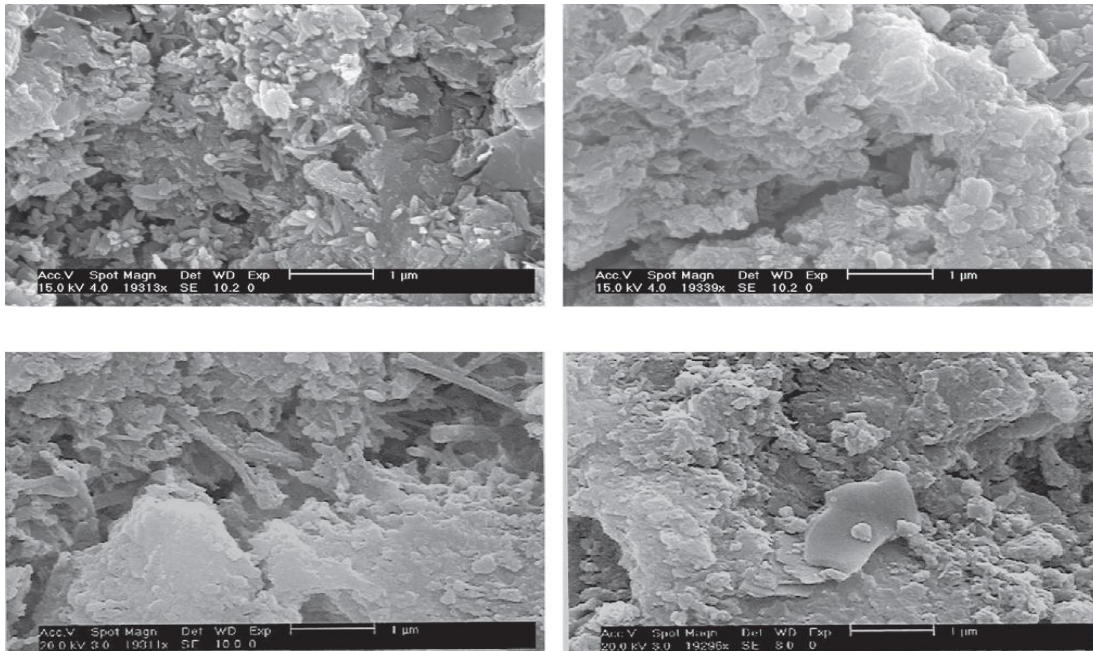


Figure 2.4 SEM micrograph of (a) CEM I mortar and (b) 50% slag mortar after 360 days of wet curing

2.1.4.3 Physical Properties Of GGBFS

Fineness

The fineness of GGBFS is a very important parameter, which is dependent on energy-saving and economic considerations, influences the reactivity of GGBFS in concrete, early strength development of concrete and water requirement. Swamy reported that an increase in fineness of two to three times that of normal PC can preserve the benefits of material fineness on a variety of engineering properties such as bleeding, time of setting, heat evolution, high strength and excellent durability.

Glass Content

The glass content of slag is considered to be the most significant variable and certainly the most critical to hydraulicity. The rate of quenching, which influences the glass content, is thus the predominant factor affecting the strengths of slag cements. Increasing crystalline contents reduce hydraulicity, but there is no well-defined or single relationship between strength and glass content, although some research has shown linear glass content–strength relationship. Although a glassy structure is essential to reactivity, researches shown that there is no exact correlation of glass content to hydraulicity, and therefore, there is no guarantee that a high glass content will produce a highly reactive slag. Several researches show that slag

samples with as little as 30–65% glass contents are still suitable, but no specific minimum required glass content appears to emerge from these tests [30].

2.1.5 Metakaolin

Metakaolin is a pozzolanic material and its use dates back to 1962 when it was incorporated in concrete for Jupia Dam in Brazil. Metakaolin is manufactured for use and is formed when china clay, the mineral kaolinite, is heated to between 600 and 800°C. It seems that metakaolin has significant potential as a beneficial addition for concrete. Because metakaolin is a very reactive pozzolana, the calcium hydroxide content of concrete can be virtually eliminated by its incorporation. A range of concrete property improvements have been recorded, including improved resistance to the penetration of chlorides, freeze-thaw resistance and reduced shrinkage; improved sulfate resistance and resistance to acids; improved strength and abrasion resistance; effectiveness in the suppression of ASR expansion; and also improvements in finish characteristics and the elimination of efflorescence [31].

2.2 Aggregates

Aggregate is the main constituent of concrete. Aggregate properties do influence concrete properties, but by and large they do not control the performance of the concrete. The essential requirement is that the aggregate remains stable within the concrete in its exposure conditions.

The strength of concrete cannot exceed the strength of the aggregate. In practice, concrete grade is likely to be much less than the strength of the aggregate, because stress concentrations are generated when the concrete stresses are shared by the aggregate and cement paste. Weak aggregates may break down during mixing, handling and compaction.

There are three main reasons for mixing aggregate with cement paste to form concrete, rather than using cement paste alone. The first and oldest reason is that aggregate is cheaper than cement, so its use extends the mix and reduces costs. Second, aggregate reduces shrinkage and creep, giving better volume stability. Third, aggregate gives greater durability to concrete. Many deterioration processes principally affect the cement paste [32].

2.2.1 Classification of Aggregates

Sources of aggregates fall into the broad categories of sands and gravels and crushed rock. Sands and gravels are the products of erosion of pre-existing rocks and are usually transported by water, or by ice in formerly glaciated regions. They are typically deposited as relatively thin layers at the foot of mountains, in river valleys or along shorelines. Crushed rock, by contrast, is obtained from rock quarries which imply that appropriate rock must occur at the Earth's surface where a quarry can be developed [33].

2.2.2 Shape and Particle Size Distribution of Aggregates

The shape of aggregate particles can affect water demand and workability, mobility, bleeding, finishability and strength. Equidimensional shapes are preferred. Flaky or elongated particles tend to be detrimental. Rounded particles tend to give better workability than crushed or angular particles.

Consistency of particle size distribution is important to the properties of fresh concrete. There is a more minor influence on hardened concrete properties. Larger maximum particle size benefits lean concrete but the optimum size is around 20 mm for normal strength concrete. Equidimensional particle shapes are the best. Shape and texture affect water demand and aggregate-cement paste bond. Aggregate must be strong enough to withstand mixing, handling and compaction without degradation. In practice, the aggregate strength usually exceeds concrete strength considerably [32].

2.2.3. Durability of Aggregates

Portland cement contains a carefully controlled proportion of gypsum (hydrated calcium sulfate), which is added during manufacture as a retarding agent. Any additional amounts of sulfate present in the aggregate could lead to reaction with cement compounds and resultant expansion and disruption of the hardened concrete, especially if the sulfates are present as the readily soluble magnesium or sodium salts [31].

Sulfates are found in natural ground, usually associated with ancient clays. On rare occasions these sulfates may be present as impurities in aggregates. High levels of sulfate can interfere with cement hydration in fresh concrete but the major concern is 'normal' sulfate attack of hardened concrete. In wet conditions, sulfates can react with components of Portland cement. The process is expansive and may lead to cracking

and spalling of concrete. The risk of sulfate attack is related to the sulfate content of the concrete expressed as a proportion of the cement content [32].

2.3 Cements

2.3.1 Definition And Some Charecteristics

Cement, in the general sense of the word, can be described as a material with adhesive and cohesive properties which make it capable of bonding mineral fragments into a compact whole. This definition embraces a large variety of cementing materials.

For constructional purposes the meaning of the term cement is restricted to the bonding materials used with stones, sand, bricks, building blocks etc. The principal constituents of this type of cement are compounds of lime, so that in building and civil engineering we are concerned with calcareous cement. The cement of interest in the making of concrete have property of setting and hardening under water by virtue of a chemical reaction with it and are, therefore, called hydraulic cements. Hydraulic cements consist mainly of silicates and aluminates of lime and can be classified broadly as natural cements. Portland cements and high alumina cements [34].

2.3.2. Portland Cement Clinker

Portland cement clinker composes limestone and clay, which are blending and grinding with several oxides like CaO , SiO_2 , Fe_2O_3 , Al_2O_3 . Then burning in a large rotary kiln at a temperature of approximately 1400°C and turns into a granule material which has 1-3 cm diameter. It has to include % 66,6 Ca-Si (calcium silicate) by the mass and CaO/SiO_2 ratio shouldn't be less than 2,0. Furthermore MgO content of mix has to be limited as 5 percent.

2.3.3. Classification of Cements

Types of Cements are altered both the quantity of used raw material and preferred manufacturing methods. We can make a classification, given below, with using national and international standards:

- Portland Cements
- Pozzolonic Cements
 - a- Ground Granulated Blust Furnace Slag Cements

b- Silica Fume Cements

c- Fly Ash Cements

- White Portland Cements
- Masonry Cement
- Sulfate Resistant Cements
- High Early Strength Cements
- Quick-setting Cements
- Low heat Portland Cements
- Low-alkali Portland Cement [35].

According to the TS EN 197-1 standards; CEM cements are collected 5 main type.

- CEM I Portland Cement
- CEM II Portland Composed Cement
- CEM III Portland GGBFS Cement
- CEM IV Pozzolanic Cement
- CEM V Composed Cement [36].

2.3.3.1 Portland Cement

Portland cement is a factory-produced binder. General purpose Portland cement made by grinding Portland cement clinker together with a controlled amount of calcium sulfate (<3.5 percent SO_3) and up to 5 per cent additional inorganic mineral, fly ash or limestone. Portland cement clinker consists of not less than 66 per cent of calcium silicates ($3\text{CaO} \cdot \text{SiO}_2 + 2\text{CaO} \cdot \text{SiO}_2$). The ratio CaO/SiO_2 shall not be less than 2,0. The maximum MgO level is 5 percent in the Portland cement clinker component [37].

History of Portland Cement

Among the numerous patents for hydraulic cements which appeared in the early nineteenth century one stands out in historic importance to the others; this was the famous patent dated 21 October 1824 by Joseph Aspdin. Aspdin was a Leeds builder or bricklayer who was conversant with building stones, and in his patent he described his material as 'Portland Cement'. This choice of name was applied because at that time Portland stone had a high reputation for quality and durability and Aspdin

wanted to direct people's attention to the resemblance of the colour and quality of his cement to Portland stone - a limestone quarried in Dorset, much favoured by Wren in the late seventeenth century. Aspdin used a hard limestone as used for the repairing of roads, crushed and calcined it, and mixed the lime with clay, grinding it to a fine slurry with water. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone.' Like Frost, he probably used a low temperature, and the product must have been of poor quality. He appears to have been guided by the idea that artificial heat applied to clay must produce a material similar in properties to the natural volcanic earths. Aspdin's early cement was nothing more than a hydraulic lime, but his 1824 patent gave him the priority for the use of the term Portland cement even though his product was not the Portland cement that we know today. Its mineralogy was completely different, as was its hydraulic activity. Nevertheless, Aspdin's patent cement was an essential link in the development that led, through technological advancement, to the calcium silicates of today which we call Portland cement [38].

Manufacture of Portland Cement

The process of manufacture of cement consist essentially of grinding the raw materials, mixing them intimately in certain proportions and burning in a large rotary kiln at a temperature of approximately 1400 °C when the material sinters and partially fuses into balls known as clinker. The clinker is cooled and ground to a fine powder ,with some gypsum added and the resulting product is the commercial Portland cement so widely used throughout the world [34].

Portland cement clinker contains four principal chemical compounds, which are normally referred to as the clinker minerals. It is the two calcium silicate minerals, C_3S and C_2S , which are largely responsible for the strength development and the long-term structural and durability properties of Portland cement. However, the reaction between CaO (lime from limestone) and SiO_2 (silica from sand) is very difficult to achieve, even at high firing temperatures. Chemical combination is greatly facilitated if small quantities of alumina and iron oxide are present (typically 5% Al_2O_3 and 3% Fe_2O_3), as these help to form a molten flux through which the lime and silica are able to partially dissolve, and then react to yield C_3S and C_2S . The reaction requiring the greatest energy input is the de-carbonation of $CaCO_3$, which takes place mainly in the temperature range 700-1000°C. For a typical mix

containing 80% limestone the energy input to de-carbonate the CaCO_3 is approximately 400 kCal/kg of clinker, which is approximately half of the total energy requirement of a modern dry process kiln.

When de-carbonation is complete at about 1100°C , the feed temperature rises more rapidly. Lime reacts with silica to form belite (C_2S) but the level of un-reacted lime remains high until a temperature of $\sim 1250^\circ\text{C}$ is reached. This is the lower limit of thermodynamic stability of alite (C_3S). At 1300°C partial melting occurs, the liquid phase (or flux) being provided by the alumina and iron oxide present. The level of un-reacted lime reduces as C_2S is converted to C_3S . The process will be operated to ensure that the level of un-reacted lime (free lime) is below 3%.

Normally, C_3S formation is effectively complete at a material temperature of about 1450°C , and the level of un-combined lime reduces only slowly with further residence time. The ease with which the clinker can be combined is strongly influenced by the mineralogy of the raw materials and, in particular, the level of coarse silica (quartz) present. The higher the level of coarse silica in the raw materials, the finer the raw mix will have to be ground to ensure satisfactory combination at acceptable kiln temperatures.

Coarse silica is also associated with the occurrence of clusters of relatively large belite crystals around the sites of the silica particles. As the clinker passes under the flame it starts to cool and the molten C_3A and C_4AF , which constitute the flux phase, crystallize. This crystallization is normally complete by the time the clinker exits the rotary kiln and enters the cooler at a temperature of $\sim 1200^\circ\text{C}$. Slow cooling should be avoided as this can result in an increase in the belite content at the expense of alite and also the formation of relatively large C_3A crystals which can result in unsatisfactory concrete rheology (water demand and stiffening) [39].

Hydration of Portland Cement

Portland cement is a multi-component system, its hydration is a rather complex process consisting of a series of individual chemical reactions that take place both in parallel and successively. The process gets under way spontaneously upon contact of the binder with water and is associated with liberation of heat.

The progress of hydration and its kinetics are influenced by a variety of factors, especially;

- by the phase composition of the cement and the presence of foreign ions within the crystalline lattices of the individual clinker phases;
- by the fineness of the cement, in particular by its particle size distribution and specific surface;
- by the water-cement ratio used;
- by the curing temperature;
- by the presence of chemical admixtures, i.e. chemical substances added in small amounts to modify the hydration rate and properties of the cement paste;
- by the presence of additives, i.e. materials interground with cement in larger amounts, such as granulated blast furnace slag or pulverised fly ash [40].

Both C_3S and C_2S react with water to produce an amorphous calcium silicate hydrate known as C-S-H gel which is the main 'glue' which binds the sand and aggregate particles together in concrete. C_3S is much more reactive than C_2S and under 'standard' temperature conditions of 20°C approximately half of the C_3S present in typical cement will be hydrated by 3 days and 80% by 28 days. In contrast, the hydration of C_2S does not normally proceed to a significant extent until 14 days [39].

Sulfate-Resisting Of Portland Cement

This type of cements can be resistible especially where the places with sulfate waters and the soils under sulfate impact, because of their low C_3A ratio ($< 5\%$). And also the concretes which are manufactured with this type of cements shows more durability against of sulfate attack. Moreover this type of concretes have long life time due to there is not ettringite existent. Since the C_3A ratio is low, their hydration temperature is lower than Ordinary Portland Cement (OPC) and their setting times are longer as well. Sulfate Resisting Portland Cement (SRC) are generally used the places influenced the sea water, sewer pipes, the places which are under impact of industrial wastes, for sustaining walls [41]

Sulfate-resisting Portland cements were developed in Germany and Canada during the 1930s and differ primarily from ordinary Portland cement in having a low calculated content of tricalcium aluminate(C_3A). This may be achieved either by using raw materials of low alumina content or by adding iron oxide in order to produce a low ratio of Al_2O_3/Fe_2O_3 , i.e. about unity or less [37].

2.3.3.2 Pozzolonic Cements

GGBFS Cements

This type of cement is made by inter-grinding Portland cement clinker and granulated blast-furnace slag, the proportion of the latter not exceeding 65 per cent of the weight of the mixture.

Slag is a waste product in the manufacture of pig iron, the amounts of iron and slag obtained being of the same order. The slag is a mixture of lime, silica, and alumina that is the same oxides that make up Portland cement, but not in the same proportions. While it is not possible to give ranges of values it may be noted that a slag known to be satisfactory had the following composition: 42 percent lime, 30 percent silica, 19 per cent alumina, 5 per cent magnesia, and 1 percent alkalis. Slag can make a cementitious material in different ways. Firstly it can be used together with limestone as a raw material for the conventional manufacture of Portland cement. Clinker made from these materials is often used (together with slag) in the manufacture of Portland blast-furnace cement. The latter cement represents the second major use of slag. Dry granulated slag is fed with Portland cement clinker into a grinding mill, gypsum being added in order to control setting. It may be noted that slag is harder than clinker so that inter-grinding presents some difficulties.

The heat of hydration of Portland blast-furnace cement is lower than that of ordinary Portland cement so that the former can be used in mass concrete structures. However in cold weather the low heat hydration of Portland blast-furnace cement coupled with a moderately low rate of strength development, can lead to frost damage. Because of its fairly high sulfate resistance, the C_3A content being low, Portland blast furnace cement is frequently used in sea water construction. Shrinkage and modulus of elasticity of concrete made with Portland blast-furnace cement are the same as when Portland cement is used [34].

At sufficiently high slag contents (60% and more) Portland–slag cement exhibits a better resistance to sulfate attack than ordinary Portland cement, whereas the resistance is scarcely affected at low substitution levels. This improved performance is mainly due to a reduced C_3A content in the cement, brought about by the replacement of a fraction of the clinker with granulated blast furnace slag. This way

the amount of mono-sulfate in the hardened paste, which is the only Al^{3+} form readily available for ettringite formation, becomes reduced [43].

Fly Ash Cements

This type of cements are composed, with grinding clinker and fly ash (10-30 % by total mass) with low amount of lime stone together. There is only one class available. They are classified by the compressive strength of 28 days. It's called UKC 32.5 in Turkey [42].

Fly ash Portland Cements, in which up to about 30% of clinker is replaced by fly ash, resist sulfate attack better than ordinary Portland cement. Different fly ashes, however, may not be equally effective, class F ashes being more effective than ashes of class C. A similar effect as with fly ashes may be attained also by combining the clinker with natural pozzolanas or with silica fume [43].

2.3.3.3. White Portland Cements

As the Turkish Standards it is in the group of Portland calcareous cements (TS EN 197-1-CEM II/B-L 42,5R) It contains approximately 25 % (by the mass) high quality pure marble powder. The whiteness of it is nearly 86 % and it's in the class of High early strength cements. They are so resistible against of alkali-aggregate reactions besides the impermeability of them, are quite high. They are usually used in the application of precast, in the furniture industry, in the glue industry, the manufacture of floor tile and producing of some art works [44].

White Portland cement often has a very low alkali content, caused by alkali loss through volatilisation in wet process manufacture as well as through the choice of pure raw materials, and also a generally higher free lime content (CaO) than is commonly obtained for most ordinary Portland cements, because of fluxing problems, and in addition lower magnesia (MgO) contents, again through the choice of purer raw materials. The C_4AF phase is normally low (commonly ≈ 1 per cent) because of the low iron content [45].

2.3.3.4. Masonry Cements

These kind of cements are produced by using clinker of Portland cement (at least 40 % by the mass), some natural pozzolans, fly ash and lime stones, which are mixed and grinding together [46].

2.3.3.5. High Early Strength Cements

Clinkers with high alite (75-95 per cent) and low belite (5-12 per cent) contents have been produced using less energy by lowering the clinkering temperature by 200°C. This has been achieved by partially substituting the aluminate and ferrite phases of conventional Portland clinker by $\text{CaF}_2\text{-CaSO}_4\text{-CaO}$ and SiO_2 . When ground with gypsum to produce a cement, high early strength properties are observed. During hydration, products such as C-S-H and ettringite from the Portland cement component and calcium aluminate hydrates from the aluminous component are formed [45].

2.3.3.6. Quick-Setting Time Cements

Quick-setting are produced either by inter-grinding Portland cement clinker with a special clinker rich in C_{12}A_7 , and suitable retarders, or by using a clinker containing Klein's compound ($3\text{CA}\cdot\text{CaSO}_4$ or $\text{C}_4\text{A}_3\cdot\text{SO}_3$). Cements which are expansive or shrinkage compensated can be obtained by inter-grinding Klein's compound with anhydrite and Portland cement clinker. The latter acts as a source of lime so that ettringite formation occurs with a degree of expansion, depending on the proportions used.

2.3.3.7. Low-Heat Portland Cement

Low-heat Portland cement is usually only manufactured to meet an individual, very large order. A, low lime saturation is employed to reduce the C_3S content and a lower limit for surface area is specified, since employing a cement which is too coarsely ground to reduce the rate of heat evolution would yield concretes prone to bleeding and segregation. Heat of hydration is limited to 250kJ/kg at an age of 7 days and 290kJ/kg at 28 days.

The maximum SO_3 content should not exceed 3.0 per cent. The specific surface must be greater than 325m²/kg. Low-heat Portland cement was developed in the USA soon after 1930 for use in mass concrete construction, such as dams, where the temperature rise caused by the heat evolved on hydration can become excessively large. A form of cement with a heat evolution intermediate between that of low-heat and the average ordinary Portland cement, but with a rate of strength development nearly comparable to the latter, was introduced in the USA in about 1934 as a

compromise to avoid some of the difficulties that had arisen in concreting with low-heat cement in cold weather.

2.3.3.8. Low-Alkali Portland Cement

The observation that certain aggregates are sensitive to attack by alkalis and that these occur much more widely than was previously thought has led to the increasing availability of low-alkali cements (<0.6 per cent equivalent Na_2O) [37].

2.3.4. Fineness of Cement

It may be recalled that one of the last steps in the manufacture of cement is the grinding of clinker mixed with gypsum. Since the hydration starts at the surface of the cement particles, it's the total surface area of the cement that represents the material available for hydration. Thus the rate of hydration depends in the fineness of the cement particles, and for a rapid development of strength high fineness is necessary.

Finer cement leads to a stronger reaction with alkali-reactive aggregate, and makes a paste, though not necessarily concrete, exhibiting a higher shrinkage and a greater proneness to cracking. However, fine cement bleeds less than a coarser one. An increase in fineness increases the amount of gypsum required for proper retardation as in a finer cement more C_3A is available for early hydration. The water content of the paste of standard consistence is greater the finer the cement, but conversely an increase in fineness of cement slightly improves the workability of a concrete mix. This anomaly may be due partly to the fact that the tests for consistence of cement paste and workability measure different properties of fresh paste; also, accidental air affects the workability of cement paste, and cements of different fineness may contain different amounts of air. We can see then that fineness is a vital property of cement and has to be carefully controlled [34].

2.3.5. Capillary Pores

The capillary porosity of the cement paste depends on both the water/cement ratio of the mix and the degree of hydration. The type of cement influences the degree of hydration achieved at a given age. The water/cement ratios higher than about 0.38 the volume of the gel is not sufficient to fill all the space available to it so that there will be some volume of capillary pores left even after the process of hydration has been completed.

Capillary pores cannot be viewed directly but their size has been estimated from vapour pressure measurement to be of the order of 1-3 μm (5×10^{-5} in). They vary in shape but form an interconnected system randomly distributed throughout the cement paste. These interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste and for its vulnerability to frost.

However, hydration increases the solid content of the paste and in mature and dense pastes the capillaries may become blocked by gel and segmented so that they turn into capillary pores interconnected solely by the gel pores. The absence of continuous capillaries is due to a combination of a suitable water/cement ratio and a sufficiently long period of moist curing. For water/cement ratios above, about 0,7 even complete hydration wouldn't produce enough gel to block all the capillaries. For extremely fine cement, the maximum water/cement ratio would be higher, possibly up to 1.0 ; for coarse cements, it would be below 0,7.

2.3.6. Gel Pores

The gel can hold large quantities of evaporable water it follows that the gel is porous, but the gel pores are really interconnected interstitial spaces between the gel particles. The gel pores occupy about 28 percent of the total volume of gel, it means that the gel pores occupy a space equal to about one-third of the volume of the gel solids. The material left after drying in a standard manner being considered as solids. The actual value is characteristic for a given cement but is largely independent of the water/cement ratio of the mix and of the progress of hydration. This would indicate that gel of similar properties is formed at all stages and that continued hydration doesn't affect the products already in existence. Thus as the total volume of gel increases with the progress of hydration the total volume of gel pores also increases. On the other hand, the volume of capillary pores decreases with the progress of hydration [34].

2.4 Self Compacting Concrete (SCC)

2.4.1 Definition and Some Characteristics

The concept of self-compacting concrete (SCC) resulted from research into underwater concrete, in situ concrete piling and the filling of other inaccessible areas. Before the advent of super-plasticizers and other admixtures, the cost of mixes for these purposes were often expensive with high cement contents required to offset

associated high water contents. The development of water-reducing super-plasticizers meant high-workability and high-strength concrete could be achieved without excessive cement contents, but excessive segregation and bleeding restricted the use of admixtures to flowing concrete having slumps of between 120 mm and 150 mm. Khayat et al. (1999) define SCC as; A highly flowable, yet stable concrete that can spread readily into place and fill the formwork without any consolidation and without undergoing any significant separation [47].

The majority of concrete cast relies on compaction to ensure that adequate strength and durability is achieved. Insufficient compaction will lead to the inclusion of voids, which not only leads to a reduction in compressive strength but strongly influences the natural physical and chemical protection of embedded steel reinforcement afforded by concrete. Concrete is normally compacted manually using vibrators, often operated by untrained labor and the supervision of the process is inherently difficult. Although poorly compacted concrete can be repaired, overall durability is more often than not reduced. The consequences of concrete compaction not only affect the material but also have health and safety and environmental [48].

2.4.2 Benefits of SCC

Feature/benefit analysis would suggest that the following benefits should result;

- Increased productivity levels leading to shortened concrete construction time.
- Lower concrete construction costs.
- Improved working environment.
- Improvement in environmental loadings.
- Improved in situ concrete quality in difficult casting conditions.
- Improved surface quality.

2.4.3 Materials of SCC

2.4.3.1 Cement

The majority of research on SCC has been carried out using Portland cement (PC) as the binder. Pioneering work by Okamura in Japan and Bartos in the UK focused primarily on the use of PC for SCC. In developing SCC, the total fines content of the mix is balanced against aggregate size and grading and, in general, the fineness

content is much higher than in conventional concrete for reasons of stability. The requirement for, a high fines content leads to high cement contents, often in the range 450-500 kg/m³.

2.4.3.2 Admixtures

SCC mixtures are produced using the same basic components as common concrete, namely cement, aggregates, water and various additives and admixtures. However, the mix design is different. The most often used fillers increasing viscosity of SCC mixtures are fly ash, glass filler, limestone powder, silica fume and quartzite filler. Some SCC mixtures contain also water retention agents such as polysaccharides to match the possible higher amount of water in the aggregates or to provide the concrete mix with thixotropic properties. Application of supplementary cementitious materials (SCM) as partial replacement of Portland cement appeared in SCC mixtures during the last decade only; previously, for instance fly ash and silica fume were considered as mere micro-fillers. At first, the main motivation for using SCM was cost reduction. More recently, environmental arguments began to prevail, in particular the need to decrease the overall CO₂ production related to the use of cement in concrete. Fly ash, ground granulated blast furnace slag and silica fume were the most frequently applied SCM in SCC. Metakaolin as an environmental-friendly material which can be prepared from kaolinic clays without CO₂ production was used only rarely in SCC mixtures, probably for economical reasons. The price of metakaolin is on most markets significantly higher than cement. Therefore, the main motivation for use of metakaolin in concrete in general is more technological or environmental than economical.

Fine particle binders such as PFA and GGBS have been used in SCC mixes. These additions are known to increase the workability of fresh normal concrete mixes and the common beneficial effects of these materials, such as reduced PC contents and lower heat of hydration, have also been exploited in practical situations. Ultra-fine particle binders such as CSF have also been used in SCC. Such binders are often associated with reducing the workability and lowering slump, however, a number of workers have used CSF in SCC, maintaining the desired workability by increasing the super-plasticizer dosage.

The increased fines content requirement of SCC has also been offset by the use of fine filler materials. The most commonly used material is limestone powder as it is generally accepted as being economically feasible. Limestone filler will help to maintain stability in a high workability mix although it will not contribute significantly to the compressive strength development of SCC. Limestone filler will also help to control the heat of hydration in mixes that have a high PC content [59].

The advent of super-plasticizers and further developments in admixture technology, have meant the production of SCC has now become easier and a variety of materials may be used. Advances in admixture technology have played a vital part in the development of SCC. Modern super-plasticizers (based on polycarboxylic ethers) promote good workability retention and can be added at any stage of the batching cycle [48].

2.4.3.3. Fine and Coarse Aggregates

The fine aggregate in SCC plays a major role in the workability and stability of the mix. The total fines content of the mix is a function of both the binder (and filler) content and the fine aggregate content with the grading of the fine aggregate being particularly important. The grading of fine aggregate in the mortar should be such that both workability and stability are simultaneously maintained. Standard concreting sands are suitable for use in SCC provided standard procedures are adhered to. Sands with fineness modulus of between 2,4 and 2,6 have been used in producing SCC. However, finer sands are recommended to ensure satisfactory segregation resistance. SCC has been made with both gravels and crushed rock as coarse aggregate. The maximum aggregate size is commonly 20 mm but smaller aggregate sizes up to 10 mm have also been used [47].

The content of coarse aggregate in SCC is a vital parameter in ensuring that the mix has excellent flow characteristics and proper mechanical properties. A high coarse aggregate content can lead to a reduction in segregation resistance and also lead to blockage of the flow. The frequency of collision and contact between aggregate particles can increase as the relative distance between the particles reduces leading to an increase in internal stresses. Limiting the coarse aggregate content reduces the potential for the formation of internal stresses leading to blockage of the mix. Okamura and Ozawa proposed that the volume of coarse aggregate in SCC be kept to

approximately 50% for the reasons mentioned above. Yarugi, proposed SCC could be obtained with coarse aggregate volumes lower than 33% providing the sand content in the mortar of the mix is in the region of 75 %. These limits are of course dependent on the maximum coarse aggregate size with coarse aggregate limits being slightly higher with lower maximum aggregate sizes [49].

2.4.4. Mix Design for SCC

Combining the constituent materials in the optimum proportions to give concrete with the required combination of fresh and hardened properties for particular application is clearly as essential part of the SCC production process. Mix design (or mix proportioning) must start with the definition or selection of the required properties.

Successful SCC needs a combination of three key distinct properties.

- Filling ability (also called unconfined flow-ability): The ability to flow into and completely fill all spaces within the formwork under its own weight. This property is a combination of total flow capacity and flow rate.
- Passing ability (also called confined flow-ability): The ability to flow through and around confined spaces between steel reinforcing bars without segregation or blocking.
- Segregation resistance (also called stability): The ability to remain homogeneous both during transport and placing (in dynamic conditions) and after placing (in static conditions).

The Japan society of civil engineers (JSCE) recommends ranking mixes according to their suitability for applications with different levels of bar spacing and reinforcement content (Table 2.4).

Table 2.4 JSCE ranking of SCC mixes according to passing ability

Rank	Reinforcing bar spacing (mm)	Normal Steel Content (kg/m ³)	U-box requirement
1	< 60	< 350	Filling Height > 300 mm with 5 bar gate
2	60-200	100-350	Filling Height > 300 mm with 3 bar gate
3	>200	< 100	Filling with 5 no gate

European Federation for Specialist Construction Chemicals and Concrete Systems (EFNARC) gives set of classes for slump-flow, viscosity, passing ability, and segregation resistance (or stability) based on the values obtained with the tests as specified in the European standards (Table 2.5).

The early development of SCC in Japan established the essential criteria for achieving the three key properties:

- A low water/cement (or water/powder) ratio with high doses of super-plasticizer to achieve high flow capacity without instability or bleeding.
- A paste content sufficient to overfill all the voids in the aggregate skeleton to the extent that each particle is surrounded by an adequate lubricating layer of paste, thus reducing the frequency of contact and collision between the aggregate particles during flow.
- A sufficiently low coarse aggregate content to avoid particle bridging and hence blocking of flow when the concrete passes through confined spaces.

Table 2.5 SCC classes proposed by EFNARC

Slump Flow		Viscosity			Passing Ability		Segregation Resistance	
Class	Slump Flow (mm)	Class	t 500	V-funnel	Class	L box ht ratio (mm)	Class	Sieve Segregation (%)
SF1	550-650	VS1/VF1	≤ 2	≤ 8	PA1	≥ 0,80 with 2 rebars	SR1	≤ 20
SF2	660-750	VS2/VF2	> 2	9-25	PA2	≥ 0,80 with 3 rebars	SR2	≤ 15
SF3	760-850							

The JSCE guidelines are summarised in Table 2.4, it is clear from this that there is greater flexibility with viscosity agent or combination-type mixes than with powder mixes [54].

Table 2.6 Limits for initial mix proportions as recommended by JSCE (for 20 or 25 mm coarse aggregate) [54].

	Powder Mixes	Viscosity Agent Type Mixes	Combination Type Mixes
Coarse Aggregate (Volume %)	Rank 1 : 28-30	Rank 1 : 28-31	Rank 1 : 28-30
	Rank 2 : 30-33	Rank 2 : 30-33	Rank 2 : 30-33
	Rank 3 : 32-35	Rank 3 : 30-36	Rank 3 : 30-35
Water Content (kg/m ³)	155-175	Minimum for required fresh properties	Sufficient for specified deformability and segregation resistance
Water / Powder ratio	0,28-0,37 by wt	Maximum for required hardened properties	
	0,85-1,15 by vol.		
Powder Content (Volume %)	16-19	Sufficient for self-compactability	> 13

Table 2.7 Summary of common factors about manufacturing SCC and laboratory investigations [48].

Property	Comments
Water Content	Typically 160-185 kg/m ³ , similar to conventional concrete. Unclear whether this is due to SCC requirements or for durability purposes.
Admixture	Superplasticizers: used to increase workability. Mainly naphthalene or melamine formaldehyde based.
	Viscosity modifiers used to control segregation in mixes with higher water/binder ratios. Cellulose or polysaccharide 'biopolymer'
Binders	Typically in range 450-550 kg/m ³ . PFA, GGBS, CSF commonly used to improve cohesion. Limestone filler also commonly used.
Water/Binder Ratio	From above, typical range is 0,30-0,36
Aggregates	Both gravels and crushed rock used. Up to 20 mm nominal size is common. Lightweight SCC has also been produced.
Workability Measurement	Numerous tests used to assess fresh properties.

2.4.5 Effects on Compressive Strength

Due to the lower water/binder ratios associated with SCC, the compressive strength of SCC is usually higher than for conventional concrete. When normal concrete is vibrated, water will tend to migrate to the surface of the coarser particles causing porous and weak interfacial zones to develop. If, SCC has been well designed and produced it will be homogeneous, mobile, resistant to segregation and able to be placed into formwork without the need for compaction. This will encourage minimal interfacial zones to develop between the coarse aggregate and the mortar phase. Thus the microstructure of SCC can be expected to be improved, promoting strength, permeability, durability and, ultimately, a longer service life of the concrete. In-situ compressive strengths, determined using cores, have shown closer correlation to standard cube strength than conventional concrete. Trials were carried out at RMC Readymix Technical Centre to examine the hardened properties of SCC, using a total cementitious content of 480 kg/m^3 at a slump flow of 700 mm, using a super-plasticizer and a viscosity modifier.

Ultrasonic pulse velocity (UPV) tests were performed over the unit and cores were taken to determine the in-situ strength and the density within the structure. The cores were also tested for chloride and oxygen diffusion. Satisfactory self-compaction of the fresh concrete was confirmed by the consistently high UPV values and densities of the core samples. The mean estimated in-situ cube strength was 81% of the standard 28-day cube strength from concrete sampled during casting. The chloride and oxygen diffusion results were 0.304×10^{-12} and 1.44×10^{-8} , respectively, which are significantly less than required by many specifications [48].

2.4.6 Effect of Mineral Admixtures On The Drying Shrinkage Of SCC

Guneyisi, Gesoglu and Ozbay carried out a study, in order to understand the drying shrinkage properties of self-compacting concretes. An ASTM Type I Portland cement (PC) was used to produce the plain SCC mixtures. In addition, the mineral admixtures, namely class-F fly ash (FA), ground granulated blast furnace slag (GGBFS), silica fume (SF), and metakaolin (MK) were used in partial replacement with cement by weight in different combinations of binary, ternary, and quaternary cementitious blends. A total of 65 concrete mixtures were designed at two water-

binder ratios of 0,32 and 0,44 with total cementitious materials content of 550 and 450 kg/m³, respectively.

According to results of this study it has obviously been seen that in the binary blends, used Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBFS) and Metakaolin (MK) with Portland Cement (PC), reduced the drying shrinkage of SCCs. However, the use of SF with PC gradually increased the drying shrinkage of SCCs. Furthermore, higher the replacement level of FA, GGBFS, and MK, leads to higher the reduction in the shrinkage of the concretes [50].

2.4.7 Durability Properties of SCC

In general, concrete structures are regularly subjected to aggressive environmental conditions. Due to their interaction with external influences, the mechanical and physical properties of concrete may be greatly diminished. Sulphuric acid (H₂SO₄) and hydrochloric acid (HCl) are classified as the most aggressive of natural threats to concrete structures. Usually, they originate from industrial processes, but they can be caused by urban activity. Significant quantities of acids are present in sewage systems. Acidic attack is affected by the processes of decomposition and leaching of cement paste constituents. A very important volume of admixtures in SCC paste can positively or negatively influence its resistance to acid aggression. Torri and Kawamura reported similar observations. They examined the effect of a 2% H₂SO₄ solution on fly ash and silica fume mortars. Fly ash mortars with 70% replacement were studied for 3 years. They observed that the effect of H₂SO₄ attack decreases with an increase in the fly ash replacement. The incorporation of natural pozzolan in SCC paste reduces the size of capillary pores through a new C–S–H gel resulting from pozzolanic activity and portlandite, hydrates resulting from cement hydration [51].

The durability of a concrete repair can depend on many factors. Those most often considered are cement reactivity with environment, low permeability, diffusion coefficient of species such as sulfate ions and compressive strength. The water absorption is also a very important factor affecting durability such as freezing and thawing. The use of mineral additives may provide a way of improving the durability of SCRM depending on the type and amount of mineral additive used [52].

2.4.8 Internal Frost Resistance Of SCC

In the case of self-compacting mixture the process of its self-compacting, depending in fact on autogenous release of random air bubbles from its volume, can significantly affect the final value of concrete porosity structure parameters.

When the SCC is air entrained it can substantially affect the frost-resistance of self compacting concrete. The high flowability of SCC can destabilize entrained-air bubbles during transport, which can affect the final air void system of the hardened concrete. The influence of this admixture must be particularly related to the characteristic of the cement and air-entraining admixture (AEA) types. As a result, self-compacting process can significantly affect the final value of concrete porosity structure parameters, and it can influence frost-resistance of self-compacting concrete [53].

2.5 Chemical Admixtures

2.5.1 Definition and Some Characteristics

Admixtures are chemical, added to concrete, mortar or grout at the time of mixing, to modify the properties, either in the wet state immediately after mixing or after the mix has hardened. They can be a single chemical or a blend of several chemicals and may be supplied as powders but most are aqueous solutions because in this form they are easier to accurately dispense into, and then disperse through the concrete [55].

Broadly speaking, admixtures may be regarded as active, interactive and passive. Active admixtures react with a solubilised component of cement such as lime to produce a derivative. It is this derivative that imparts the admixture effect. Accelerators, retarders and water-proofers would comprise this category.

Interactive admixtures are usually surface active and associate with the liquid-air and solid-liquid interfaces, resulting in orientation and adsorption. The active component of the admixture is not changed by these events. Examples are plasticisers, super-plasticisers and air entrainers.

Passive admixtures do not change their form in passing into solution or remaining in suspension. Their contribution is mainly physical, by way of molecular entanglement and solvent association in the case of viscosity modifiers, or simply light absorption and reflection in the case of pigments [56].

Admixtures are usually defined as being added at less than 5% on the cement in the mix but the majority of admixtures are used at less than 2% and the typical range is 0.3- 1.5%. This means the active chemicals are usually present at less than 0.5 % on cement or 0.02% on concrete weight.

Table 2.8 Proportions of Concrete Mix Constituents

Proportions Of Concrete Mix Constituents	By Weight	By volume
Cement	15%	11%
Water Required For Cement Hydration	3%	8%
Additional Water To Give Workability	5%	11%
Aggregate	77%	70%

The most important factor in this typical mix design is the 11% by volume of water that is added, only to give the mix workability. This water does not react with the cement but remains unbound and free in the concrete after hardening. This forms interconnecting water-filled voids called capillaries that reduce strength, increase permeability to water and provide paths for diffusion of chlorides, sulphates and other aggressive chemicals. As the water slowly evaporates from the capillaries, it causes drying, shrinkage and cracking.

2.5.2 Main Purposes of Using Admixtures

The benefits obtained from using the admixture are often in the hardened properties. However, with the possible exception of the last bullet point, these actions all affect the properties of the wet concrete between the time of mixing and hardening in one or more of the following ways:

- Affect water demand- Plasticizing or water reducing
- Change the stiffening rate- Accelerating/retarding
- Change the air content- Increase (or decrease) entrained air.
- Change the plastic viscosity- Cohesion or resistance to bleed and segregation of the mix.

One of these effects will usually be the primary property, the property for which the admixture is being used. However, the admixture can also affect one or more of the

other wet properties. These are called secondary effects and it is often these which are key to admixture selection within an admixture type.

For example, a water-reducing admixture may be required to give low water:cement ratio for durability but if the concrete mix lacks cohesion and is prone to bleed, a water reducing admixture which also increases cohesion would be appropriate to prevent the bleed. The primary function is as a water reducer; the secondary function is to improve cohesion. Incorrect admixture selection could make the bleed worse.

2.5.3. Classifications of Admixtures

2.5.3.1 Dispersing Admixtures

These dispersing admixtures all function by adsorption onto the cement surface in a way that causes the cement particles to distribute more uniformly throughout the aqueous phase, reducing the yield value for a given water content and so increasing the fluidity of the mix. They may also have a small effect on the plastic viscosity or cohesion of the mix. They are used in one or more of the following ways:

- To increase the fluidity of the mix at a given water content. (Plasticizing or super-plasticizing action)
- To reduce the water content of the mix at a given fluidity, improving strength and durability. (Water reducing or High Range Water Reducing)
- To reduce the cement content by reducing water and maintaining water : cement ratio to give equivalent strength. (Cement reducing).

Dispersing Mechanism

When water is added to cement, the grains are not uniformly dispersed throughout the water but tend to form into small lumps or flocs. These flocs trap water within them causing the mix to be less mobile and fluid than would be the case if the cement were in the form of individual grains. This is analogous to the situation where people are walking both ways along a narrow pavement. If groups of people walking in one direction hold hands, then it is hard for people walking the other way to pass, especially if they are also holding hands. If everyone stops holding hands and walking in groups, then it is easy for people going in opposite directions to move round each other and pass. Admixtures adsorb onto the cement surfaces and break up

the flocs, leaving individual cement grains, which can pass each other easily, making the mix more fluid.

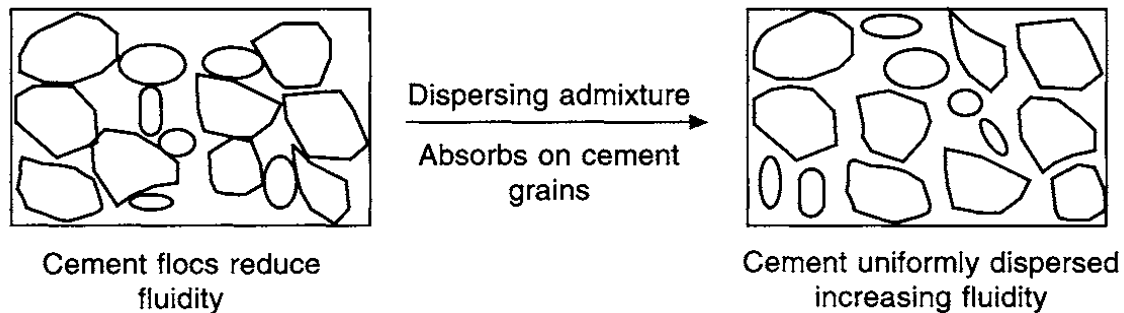


Figure 2.5: Dispersing Mechanism Of Admixtures

If water is now removed from the system, the fluidity can be reduced back to what it was before the admixture addition. However, the average inter-grain distance will also reduce, so less hydration will be necessary before the space between the cement grains is filled with hydration product to give setting and strength development. This leads first to a higher early strength. With continued hydration, more inter-grain space eventually becomes filled with hydration products so late age strength is also improved. Finally, there will be less void space, not filled with any hydration product resulting in fewer capillaries and therefore better durability [55].

Normal Plasticizers

When added to concrete or mortar at the prescribed dosage, these admixtures have no significant effect on the subsequent hydration of the cement. However, the improved dispersion of cement grains can cause a shortening of the stiffening time and enhanced early strength at a constant water/cement ratio. At high dosage levels, some admixtures used in combination with certain cements (particularly those with low C_3A content, i.e. sulfate-resisting) may cause retardation. This can be offset by incorporating small amounts of an accelerator into the formulation, such as calcium chloride, calcium formate or triethanolamine. [56].

Normal plasticizers are extensively used by ready-mix companies to optimize their mix designs, especially at low to medium slump (up to about 130 mm). Admixture performance always depends on the concrete materials and mix design being used as well as the dosage of the admixture. Normal plasticizers may be modified to enhance performance when slag or pfa binders are being used; they may also contain an air de-trainer to control the air content of the mix. Typically, normal plasticizers will

give 8-10% water reduction. Depending on retardation this will translate to a 120% strength improvement at 24/36 hours and 112% at 28 days. Most normal plasticizers will increase the air content by between 1% and 2%, which will give some additional cohesion to the mix and may reduce any tendency to bleed especially if the plasticizer is being used to increase workability. The higher the air content of the mix without admixture, the greater will be the additional air that is entrained by an admixture [55].

Super-plasticizers

These admixtures can be used at considerably higher dosages than ordinary water-reducing admixtures without adverse side effects such as gross retardation of set. A much greater reduction in the volume of mixing water can therefore be made in the case of concretes of normal workability (≈ 30 per cent) or alternatively, 'flowing concrete' can be obtained without excessive addition of water to the mix. All super-plasticizers consist of high molecular weight, water-soluble polymers, the majority being synthetic chemicals.

Workability is greatly enhanced by delayed addition of the super-plasticizer, rather than adding it with the mixing water. This allows time for the normal reactions between gypsum and clinker to occur without competition from the super-plasticizer. A delay of only a few minutes is adequate for ettringite formation and the establishment of a 'dormant' period during which only slow changes take place.

The effect of super-plasticizers on cement hydration is mainly due to physical factors rather than chemical interaction. Better dispersion of individual cement grains leads to more efficient hydration and better early strength where no reduction in water content is made. When large reductions in water content are made possible by the use of a super-plasticizer, improved strength and reduced permeability of the resulting concrete are an obvious benefit. More controversially, improved freeze-thaw durability has been claimed for high-strength concrete [56].

There are currently three main chemical types: the sulphonated polymers of naphthalene or melamine formaldehyde condensates and the polycarboxylate ethers. These basic chemicals can be used alone or blended with each other or with lingo-sulphonate to give admixtures with a wide range of rheological properties. They can also be blended with other chemicals to increase retardation, workability retention,

air entrainment and other properties. Super-plasticizers find use in the pre-cast and ready-mix concrete industries as well as in site-mixed concrete. In pre-cast they are used mainly as water reducers to give high early strength. On site mixed they may be used:

- To give high workability where there is dense reinforcement
- For low water contents to give high early or later age strength
- For low w/c to give low-permeability durable concrete.

Sulphonated melamine formaldehyde condensates (SMF) give 16-25%+ water reduction, they tend to reduce cohesion in the mix, increasing the tendency to bleed and segregate but can be very effective in improving mixes which, because of the materials/mix design, are already over-cohesive and sticky. SMF gives little or no retardation, which makes them very effective at low temperatures or where early strength is most critical.

Sulfonated naphthalene formaldehyde condensates (SNF) typically give 16-25% + water reduction. They tend to increase the entrapment of larger, unstable air bubbles. This can improve cohesion but may lead to more surface defects. Retardation is more than with SMF but will still not normally exceed 90 minutes over a control mix, even at the highest dosages. Workability retention is quite good but can be significantly improved if modified with other plasticizers/retarders.

Poly-carboxylate ether super-plasticizers (PCE) typically give 20-35%+ water reduction. They are relatively expensive per litre but are very powerful so a lower dose (or more dilute solution) is normally used. The PCEs are the most recent super-plasticizer development and are still establishing their position in the market, with development continuing to optimize their performance [55].

2.5.3.2 Retarding Admixtures

Their main function is to delay the setting time of concrete without adversely affecting subsequent strength development, whilst at the same time permitting a substantial reduction in water/cement ratio. Materials which can slow down the hydration of cement usually work by enhancing the early hydration sheath that surrounds cement grains. They can do this by complex with the calcium that is liberated on hydration and/or by adulterating the early gel membrane itself. Materials

that cause the latter effect are heavy metal salts of tin, lead and zinc. Their action is prolonged and difficult to control [56].

Accidental overdosing of a retarding admixture can significantly delay the setting and strength development. As soon as the error is spotted, the following actions should be taken:

- Protect the surface from evaporation by effective curing
- Re-vibrate the concrete up to the time of initial set to prevent settlement cracking
- Contact the admixture manufacturer for advice on the likely retardation time at the actual dosage used.

Unless an extreme overdose was used, most concrete will set and gain strength normally within 3-5 days. Beyond 5 days, the potential for the concrete not to gain full strength increases significantly [55].

2.5.3.3 Accelerating Admixtures

Accelerating admixtures consist of chemicals which principally influence the rate of hydration of the alite phase of Portland cement, resulting in an increase in heat evolution and C-S-H gel formation at an early age [56].

Accelerating admixtures can be divided into groups based on their performance and application:

- Set accelerating admixture, reduce the time for the mix to change from the plastic to the hardened state.

They can be subdivided into two groups:

- a-** Sprayed concrete accelerators, which give very rapid set acceleration (less than 10 minutes).
- b-** Concrete set accelerators which, according to EN 934-2, reduce the time for the mix to change from the plastic to the hardened state by at least 30 minutes at 20°C and at least 40% at 5°C.
- Hardening accelerators, which increase the strength at 24 hours by at least 120% at 20°C and at 5°C by at least 130% at 48 hours.

Calcium chloride is the most effective accelerator and gives both set and hardening characteristics. Unfortunately, it also reduces passivation of any embedded steel, leading to potential corrosion problems. For this reason, it should not be used in concrete where any steel will be embedded but may be used in plain unreinforced concrete [55].

2.5.3.4 Air Entraining Admixtures

These admixtures comprise a group of surfactants which act at the air-water interface in cement paste, thereby stabilising air entrapped during the mixing process in the form of tiny discrete bubbles [56].

Strength is reduced by entrained air, typically 5-6% reduction for each 1% of additional air. For this reason, air should normally be limited to the lowest level necessary to achieve the required properties. However, in low cement content, harsh mixes, air may improve workability allowing some water reduction that can offset part of the strength loss [55].

Factors Affecting Air Entrainment

As a general rule the volume of air entrained decreases with increasing cement content and fineness but increases with increasing alkali content of the cement (peaking at 1.5 per cent equivalent Na_2O). The latter effect may be connected with the increasing pH of the aqueous phase.

Air content also increases with increasing sand content in a mix, and with a decreasing proportion of sand with a particle size $< 150 \mu\text{m}$. Higher temperatures lead to a lower air content, as does a high degree of workability.

The sand content and grading undoubtedly has the greatest influence on air entrainment. It is almost impossible to entrain a significant amount of air into a neat cement paste (except by the use of a pre-foam system). As the sand content increases, so does the amount of air under otherwise equal conditions, with an optimum level being reached at about 1:3 cement to sand. Entrained air is very similar in size to the bottom third of most sand gradings.

Dust in any of the aggregates should be avoided. Because air is similar in size to the finer sand, it acts in a similar way, increasing cohesion. In already cohesive mixes (high cement content or fine sand) it may be necessary to reduce the sand content of

the mix to reduce cohesion but if the cement/sand ratio falls to about 1:2 problems with consistency and stability of air content may be encountered [56].

2.5.3.5 Water Resisting (Waterproofing) Admixtures

These admixtures (also known as integral permeability reducers, water-proofers or damp-proofers) consist of materials which reduce the hydraulic permeability of concrete and mortar, and often confer water repellency to the exposed surfaces [56].

All these 'waterproofing' admixtures reduce surface absorption and water permeability of the concrete by acting on the capillary structure of the cement paste.

Pore blocking can be achieved by the addition of very fine un-reactive or reactive additions such as silica fume or by the use of insoluble organic polymers such as bitumen introduced as an emulsion.

However, if the added mix water can be reduced to a w/c of below about 0.45 (or 160 liters per cubic meter of added water) the capillary system loses much of its continuity and pressure permeability is significantly reduced. The best way of achieving this reduced level of water is to use a water-reducing admixture that can also be used to ensure sufficient workability for full compaction and reduce shrinkage cracking [55].

2.5.3.6 Corrosion Inhibiting Admixtures

The most common cause of reinforcement corrosion is pitting corrosion due to the ingress of chloride ions through the covering concrete and subsequent diffusion down to the embedded steel. When the amount of chloride at the steel surface reaches a critical level, the passivation of the steel breaks down and corrosion starts. Carbonation of the concrete leads to a lowering of the alkalinity around the steel and when the pH drops below a critical level this causes a loss of passivation that results in general reinforcement corrosion. Corrosion inhibitors increase the 'passivation state' or 'corrosion threshold' of the steel so that more chloride must be present at the steel surface before corrosion can start.

Although corrosion inhibitors can raise the corrosion threshold, they are not an alternative to using impermeable, durable concrete and are not cost-effective unless used in a high quality mix [55].

2.5.3.7 Shrinkage Reducing Admixtures

Shrinkage-reducing admixtures can significantly reduce both the early and long-term drying shrinkage of hardened concrete. This is achieved by treating the 'cause' of drying shrinkage within the capillaries and pores of the cement paste as water is lost. This type of admixture should not be confused with shrinkage-compensating materials which are normally added at above 5% on cement and function by creating an expansive reaction within the cement paste to treat the 'effects' of drying shrinkage. The dosage is largely independent of the cement content of the concrete and is typically in the range 5-7liters/m³.

Shrinkage-reducing admixtures can be used in situations where shrinkage cracking could lead to durability problems or where large numbers of shrinkage joints are undesirable for economic or technical reasons [55].

2.5.3.8 Anti Washout/Underwater Admixtures

Underwater concrete anti-washout admixtures are water-soluble organic polymers which increase the cohesion of the concrete in a way that significantly reduces the washing out of the finer particles, i.e. cementitious material and sand from fresh concrete when it is placed under water. They are often used in conjunction with super-plasticizers to produce flowing self-levelling concrete to aid placing and compaction under water.

Anti-washout admixtures were developed to provide a higher integrity of concrete placed under water and to reduce the impact that the washed-out material can have on the marine environment. Anti-washout admixtures work on the mix water but are more effective if the base mix is cohesive. Cement contents should be at least 400 kg/m³ but this can include blended cement. The increased cohesion provided by very fine binders such as silica fume have been found particularly effective in some applications. Sand contents should also be high, typically 45% or higher, and need to have a uniform medium or fine grading [55].

2.6. Durability of Concrete

2.5.1 Definition and Some Characteristics

Concrete is a material of widespread utility, adaptable to many purposes, but there are situations in which it may be used where precautions must be taken to provide

protection against potentially destructive agencies, which may be physical in action, for example frost, or chemical. Damaging chemical substances are numerous, and include those which occur naturally in soils and waters, and those which are of industrial origin. Briefly, it is the weathering of concrete, interpreting weathering in a wide sense to include both natural agencies and artificial conditions, which will be considered here [57].

2.6.2 Principal Causes of Concrete Deterioration

Deterioration of concrete may be caused by chemical and physical processes, or their combination. Chemical mechanisms include leaching of paste components, carbonation of calcium hydroxide and C-S-H, paste deterioration by exposure to aggressive chemicals (acids, agricultural chemicals, sulfates), corrosion of steel reinforcement, and alkali-aggregate reactions. Physical or mechanical causes of concrete deterioration are represented by abrasion, erosion, cavitation, most important, by freezing and thawing cycles. Most chemical mechanisms of deterioration involve damage to the cement paste matrix, but deterioration of the paste-aggregate interface, the aggregate itself, or the pore structure often accompanies the paste deterioration. When examining concrete deterioration, one has to take into consideration the local microclimate the concrete is exposed to. The concrete surface durability may depend on the local temperature and humidity, thus an important consideration is exposure or lack of exposure to rain, direct sun, etc.

Ingress of external species into concrete and the subsequent removal of the reaction products from the system are clearly porosity and permeability dependent. In the absence of a permeable pore structure or, better, if the rate of penetration through the concrete matrix pore structure is low, the probability of deterioration is dramatically decreased.

For all types of external chemicals, whether organic or inorganic in nature, the probability of deterioration is minimized if the concrete has low permeability and is placed in a dry environment at constant temperature and humidity.

Understandably, such conditions are uncommon in most applications. It is important, therefore, to recognize the above facts and consider right at the design phase materials and processing conditions that will minimize the potential damage. Recognition of potential problems is especially important for construction in

geographical areas known to have soils containing aggressive components, and in some industrial and agricultural applications [58].

2.6.3 Sulfate Attack

Sulfate attack is the term used to describe a series of chemical reactions between sulfate ions and the components of hardened concrete, principally the cement paste, caused by exposure of concrete to sulfates and moisture. First we would like to emphasize that the chemistry of sulfate attack is independent of the source of sulfate; as will be shown later, the processes are governed by the same physico-chemical principles. The differences in the consequences of any sulfate attack are caused by the environmental and physical conditions under which these reactions proceed [58].

The sulfate attack is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. The gypsum and ettringite formed as a result of a sulfate attack are significantly more voluminous (1.2–2.2 times) than the initial reactants. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. In addition to the formation of ettringite and gypsum and its subsequent expansion, the deterioration due to a sulfate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to a loss of C–S–H gel stiffness and overall deterioration of the cement paste matrix [59].

Concrete deterioration due to sulfate attack is a serious problem throughout the world. Soluble sulfates, principally those of sodium, calcium and magnesium occur in nature. Environmental conditions such as those met in sulfate-rich soils and some natural waters require concrete to be designed to resist deterioration due to sulfate attack.

The sulfates resulting in degradation of concrete may come from external sources or internal sources. External sulfate attack occurs when sulfates diffuse or permeate from the outside environment through capillary pores and cracks into the microstructure of the concrete. Significant symptoms of attack do not occur until sufficient sulfate enters the microstructure and reacts. The characteristic mode of attack is therefore an incubation period during which sulfates diffuse into concrete and react, followed by an acceleration of expansion and cracking when the extent of

local damage reaches a sufficiently high level. External sulfate attack may also take the form of a progressive loss of strength and loss of mass due to deterioration of cohesiveness of the cement hydration products. The internal form of chemical sulfate attack is likely very similar to the mechanism of external sulfate attack, except that the diffusion of sulfate from outside of the concrete is not necessary precursor, the sulfate is already within the concrete at the time of hardening [60].

The sulfate attack chemical interaction depends on many parameters including the concentration of sulfate ions, ambient temperature, cement type and composition, water to cement ratio, porosity and permeability of concrete, and the presence of supplementary cementitious materials. The incorporation of supplementary cementitious materials such as natural pozzolan, blast-furnace slag, fly ash, and silica fume as partial replacements for ordinary cement has been found to be a beneficial technique to enhance the resistance of concrete to a sulfate attack [59].

2.6.3.1 Action of Sulfates

According to ACI's Guide to Durable Concrete (ACI 1992), there are two mechanisms that can be considered to be sulfate attack: formation of gypsum and formation of ettringite. Both of these reaction products are believed to damage concrete by increases in overall solid volume.

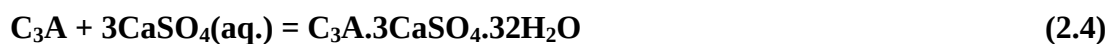
In numerous literature sources, sulfate attack is categorized into chemical versus physical and into internal versus external. Chemical sulfate attack is considered to be the result of chemical reactions involving sulfate anion, SO_4^{2-} . Example of such reaction is formation of ettringite from monosulfate and gypsum, according to the following stoichiometric reaction:



Monosulfate Gypsum Water Ettringite

where C is CaO, A is Al_2O_3 , S is SO_3 , and H is H_2O . The reaction is known to result in an increase in solid volume of the system, and may or may not lead to the expansion of concrete [58].

Portland cements contain sulfates to control the reaction rate of the C_3A . Alkali sulfates from the clinker and the added gypsum dissolve rapidly and in the presence of this high concentration of sulfate ions the C_3A reacts to form ettringite.



In cement hydration pure phases are rarely found and the ettringite phase is often referred to as AFt (alumino-ferrite-tri). If the cement contains sufficient C_3A to react with more sulfate than is available, further reaction converts the AFt to AFm (alumino-ferrite-mono) or monosulfate.



The ettringite crystal contains a lot of water and its formation involves a large increase in solid volume. However, in the early stages of hydration this is easily accommodated. A reasonably mature concrete will contain a mixture of AFt, AFm, some unhydrated C_3A , rather more unhydrated CaAF and some other aluminate and alumino-ferrite hydrates, such as hydrogarnet phases (C_3AH_6 and related solid solutions).

External sulfate ions can react to form the same phases as the internal sulfate. In particular, reaction with unreacted C_3A or AFm to form AFt will lead to a solid volume increase that may be disruptive. An additional reaction with external sulfates is with CH to form gypsum.



Sulfates of various bases occur naturally and are also extensively used in industry. Their solutions enter into chemical reactions with compounds present in set cements, causing expansion, cracking or spalling of the concrete or softening and disintegration. Ordinary Portland cement is the most vulnerable to attack, but while sulfate-resisting Portland, pozzolanic and Portland blast-furnace cements have greater resistance, they are not immune to attack in all situations and at all concentrations of sulfate solutions.

The action of sulfates and the protection of concrete against their damaging effects are therefore matters of considerable concern, and have been the subject of extensive investigation. Calcium, magnesium, sodium and potassium sulfates are found throughout the world in clays and other soils, frequently in considerable quantities. The distribution of sulfates in clays is often very irregular, and concentrations may vary between points only a few metres apart. In clay soils gypsum frequently occurs as discrete crystals or clusters of crystals. There can also be a considerable variation in sulfate concentration with depth, depending on climatic conditions. In temperate

zones, where rainfall exceeds evaporation, sulfates are mainly absent from the top 1 m of soil as a consequence of gradual leaching by rain water. In drier regions, where rates of evaporation are high, there may be a greater concentration of sulfates near the surface. In hot, arid regions, where the excess of evaporation over rainfall leads to continual upward movement, salts carried in solution crystallise at the surface in deposits, which can be of considerable thickness.

The concentration of sulfates in ground water also varies widely. The sulfate content of the soil and the movement of the water are important, but the chief factor that determines how much sulfate may be present is the solubility of the sulfate salt. Calcium sulfate is of limited solubility in water (2g/L) and this sets a limit of 1.2 g/L SO_3 to which it can give rise in ground water [57].

2.6.3.2 Internal Sulfate Attack

Internal sulfate attack refers to situations where the source of sulfate is internal to concrete. The source of sulfate can be the cement, supplementary materials such as fly ash or slag, the aggregate, the chemical admixtures, or the water. Two examples of such internal sulfate attack are the classical attack by excess (with respect to the clinker aluminate phase) of cement sulfate and the so-called delayed ettringite formation (DEF).

Internal Sources

Calcium sulfate is an important component of all Portland cements. Various forms of calcium sulfate (anhydrite, hemihydrate, dihydrate; sulfate-bearing industrial by-products) are added to clinker during cement grinding to enable control of cement setting characteristics. Sulfates are also known to accelerate hydration of the calcium silicates present in Portland clinkers, thus potentially increasing early strength of cement. Sulfate may be added in the form of natural or industrial-grade calcium sulfate dihydrate (gypsum) or anhydrite.

Additional sulfates originate from clinker, in which they are formed during clinker manufacturing from raw materials and fuel combustion products. They are predominantly present in clinker in the form of alkali- and calcium alkali sulfates and, occasionally, in the form of calcium sulfate anhydrite or other phases. The most common sulfate phases present in clinkers are arcanite, K_2SO_4 , calcium langbeinite, KC_2S_3 , and aphthelite K_3NS_4 .

Occasionally, the source of sulfate in concrete may be the sulfates (e.g. gypsum) or sulfides present in aggregate. Typical example of a sulfide is iron sulfide (pyrite).

In the presence of oxygen and moisture, pyrite may oxidize to form a low-pH sulfate solution that may contribute to concrete degradation by both sulfate and acid attack: [58].



Internal Sulfate Attack With Clinker Aluminate Phase

Most national and international standards put restrictive limits on both sulfate and C_3A contents of cements, the purpose of this double restriction being, among others, prevention of internal sulfate attack. The importance of such restriction was recognized when it was observed that extensive expansion might occur in the absence of external source of sulfate. The recent ASTM standard for Type V sulfate resisting cement limits the C_3A content to 5%, the $\text{C}_4\text{AF} + 2(\text{C}_3\text{A})$ content to 25%, and the SO_3 content to 2.3%.

The main sulfate constituent in Portland cement is calcium sulfate, inter-ground to the cement in the course of manufacturing. It is usually present in form of hemi-hydrate or anhydrite and rarely also as dihydrate. Distinct, but limited amounts of sulfate ions are also incorporated into the crystalline lattices of clinker minerals. Most of the sulfate ions are incorporated in the belite phase followed by alite and tricalcium aluminate, whereas the amount present in the ferrite phase is small enough to be ignored. For clinkers with up to 3% SO_3 , the concentrations are below 0.5% in alite and rarely exceed 2.0% in belite. Sulfates bound within the clinker minerals are released into the liquid phase slowly and thus have the potential to act deleteriously, however only at excessively high overall SO_3 contents in the mix. In concrete mixes, additional amounts of SO_3 may be introduced as constituents of the aggregate employed. Obviously, rocks containing distinct amounts of SO_3 may be used as concrete aggregate without concern only if the sulfate is present in a sufficiently insoluble form such as, for example, in the form of baryte [BaSO_4], whereas aggregates containing even a moderately soluble sulfate phase, such as anhydrite [CaSO_4], must not be used.

Also, some rocks may contain sulfur in sulfide form, such as pyrite [FeS_2]. If used as concrete aggregate, a gradual oxidation of this constituent to sulfate by the oxygen of

air may cause an expansion of such aggregates, and act deleteriously even before a chemical interaction with constituents of the cement may get under way.

Internal sulfate attack caused by excessive sulfate in clinker and cement, or possibly in other concrete making materials, is uncommon. However, because of the documented increased amounts of sulfates, primarily alkali sulfates, in modern cements, all necessary precautions should be taken. Such precautions include selection of quality concrete ingredients, proper proportioning of the concrete mixture, adherence to best curing practices to give dense and impermeable concrete, and proper maintenance – all relative to the conditions of the concrete use. This is specifically recommended for concrete that might be heat cured or exposed to changing temperature and humidity.

Finally, SO_3 present in the mixing water may also contribute to internal sulfate attack, but a contribution if this constituent of the concrete mix is in most instances negligible and may become noticeable only at extremely high SO_3 concentrations.

Measures To Protect Concrete (DEF)

Cement itself may be a source of excessive sulfate in concrete. This is the reason why requirements of CEN, ASTM (see ASTM C150; ASTM C1157, BS 5328) and other standards on cement and clinker composition should be closely followed; this will assure proper concentrations and ratios of the relevant clinker minerals to give sulfate levels that will not lead to excessive expansion.

Aggregates and mineral additives are other potential sources of excessive sulfate. Selected aggregates and intermixed mineral admixtures should not contain sulfate-bearing compounds that may later become available for reaction with cement components of the concrete mixture[58].

Proper mixture design is one way of protecting concrete against degradation by heat-induced internal sulfate attack. The materials used in designing concrete mixtures (cement, aggregate, supplementary materials, admixtures) must pass the existing specifications and have proven history of satisfactory performance. The lowest possible w/cm is recommended.

Exposed concrete surfaces should be kept wet, but condensed water should not drip on them. Pre-curing or preset time must be adequate to allow the cement used in making the concrete to set properly. Depending on the type of cement used, this may

be between two and four hours. It should be kept in mind that prematurely heated fresh concrete will develop lower strength and may lead to decreased durability.

Heating rate of concrete should be steady (limited to about 15–20 °C, or about 25–35 °F, maximum per hour) and the temperature rise uniformly distributed for the whole member as well as within the curing chamber; such curing procedure will prevent formation of micro-structural faults and cracks that may adversely affect long-term durability of the treated concrete member. In designing concrete to be exposed to heat treatment, the heat of hydration of the cement should always be taken into consideration: it is the total heat input (heat of the ambient temperature plus heat of hydration plus heat added during curing) that controls the quality of the product.

The difference between the external and maximum internal temperature of a member should never exceed 20 °C or about 35 °F [58].

Internal Sulfate Attack Related With Delayed (DEF)

As is often the case in discussion of newly described phenomena, the terminology and nomenclature used in the literature to describe the DEF induced deterioration is confusing.

First of all, it should be recognized that the phenomenon is clearly an internal form of sulfate attack because it is triggered by sulfate that is internal to concrete. All necessary ingredients (sulfate, alumina, calcium, and water) are present in the system at the time the concrete is produced, although additional water may be required to produce the damaging expansion; such water is supplied during post-curing storage or field use.

Available information shows that heat-induced sulfate attack (DEF), in line with all localized sub-microscopic volume increases, is characterized by map cracking, longitudinal cracking, occasional warping of the concrete structure or product, and some spalling. Because in the majority of the known cases internal sulfate attack and ASR were operative simultaneously, it is difficult to make any definitive statement credibly characterizing the “DEF” damage caused by sulfate reactions alone.

One of the characteristic features of heat-induced sulfate attack is the formation of circular or peripheral cracks (gaps, bands), around the aggregate particles. There is some evidence to show that the width of these gaps is proportional to the aggregate

size, this fact implying that the formation of the gaps is related to homogeneous expansion of the cement paste [58].

2.6.3.3 External Sulfate Attack

External sulfate attack is caused by a source external to concrete. Such sources include sulfates from ground water, soil, solid industrial waste, and fertilizers, or from atmospheric SO_3 , or from liquid industrial wastes. In external sulfate attack, sulfates from an external source enter the hardened concrete, causing its impairment.

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. Here, the sulfate anions are most commonly combined with alkali or calcium cations. In some waters the amount of present Mg^{2+} ions may also be significant.

In addition to ground water, water of rivers and lakes may also serve as source of sulfates that may cause external sulfate attack. The chemical composition of these waters varies within the range commonly seen also in ground waters, in most instances. Industrial waste waters have to be considered to be a special case. Their composition may vary greatly, depending on the kind of industry involved, and along with it also varies their harmfulness.

A special consideration has to be given to sea water, as it contains a variety of constituents, including sulfate ions, and its overall content of dissolved species is significantly higher than is common in ground, lake or river waters [58].

Many authors (Hamilton and Handegord 1968; Harboe 1982; Price and Peterson 1968; Terzaghi 1948) reported marked losses in compressive strength for concrete structures exposed to sulfate-laden soils or sea water.

Curiously, it appears that the shear resistance and tensile strength of concrete are more sensitive to external sulfate attack than compressive strength. This phenomenon can probably be explained (at least in part) by the layered damage resulting from external sulfate attack. The tensile strength and the shear resistance of concrete are more sensitive by internal defects than compressive strength [58].

External Sources

The primary sources of external sulfate are natural sulfates of calcium, magnesium, sodium, and potassium present in soils or dissolved in ground water. Occasionally, sulfides may be present, such as pyrite, which may oxidize to form water-soluble sulfates. In arid areas, concrete structures in contact with ground water, having one face exposed to air, are particularly endangered due to increasing concentrations of sulfates at the air-exposed surface through evaporation of surface moisture. The probability of such increase in sulfate concentration decreases with concrete impermeability, i.e., decreasing water–cement ratio.

Additional sources of sulfate are solid industrial wastes exposed to precipitation or ground water. Examples are wastes from mining industry (e.g. cinders, oil-shale residues), combustion of coal (refuse from incineration, bottom ash, pulverized fuel ash), and metallurgical industry (e.g. low-quality blast-furnace slag). Ready availability of these sulfates to cause damage to concrete depends on their concentration and solubility, access and mobility of contact water, and environmental conditions.

Industrial or agricultural waste waters may contain sulfates too; for example, water from some cooling towers may under certain conditions reach relatively high sulfate concentrations. Agricultural waste is a well-known source of aggressive chemicals, although sulfate (e.g. from fertilizer) is not one of the most common ions present.

Finally, sulfates may originate from atmospheric pollution and, depending on the atmospheric conditions (temperature, humidity, wind, etc.), may contribute to increased sulfate concentration of the soil and ground water, thus increasing the potential for causing sulfate attack.

Measures To Protect Concrete Against External Sulfate Attack

One of the primary conditions for the proper design and erection of a concrete structure is the full understanding of all aspects of the local environment. Understanding of the ranges and fluctuations in temperature and humidity enables proper selection of concrete quality needed in the given environment.

Therefore, these environmental/atmospheric conditions should be taken into consideration right at the design stage, to assure proper concrete mix design and structural design, minimizing the access of ground water to the structure.

Understandably, good workmanship during the structure erection is crucial. It is important to remember that the potential negative effect of atmospheric conditions can be completely negated if concrete quality compatible with the environment is delivered.

The three main strategies for improving resistance to sulfate solutions are:

- Making a high quality, impermeable concrete;
- Using a sulfate-resistant binder; and
- Making sure that concrete is properly placed and cured on site.

As specified by many standards and codes, concrete should be designed to give dense, low porosity concrete matrix that can resist penetration of aggressive chemical species into hardened concrete. Depending on the sulfate concentration in the environment of use, maximum w/cm of 0.5, but possibly as low as 0.4, is recommended. It should be also taken into consideration that achievement of the specified minimum compressive strength may not be an adequate measure of durability under the given environmental conditions. Therefore, an increase in cement content above that needed to achieve the minimum strength (while keeping the w/cm low) should be considered.

The sulfate-resisting cements should be used with the understanding that they are not a panacea against sulfate attack unless used with quality concrete. Sulfate resisting cements are not a substitute for proper concrete making. Their use is recommended to give a secondary level of protection in addition to (not instead of!) protection given by low water–cement ratio, adequate cement content, and overall proper mix design and good workmanship.

In addition, in severe sulfate environments, the use of appropriate and tested mineral admixtures may be desirable. However, special care should be taken to select the proper source of fly ash and/or slag [58].

2.6.3.4 The Prospective Reasons and Results of Sulfate Attack

The interaction between sulfates on one hand and the constituents of unhydrated cement or hydrated cement paste on the other hand is very complex and depends on a variety of factors. A multitude of chemical reactions, taking place concurrently or subsequently, may be involved. The factors affecting the process include:

- The composition of the cement or hardened cement paste;
- The form of sulfate participating in the process;
- The type of interaction, i.e. whether the sulfate is a constituent of the cement or concrete mix undergoing hydration (internal sulfate attack) or enters into the hardened paste/mortar/concrete from outside (external sulfate attack);
- Temperature at which the interaction takes place, etc.

The reactions involved may result:

- in an expansion of the paste;
- in chemical degradation of the present hydrate phases associated with a worsening of the intrinsic strength properties of the hardened cement paste;
- in crack formation within the hardened material, in surface scaling, spalling or delamination of the hardened material [58].

When damage occurs, it is always the consequence of incorrect construction that enables penetration into concrete of aqueous salt solutions needed to initiate and feed the attack.

Most of the codified recommendations are based on prescription of maximum values for water–cement ratio, maximum levels of C_3A in cement and, in some cases, of minimum cement content and addition of supplementary materials such as selected pozzolans or slags or both.

According to Mehta and Monteiro, a well-constructed, impermeable concrete structure will not suffer from sulfate attack regardless of the prevailing environmental conditions and physico-chemical mechanisms (e.g. potential for ettringite, thaumasite, gypsum, or efflorescence formation). The quality of concrete, specifically a low permeability, is the best protection against sulfate attack. Adequate concrete thickness, high cement content, low water/cement ratio and proper compaction and curing of fresh concrete are among the important factors that contribute to low permeability. In the event of cracking due to drying shrinkage, frost

action, corrosion of reinforcement, or other causes, additional safety can be provided by the use of sulfate-resisting cements.

In other words, properly designed and constructed concrete will be stable under most aggressive conditions unless the concentration of sulfates in the soil or the water in contact with the concrete is extreme. Under such conditions additional measures have to be taken to prevent direct contact between the concrete and the SO_4^{2+} source. However, problems do occur, and sulfate attack may become a real issue when concrete is improperly proportioned, designed, cured and placed in a hostile environment, or both [58].

The expansion of concrete is usually accompanied by the development of cracks into the material. Numerous studies indicate that cracking is usually initiated near the surface and gradually evolves towards the central portion of the sample. According to Lagerblad, cracks can be detected by a visual inspection when the linear expansion of the sample exceeds 0.7 %. At later stages of degradation, severe cracking often is accompanied by de-lamination and exfoliation, and may eventually lead to the total disintegration of the sample.

As emphasized by Hamilton and Handegord, the degradation of field concrete by sulfate attack does not usually result in the sudden failure of the structure. The detrimental action of sulfates is a progressive process of deterioration that often leads to collapse or to the necessity of demolition. Field reports indicate that the rate of deterioration can be particularly rapid and severe when concrete exposed to sulfates is continuously kept in saturated (or nearly saturated) conditions.

According to Haynes, the mechanisms of degradation involve the penetration of sulfate solutions either by simple diffusion or by capillary suction when pore water evaporates from above-ground surfaces, the sulfate concentration becomes sufficiently high to cause crystallization.

Changes in ambient temperature and relative humidity cause some salts to undergo cycles of dissolution and crystallization, which may be accompanied by volume expansion.

For instance, using X-ray microanalyses, backscattered electron imaging and scanning electron microscopy, Gollop and Taylor (1992) found that laboratory samples immersed in sodium sulfate and magnesium sulfate solutions were characterized by a succession of layers (or zones) starting from the outer surface of

the specimens. Each zone was found to be the result of a series of reactions between the external sulfate ions and the aluminate and calcium-bearing phases initially present within the material.

The authors found that the cement content of the mixture influenced the admissible expansion beyond which the compressive strength of mortar was detrimentally affected. They proposed the following relationship to predict the value of critical expansion (noted E and expressed in mm/mm):

$$E = 0.0026 + 0.01C \quad (2.8)$$

Where, C is the cement content (expressed as a percentage of the total mass of the mixture) [58].

2.6.3.5 Tests for Determining Sulfate Attack On The Concrete

The degree of complexity of the modern cementing system in concrete indicates the need for the increasing the performance of specifications and prescription specifications for cementing system and the concrete. ASTM tests that are relevant to resistance of cement against sulfates are:

1. C 452 – Standard Test Method for Expansion of Portland Cement Mortars Exposed to Sulfate.
2. C 1012 – Test Method for Length Change of Hydraulic Cement Mortars to a Sulfate Solution.
3. C 1038 – Test Method for Expansion of Portland Cement Mortar Bars Stored in Water.

Among these three tests, ASTM C 1012 has become predominant for estimating the potential for sulfate attack for cementing systems containing various combinations of Portland cements and pozzolans. The potential sulfate resistance of ordinary Portland cement has been determined by ASTM C 452 test. For systems consisting of only Portland cement, ASTM C 452 test method is still used because of its short duration [60].

In the US ASTM C 452 (ASTM, 1995) describes a method, which is referenced by C-150, Standard Specification for Portland Cement (ASTM, 1999). This method is based on the preparation of mortars with gypsum added to the cement to raise its SO_3 content to 7%. Expansion between 24 hours and 14 days is measured. Cements

giving an expansion of less than 0.04% have high sulfate resistance, equivalent to the Type V cements with a C₃A limit of 5%. However, this test method is not suitable for cements containing slag or pozzolans. For these cements the method in C1012 (ASTM, 1995) is referenced. In this test mortar prisms are stored in sulfate solution and expansion determined after 6 months and 1 year of exposure. To ensure that the mortar is sufficiently mature to give a realistic measure of its long-term performance the prisms are only placed in the sulfate solution after cubes cast from the same mortar have reached a specified strength [61].

2.6.3.6 Action of Magnesium Sulfate

Magnesium sulfate has a more far-reaching action than other sulfates and decomposes the hydrated calcium silicates in addition to reacting with the aluminates and calcium hydroxide. If tri- or dicalcium silicate is placed in magnesium sulfate solution, formation of gypsum crystals occurs rapidly [57].

The primary step in the interaction between hydrated cement paste and a magnesium sulfate solution is a reaction of the sulfate with calcium hydroxide of the paste, yielding magnesium hydroxide [brucite, Mg(OH)₂] and calcium sulfate in form of gypsum [CaSO₄ · 2H₂O]:



The action of magnesium sulfate is accompanied by a migration of hydroxide ions towards the surface to produce insoluble brucite and by a migration of sulfate ions inwards to form gypsum, and in deeper regions and in smaller amounts also ettringite.

Table 2.9: Harmful effectiveness level of sulfate ions according to TS 3340

Effectiveness Level	SO ₄ ⁻² mg/l in water	SO ₄ ⁻² mg/kg in water
Weak	200-600	2000-5000
Strong	600-3000	> 5000
Very Strong	> 3000	-

The calcium ions needed for the formation of these phases are supplied primarily by the decomposition of calcium hydroxide and, especially after exhaustion of this phase, also by the decalcification of the C-S-H phase. Eventually, a double surface

layer is formed consisting of an external layer of brucite, followed by a layer of gypsum [58].



Figure 2.6 Penetration of sulfate-bearing ground water through a retaining wall exposed to atmospheric changes (wetting–drying, heating–cooling)

2.6.3.7 Conditions Affecting Sulfate Attack

- Quality and proportion of the concrete mixture ingredients, including cement, supplementary materials, fine and coarse aggregate, chemical and mineral admixtures, and water.
- Processing conditions, including mixing, placing, curing of fresh concrete, and maintenance of hardened concrete. Special emphasis has to be placed on those processes that control the water tightness, e.g. proper consolidation and curing.
- Environmental – atmospheric conditions in which the concrete structure is being used. Not only are the temperature and humidity of great importance; so are their variations with time, especially in climates where capillary suction and evaporation may cause super-saturation and crystallization in the concrete above ground [58].

2.6.3.8 Improvement of Sulfate Resistance Of Concrete

Early efforts to improve the sulfate resistance of Portland cement concretes were concentrated on the effects of physical factors, such as steam curing, the duration of water curing or allowing the concrete to dry in air to give an impermeable carbonate skin before exposure to sulfate solutions. While having some beneficial effects, these

measures were limited in their practical application to precast units. Significant improvements in sulfate resistance came with a change in the composition of the cement, whereby the compound tetra-calcium aluminoferrite largely replaced tri-calcium aluminate.

The value of reduced tri-calcium aluminate content in increasing the sulfate resistance of Portland cements was demonstrated by a number of field and laboratory trials of concretes made with different cements and exposed to sulfate solutions for lengthy periods.

The general findings of the work confirmed the results obtained in other investigations. They showed that little benefit was derived from the use of air-entraining agents or of other additives, and that thin surface coatings, while giving some early protection to the concrete, retained little protective effect after about 5 years.

High-temperature steam curing, at 175°C for 6h, increased the resistance to sulfate attack to such a degree that almost complete immunity for 17 years was obtained. Lower temperatures or shorter times of curing gave only limited improvement in durability. The importance of high-quality concrete with low permeability and freedom from honeycombing in giving maximum resistance was clearly demonstrated.

Both the cement content of the concrete and the C_3A content of the cement were considered to influence durability in trials conducted at Sacramento, California, as part of the American Long-time Study of Cement Performance. Large concrete prisms were partially buried in two soils, each containing about 10 per cent soluble salts, but in one these were composed of 85 per cent sodium sulfate with 10 per cent sodium carbonate and little magnesium sulfate, and in the other about one-third of the sodium sulfate was replaced by magnesium sulfate. The beds were flooded periodically during the summer, resulting in crystallization of salts by evaporation over the exposed surfaces. After about 5 years under these conditions the factor of major importance was the cement content of the concrete, while the type of Portland cement was secondary to this. Lean concretes of about 224kg/m³ deteriorated badly and many disintegrated completely in a shorter period. With medium concretes of about 310kg/m³ the deterioration after 5 years varied from slight to severe, while

most of the rich mixes with about 390kg/m^3 cement content showed only slight deterioration. In the concretes of low and medium cement content there was a general relation between degree of deterioration and the calculated C_3A content of the cement [58].

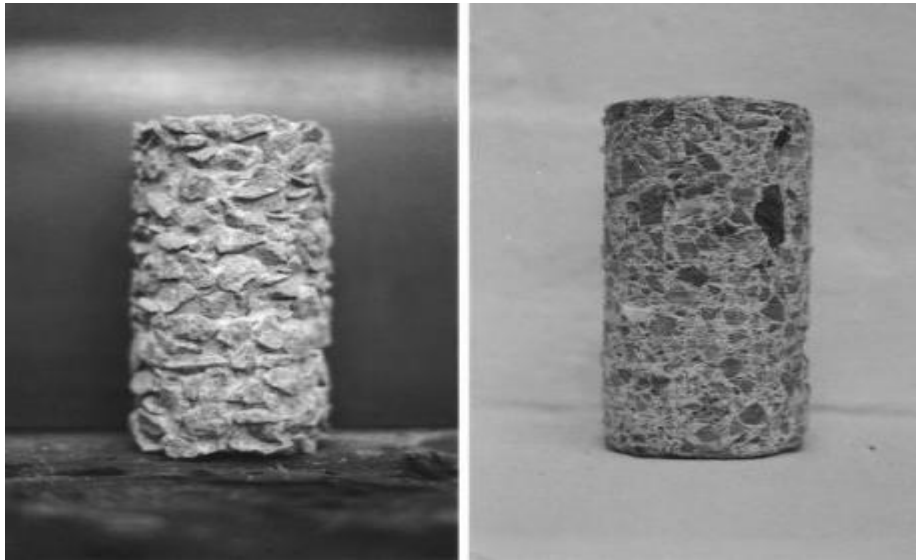


Figure 2.7 a, b Laboratory concrete samples attacked by sulfuric acid; readily soluble: (a) Sample with dolomitic (acid-soluble) aggregate; and paste portion (b) sample with silicious (insoluble) aggregate .

2.6.3.9 Influence of the Water to Concrete Durability

Water is a necessary component of all hydraulic concrete. It is usually used in amounts of 25–50 weight per cent of the cement. It has two engineering purposes: to enable

- Proper mixing, consolidation and finishing of the fresh mixture (workability); and
- The chemical processes of hydration that, are responsible for development and maintenance of the desired physical properties (setting, hardening, maturity).

For complete hydration of a typical Portland cement, about 20–22 weight per cent of water relative to the cement content is required. Any water in excess of that is theoretically needed will increase to cement paste porosity. Because of its molecular structure and chemical nature, water is an excellent solvent capable of dissolving

more chemical substances than any other liquid it exists in three phases at ambient temperatures, and is capable of penetrating even the finest pores.

This makes water the most important medium also from the point of view of durability, for it is the carrier of chemical species into and out of the concrete microstructure. Without water most mechanisms of concrete deterioration could not proceed. The following water-related items should be considered in design, production, and protection of any concrete or concrete structure: chemical nature of the water (presence of organic or inorganic components, aggressivity, alkalinity or acidity, etc.), humidity and its changes, flow rate, action of waves, and repeated drying and wetting.

2.6.3.10 Development Of Physical Properties

The most important property of fresh concrete is its workability. It can be defined as the resistivity of the fresh concrete mixture against forces of deformation, and is observed in the field as the ease of mixing, transporting (pumping), and finishing. Workability of concrete depends on the fluidity of the cement paste and the quality, amount and mixture proportions of the used aggregate. Change with time of concrete workability is usually characterized by its flow-ability (e.g. flow table, slump) and setting characteristics (e.g. Vicat and Proctor tests).

Like other concrete properties, the change of fresh concrete workability with time is directly influenced by the chemical reactions of hydration. As hydration progresses and more cement components transform into hydration products, the overall porosity, thus the free space between particles of the newly formed compounds, decreases; this increases the friction within the paste and between the paste and other concrete components, thus increasing the resistance to external forces. It is important to recognize that during this process of setting the concrete system may easily be damaged by excessive deformation, and this deformation may negatively influence the hardened concrete durability at later ages.

Hardened concrete, concrete that has set and can resist force without deformation, has to be durable – meaning it has to maintain its desired chemical and physical properties for a long time. Please note the emphasis on durability: it is a mistake to assume that strong concrete is also durable.

In the majority of cases, concrete designed and processed for good durability also guarantees maintenance of concrete quality represented, typically, by volume stability and strength, whereas strength per se is not an appropriate or adequate measure of durability.

The most important engineering properties of hardened concrete include strength, modulus of elasticity, water tightness, and volume stability. In other words, durability is a measure of resistance of a concrete product or structure to physical and chemical “pressures.” A durable structure will maintain its expected chemical, physical and engineering properties for the whole duration of its projected service life.

Chemical durability is the measure of stability of the concrete components, paste and aggregate, in the environment of its use; specifically, it is the resistance against external or internal, surface or bulk reactions that may lead to exchange of chemical species between the concrete and the environment. Such exchange may include carbonates, sulfates, chlorides, and other inorganic and organic species. The reactivity of concrete components with the above species is moisture- and temperature-dependent, thus the conditions of future use have to be considered already at the design stage and during concrete processing [58].

2.6.4 Alkali-Aggregate Reactions

Apparently spontaneous and often serious long-term cracking of concrete structures was investigated in the USA in the 1930s and eventually found to be caused by an expansive reaction between cement and aggregate. It was found that the combination of cement with a relatively high content of alkali hydroxides and aggregates containing certain potentially reactive forms of silica reacted to form an alkali-silica gel, which could swell on the absorption of water, giving rise to expansive stresses. This initial discovery gave rise to the rapid development in the USA of various tests for aggregate reactivity and preventative controls primarily based on using cements with relatively low alkali contents.

AAR arises as a result of an inappropriate combination of potentially incompatible constituents of concrete and should not be characterized as being caused by one or other of these components, each one of which is stable in isolation.

2.6.4.1 Alkali Silica Reactivity

The most prevalent alkali-aggregate reaction is alkali-silica reaction, ASR, characterized by the reaction of OH^- ions with silica contained in reactive amorphous silicates in aggregate. The reaction leads to breaking of the -Si-O-Si- bonds in the silicate structure and formation of calcium-alkali-silicate gel of variable composition that, may, under certain conditions, lead to cracking of the aggregate, expansion of the cement paste matrix and, ultimately, to cracking and complete destruction of the concrete structure [58].

2.6.4.2 Reasons and Results of ASR Formation

The alkali silica gel which composed after the reaction absorb a big quantity of water and expand thereby it leads on the concrete swelling and cracks. In order to occur ASR, aggregate need to include reactive silica high range alkali pore solution and sufficient amount of humidity in the ambient. If not one of these conditions don't exist, there will be no expansion because of ASR. The quantity of gel in the concrete depends on the sort and amount of silica and the concentration of alkali hydroxide. The reaction is developed by ASR happens in two stage;



If the concrete is getting dry during its service life ASR couldn't be serious problem. The researches demonstrate that ASR fall out on the concrete when the relative humidity ratio over the 80% [62].

ASR in concrete, and especially ASR leading to damage, is rarely inevitable and depends on the coexistence in a given circumstance of a number of conducive factors. Three crucial factors are;

- Sufficient moisture to initiate reaction and then promote swelling of the gel,
- Sufficiently high alkali hydroxide concentrations to trigger and sustain reaction,
- The presence of potentially reactive silica in a critical proportion. Some other factors can influence the likelihood, rate and severity of reaction and/or resultant damage [63].

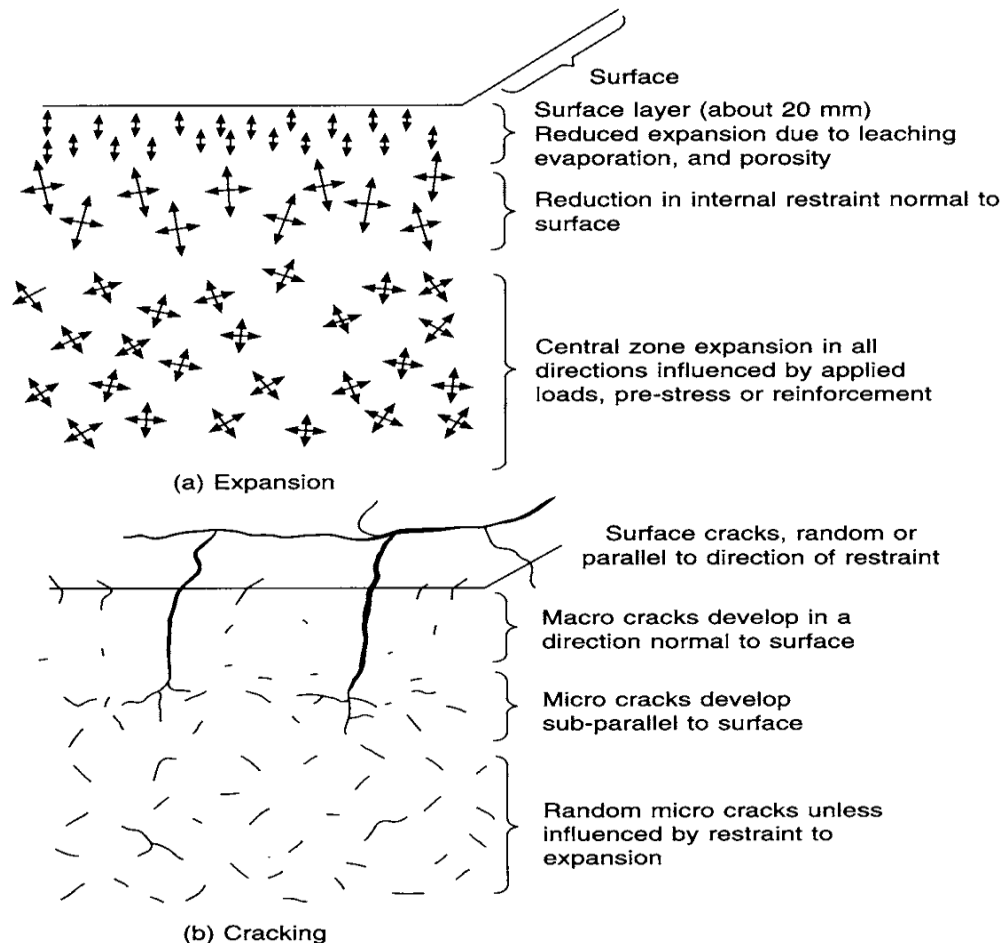


Figure 2.8 Diagrams illustrating the development of cracking caused by ASR

2.6.4.3 Component's Influence to the ASR Formation

Moisture

In most cases, the mix water provides sufficient excess moisture to initiate any reaction. However, it has generally been considered that significant damage will only occur in conditions sufficiently humid to facilitate swelling of the gel reaction product. Any relative humidity in excess of about 75% is regarded as conducive to ASR damage, which, in practice, means that any exterior concrete in a temperate or other wet climate is at risk, if the concrete contains a reactive mix.

Alkalis

It is a convention in cement and concrete chemistry to assess alkalis on the basis of acid soluble 'equivalent soda' (Na_2Oeq), which is expressed as $\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$. Portland cement always contains soluble alkali salts that enter the pore solution very early in the hydration process. It is these alkali hydroxides in the concrete pore

solution that are available to participate in ASR. Portland cement is thus the predominant, and frequently the only significant, source of alkalis in cases of ASR. Early experience demonstrated that usually only high-alkali cements (say $\text{Na}_2\text{O}_{\text{eq}} > 1.0\%$ by mass) were involved in damaging ASR, leading to pragmatic control measures in the USA and elsewhere based on using 'low-alkali' cement, defined as $<0.60\%$ by mass.

Aggregate

From a purely chemical standpoint, ASR is not surprising, as any silica is reactive with, and ultimately soluble in, highly alkaline (caustic) solutions. However, most forms of silica are essentially stable within the normal range of internal concrete environments, under normal atmospheric conditions and for the foreseeable service life of any structure. Silica reactivity seems to depend upon high internal surface area and/or some degree of atomic disorder; the entropy of a partially or poorly crystalline fine-grained silica may be greater than that of a purely amorphous material. The most reactive natural silica is opal (or opaline silica), which is fairly common worldwide (in non-gem quality forms) and is a hydrous and virtually non-crystalline or highly disordered form of silica related to cristobalite. Similarly, silica-rich volcanic glasses, or especially their partially or completely devitrified equivalents, can be very reactive.

Early research into ASR discovered that there was no simple relationship between the proportion of potentially reactive constituents in the aggregate and the resultant magnitude of reaction and expansion. Indeed, in many cases, the maximum expansion occurred at a relatively low proportion of reactive material in the aggregate; this critical proportion has been termed the 'pessimum'. A wide range of pessimum values has been identified for different aggregate types, for example, ranging from just a few per cent for opal, through maybe 15 to 35% for flint and up to 100% (i.e. no pessimum) for some crushed glassy andesites [63].

2.6.4.4 Symptoms of Alkali Silica Reactions

The shape of ASR cracks is different from the other construction cracks which are formed by reason of soil loads or several structure loads. It has been obviously distinguished from the compressive, tension, shear and shear loads. The potential energy, stored in the concrete because of ASR gels water absorption, is run out with

these cracks. The surface or near to surface fractions behave as a pop-out happening and compose small holes on the concrete surfaces. If the ASR gel, exist on the pop-out area, it is a crucial evidence to ASR. The coloration and discoloration is appeared with these map cracks on the concrete surface. Dark colored or black areas are usually sourced from ASR. There might be seen along the crack areas being white, brown, or pink colors. ASR is more disruptive, on bridges, on underground roads, cross-points, on the bottom side of concrete pavements, on the quay's near to water zone surfaces [64].

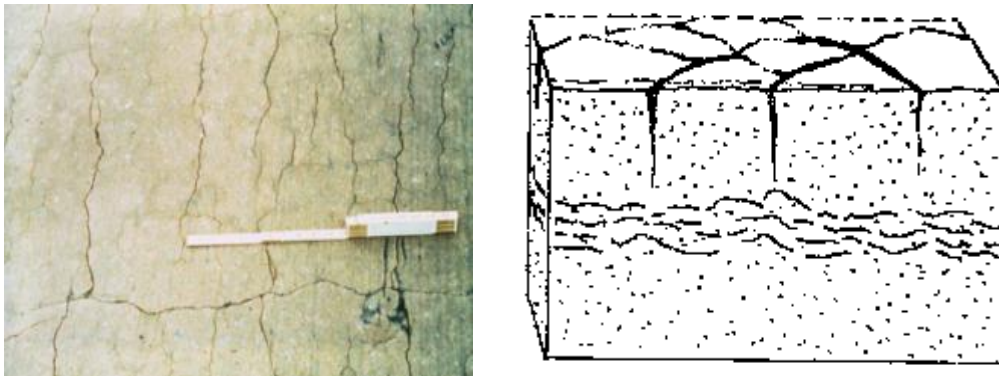


Figure 2.9 Map cracks sourced by AAR

2.6.4.5 Major Preventative Options

Eliminating, one of the three key factors for damaging ASR: sufficient moisture, sufficient alkalis, or a critical proportion of reactive aggregate. In the case of most exterior concrete, it will be impracticable adequately to restrict moisture to a level continuously lower than 75% relative humidity. However, some internally exposed concrete could be considered sufficiently dry and well ventilated, after curing, for ASR damage to be prevented.

Adequately low alkali contents may be achieved by adjusting the cement content, the composition of the cement (which might be a factory-blended cement) and/or the combination of the cement with additions of GGBS or suitable PFA. Although these GGBS and PFA materials certainly act as diluents in respect of reactive alkalis, there is at least empirical evidence that these additions can also inhibit expansion through other mechanisms, probably including reaction with calcium hydroxide, causing the gel products from any ASR to be less expansive [63].

A. Bouikni, R.N. Swamy , A. Bali have carried out a research and they had tried to understand the affect of GGBS on the concrete for preventing or declining ASR

influences on it. They had manufactured 50% slag content (by the mass) and 65 % slag content concretes. After their experiments they showed that both concretes suffered major losses in flexural strength, whereas the eventual loss in compressive strength was only about 10% for the 50% slag concrete whilst the concrete with 65% slag registered an increase in compressive strength of almost 25%. Furthermore, concretes with 65% slag performed better in resisting the effects of cracking due to ASR than concretes with 50% slag [65].

2.6.5 Frost Attack

2.6.5.1 Causes of Frost Damage

There are various explanations of frost damage. In earlier theories the damage was attributed directly to the empty space available being insufficient to accommodate the additional solid volume produced when the water in the concrete freezes. Damage is related to the degree of saturation. For example, a high permeability would allow easier flow of water and, since it will arise from larger capillaries, more room for ice growth, but such a concrete would readily become highly saturated. In practice, frost resistance is high for dense impermeable concretes and for open-textured or very porous concretes, such as no-fines and some lightweight concretes, and is lower for the more permeable 'dense' concretes.

2.6.5.2. Factors of Effecting Frost Resistance

The resistance of concrete to frost depends on the quality of the cement mortar and, to some extent, of the aggregate. Fairly wide variations in the quality of the coarse aggregate can be tolerated, for there is no close correlation between the durability of aggregates and the concrete made from them, but argillaceous or soft, porous limestones, gravels containing too much weak material, such as particles of porous chert, shales and friable sandstones are susceptible to breakdown by frost action.

There is no close relation between the total porosity or absorption of aggregates and their frost resistance, for it is the character of the pores which is of predominant importance. The larger pores are not necessarily detrimental, and it is the finer pores, for example, $< 5 \mu\text{m}$ in diameter which, if present in abundance, have most influence in reducing the frost resistance of concrete, since they tend to remain full of water. This leads to an expectation that aggregates with a large internal, but accessible

surface area should tend to be less frost resistant, and there is some evidence to support this [57].

As water turns to ice at its freezing point of 0°C , there is an increase in volume of about 9%. When porous material is saturated with water this expansion on freezing can lead to disruption of the material if its strength is insufficient to resist the forces involved. Unless the material is more than 92% saturated, however, disruption does not occur since there is empty space to accommodate the expansion.

The saturation need not be over the whole volume of the material and surface layers can suffer frost attack even though the main body is unaffected.

In saturated concrete the water filling the gel pores will not freeze under normal conditions because its freezing point is far too low. This is because the liquid in the very fine gel pores is under high surface tension forces which prevent the formation of the nuclei of ice responsible for initiation of ice growth. Water in the capillary pores freezes and as the ice grows it forces unfrozen water into the surrounding gel pores. Since a particular section of gel will be surrounded by capillaries all trying to push water into it, the hydraulic pressure build-up can be sufficient to disrupt the gel system [62].

2.6.5.3 Assessment of Frost Resistance

One of the main difficulties in attempting to relate frost resistance to the absorption, or the degree of saturation, lies in the definition of these terms. Porosity arises from the following.

- Voids in the aggregate particles.
- Spaces between the aggregate particles and the cement paste.
- Capillaries in the set cement gel. These are the spaces originally occupied by water and which are too fine to have allowed hydration products to form and fill them. The gel capillaries vary in size from several tens of nanometers up to $1\text{ }\mu\text{m}$.
- Gel pores, which are ultrafine slits, less than $2\text{ }\mu\text{m}$, and smaller than the solid particles.
- Air bubbles entrapped in the concrete during making [57].

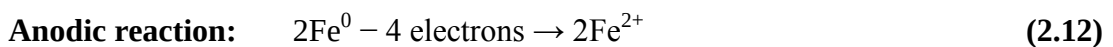
2.6.5.4. Precautions Against to Freezing

Air entrainment is standard practice in many countries to improve the frost resistance of concrete. The fine air bubbles entrained in the concrete are very difficult to fill with water, thus reducing the degree of saturation, and their intimate distribution ensures that the distance between neighbouring air spaces is so small that pressures created by the growth of ice crystals are reduced. It is usual to aim at an air content of 5-6 percent by volume in the concrete. For good frost resistance the distance between individual air bubbles should not exceed about 0.25 mm.

Occasional large air voids do not have the same beneficial effect of small, closely spaced bubbles, even when the total void space is the same [57].

2.6.6. Corrosion of Embedded Steel

The function of the steel is to give concrete structures certain properties that cannot be achieved by concrete itself, adequate flexural strength, modulus of elasticity, etc. Under regular field conditions, the reinforcement in good quality concrete is protected from aggressive corroding environment by the alkaline environment of the concrete cover and by use of otherwise protected steel surface, or both. The steel surface itself is covered by an oxide layer that is stable in alkaline, but not under more acidic conditions. Under field conditions, however, the ideal conditions are often not met. In lower quality concrete, for example concrete made with excessive water and thus possessing high porosity and permeability, the reinforcing steel may undergo oxidation resulting in electrochemical (cathodic plus anodic) removal of Fe atoms from the surface.



Dissolution of Ions in solution
Fe atoms



Dissolved oxygen Ions in solution
molecules

Under such conditions the protective iron oxide layer may get damaged, leading to excessive formation of one of several varieties of rust, followed by expansion and delamination of concrete. High concrete porosity and high concentration of cracks reaching the depth of reinforcement increase also the rate of carbon dioxide ingress,

this leading to carbonation of the calcium hydroxide, Ca(OH)_2 , present in the cement paste, to form calcium carbonate, CaCO_3 .



This may result in a drop of pH in the cement paste that is in immediate contact with the steel surface, thus allowing the corrosion of steel to take place. Corrosion of reinforcement steel may be accelerated under conditions where other mechanisms of damage are in action simultaneously. For example, simultaneous freeze–thaw conditions or exposure of concrete to aggressive sulfates may accelerate the rate of corrosion. In a similar manner, chemical deterioration of concrete may be aided by conditions leading to reinforcement corrosion, such as access of chlorides and sulfates [58].

3. EXPERIMENTAL STUDY

In this part, it has been explained study's materials and the main properties of the, mix design of concrete and also the methods of applied experiments with their results on the samples.

3.1. Materials Of Study

3.1.1Aggregate

The types of aggregate which was used in this study are natural sand, crashed sand, and crashed stone I. The physical properties, sieve analyses and the sources of these aggregates are showed at Table 3.1. Additionally grading size curve is given below as Figure 3.1 .Aggregate's grading curve is considered between the A16 and C16 curve as close as possible to B16 curve..

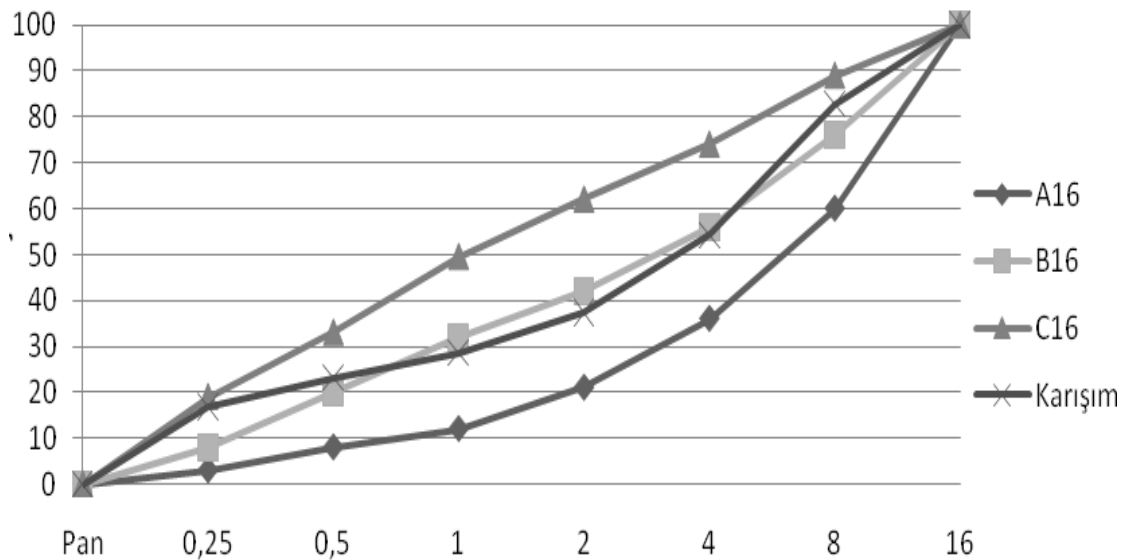


Figure 3.1: Grading Size Curve of Aggregate

Table 3.1: Sieve Analyses of aggregates

Material		Natural Sand	Crashed Sand	Crashed Stone I	Mix
The Area Of Quarry		AKPINAR	ÖMERLİ	DARICA	
Dry Weight		2000	2000	2000	
Cleaned Dry Weight		1995	1900	1986	
% Passed		%4,0	%5,0	%0,7	91.42
Sieve		%	%	%	82.83
Number	Distance(mm)	Passed	Passed	Passed	
62/25"	63	100	100	100	100
31/25"	31,5	100	100	100	100
5/8"	16	100	100	100	100
5/16"	8	100	100	57,08	82,83
No:5	4	89,22	89,25	1,73	54,23
No:10	2	79,95	43,96	0,7	37,45
No:18	1	69,92	25,63	-	28,66
No:35	0,5	59,90	17,58	-	23,24
No:60	0,25	49,87	6,50	-	16,91
No:230	0,063	19,80	5,00	-	7,44
Fineness Modulus		1,5	3,2		

3.1.2 Cement

CEM I 42.5 Portland Cement which possess $3550 \text{ cm}^2/\text{g}$ specific surface is utilized for all samples in this investigation. Chemical properties of used cement are given below at the Table 3.2.

Table 3.2: Chemical content of CEM I 42,5 Portland Cement

Components	% By volume
SiO ₂	20,63
Al ₂ O ₃ (%)	4,71
Fe ₂ O ₃ (%)	3,41
CaO (%)	63,64
MgO (%)	1,24
SO ₃ (%)	2,98
K ₂ O (%)	0,91
Na ₂ O (%)	0,23
Cl	0,0357
LOI	1,25
Free CaO	1,1

Table 3.3: Compressive Strength Results of Cement

Day	Compressive Strength (N/mm ²)	TS EN 197-1 Standard
2	27	min. 20
7	40	-
28	51	min. 42.5
		max. 62.5

3.1.3 Mineral Admixtures

F type Fly Ash, Lime Stone filler and Sand Stone fillers are used in this study. The physical properties of both aggregates and minerals are given below at Table 3.4.

Table 3.4 Unit Weight and Water Absorption Capacity of Aggregates and Filler

Types And Size Of Material	Specific Gravity (gr/cm ³)	Water Absorption %
F Type Fly Ash (0-100 mm)	2,12	-
Lime Stone Filler (0-100 µm)	2.71	1.4
Sand Stone Filler (0-45 µm)	2.64	1.5
Natural Sand (0-4 mm)	2.63	0.9
Crashed Sand (0-4 mm)	2.71	1.4
Crashed Coarse Aggregate(4-16 mm)	2.72	0.8

3.1.4 Chemical Admixtures

Super-plasticizer “Glenium 51” which is based on poly-carboxylic ether and “Rheomatrix 100” viscosity regulator admixture was used in all mixes with the same amounts. The technical properties of both admixtures are shown at table 3.5 and 3.6

Table 3.5: Technical Properties Of Glenium 51 [66]

Structure Of Material	Poly-Carboxylic Ether
Colour	Brown
Density	1,082 - 1,142 g/cm ³
Chlorine Content % (EN480-10)	< 0,1
Alkali Content % (EN 480-12)	< 3
pH Value	6.6

Table 3.6: Technical Properties of Rheomatrix 100

Structure Of Material	Water solution Of High molecular weight synthetic
Colour	Brown
Density	1,082 - 1,142 g/cm ³
Chlorine Content % (EN480-10)	1,0 - 1,02 g/cm ³
Alkali Content % (EN 480-12)	< 0,1
pH Value	6,6

3.1.5 Mix Water

City water supply, which has 7 pH values, was used not only for manufacturing process but also curing process of all samples.

3.2 Mix Design

Four kind of Self Compacting Concrete (SCC) was manufactured as 10 different mix in this study. The first of them was consisted of only Portland Cement for binder material. It was called as “Reference concrete” and it was produced for making comparisons with the others. Besides reference concrete, 3 other kind of concrete with 9 different mix were produced by reducing the cement amount and adding Fly Ash, Lime Stone filler and Sand Stone filler instead respectively. While Fly Ash content mixes were replaced with cement as 20, 30, 40 % by weight, Lime Stone filler and Sand Stone filler content samples were produced with 24, 36, 48 % replacement ratios by weight. This changes, is sourced from different unit weights of each materials. Fly ash possesses $2,12 \text{ g/cm}^3$ unit weight, Lime Stone filler and Sand Stone filler have $2,71 \text{ g/cm}^3$ and $2,64 \text{ g/cm}^3$ respectively. Therefore, in order to achieve same replacement values by volume in the mix, replacement levels were increased 24, 36, 48 respectively for Lime Stone and Sand Stone added mixes.

Water/dust ratio, super-plasticizer amount and Viscosity regulator amounts are the same for all ten mix. Air content was assumed 1,8 % by volume. The aggregates content ratio by volume are % 30 Natural sand, % 30 Crashed Sand, % 40 Crashed Stone for all mixes. Binder content and Aggregate content of the mixes are showed below as Table 3.7 and Table 3.8.

Table 3.7: Fineness and Admixture Content of All Mixes

Mix Code	Cement (kg/m^3)	Fly Ash(kg/m^3)	Aggr. Filler (kg/m^3)	Type Of Filler	Air Cont. (%)	Superplast. (%)	Viscosity Reg. (%)	Water/Dust
R	500	-	-		1,8	1,2	0,1	0,4
F20	400	100	-		1,8	1,2	0,1	0,4
F30	350	150	-		1,8	1,2	0,1	0,4
F40	300	200	-		1,8	1,2	0,1	0,4
L24	400	-	120	Lime stone	1,8	1,2	0,1	0,4
L36	350	-	180	Lime stone	1,8	1,2	0,1	0,4
L48	300	-	240	Lime stone	1,8	1,2	0,1	0,4
S24	400	-	120	Sand stone	1,8	1,2	0,1	0,4
S36	350	-	180	Sand stone	1,8	1,2	0,1	0,4
S48	300	-	240	Sand stone	1,8	1,2	0,1	0,4

Table 3.8: Aggregate Content of All Mixes

Mix Code	Nat.Sand(kg/m ³)	Crash.Sand (kg/m ³)	Crash.Stone(kg/m ³)
R	488	502	672
F20	476	491	657
F30	471	485	649
F40	465	479	641
L24	472	486	651
L36	464	478	640
L48	456	470	629
S24	472	486	651
S36	464	478	640
S48	456	470	629

3.2.1 Concrete Production

Vertical axis concrete mixer, which is available in Istanbul Technical Universities Building Material Laboratory, was utilized for concrete manufacturing. Producing process is given below:

At first cement, aggregate and mineral admixtures were put and mixed at the cement mixer in dry conditions. Half of mix water added to mix slowly in order to prevent gathering and to provide a homogeneous mix. Super-plasticizer and Viscosity regulator was added to remain water and mixed together. All mixes were mixed 7 minutes. Finally concrete was moulded after made the fresh concrete tests.

3 cylinder with 100 mm X 200 mm dimension, 1 cylinder with 150 mm X 300 mm dimension, 3 prismatic 70 mm x 70 mm x 280 mm dimension, 2 prismatic 100 mm x 100 mm x 510 mm dimension and 1 cube 100 mm x 100 mm x 100 mm were manufactured for tests. After 24 hours moulding process, the samples were demoulded and moved to water pool with 20 °C for curing. The samples were cured in the water pool till 28 days old. And air cure was applied till 35 days old when the tests were started.

3.3. Test Methods

3.3.1 Fresh Concrete Experiments

There are several tests available in order to measure the fresh concrete properties of SCC. The most common and wide spread ones are mentioned below.

3.3.1.1 Slump -Flow Test

During more than ten years of the widespread use of SCC, the well known slump flow test method has been the primary base for technical development of concrete mixes, production technique and for quality assurance at building site as well as for various demonstration. This very simple method gives the total spread diameter after lifting the standard slump cone and indicates the filling ability of the concrete [67].

Application steps of the test are given below;

- Place the base-plate on a firm surface and check that it is in a horizontal position.
- Wet the surface of the base-plate and wipe off the moisture with a cloth.
- The conical mould is placed onto the central of the 200 mm diameter circle.
- Press the mould firmly down by standing on its foot-holds or fit the holding-down collar.
- Fill the conical mould with concrete using the scoop, without any tamping or other compaction, ending with a minimum of surplus material above top edge of the mould.
- Strike off any surplus concrete from the top off the cone and remove any spilled concrete from the base-plate.
- Lift the conical mould vertically in a single and smooth action within approximately 30 s of filling the mould.
- Allow the concrete to spread and once its movement has stopped, use the ruler to measure the largest diameter of the spread and record its value d_m to nearest 10 mm. Follow this by measuring the diameter of the spread in a direction perpendicular to the first one. Record its value as d_r (to nearest 10 mm).
- Carry out a visual check of the spread concrete. Note any indicators of potential segregation such as a zone of paste or mortar without coarse aggregate around the edge of spread concrete and any pile up of coarse aggregate in the centre.

If the difference between the values of d_r and d_m exceeds 50 mm the result of the test is rejected as unreliable. It means the test procedure should be repeated and if the difference between the diameters remains excessive, we consider either the slump-flow test in principle or equipment used as unsuitable for the concrete tested. After the calculation of the arithmetic mean value of d_r and d_m that is recorded at the resulting slump-flow spread SF (mm) to the nearest 10 mm [54].

Most SCCs require 650 > mm flowing value in order to achieve an adequate filling ability.

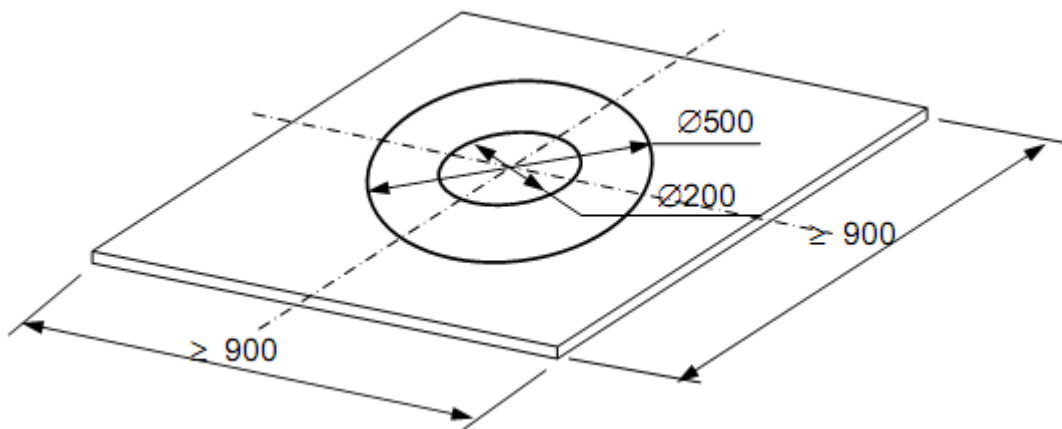


Figure 3.2: Slump-Flow Test Table [68].

3.3.1.2 V-Funnel Test

This method is also said to determine the filling ability of SCC by specially detecting the viscosity of the concrete. It was originally developed in Japan and has often been used for concrete mix design in laboratory and at concrete plant, and for quality control on building site [67].

Application steps of the test are given below;

- Set up the V-funnel apparatus on a firm ground.
- Place the receiving container below the V-funnel.
- Dampen the inside of the apparatus, ensuring that any surplus water drains out of the funnel.
- Close the gate and fill the apparatus with concrete without any compaction or assistance. Immediately strike off surplus concrete with the straight edge. Prepare for timing.

- Wait approximately 10 s from the completion of filling of apparatus. Quickly open the gate and simultaneously start timing the flow.
- Look down inside the funnel and stop timing once daylight shows through the orifice.
- Record the V-funnel flow time t_v to nearest 0,1s.

As a consequence of these steps a direct test result (V-funnel flow time t_v) is obtained. So there is no need for further processing [54].

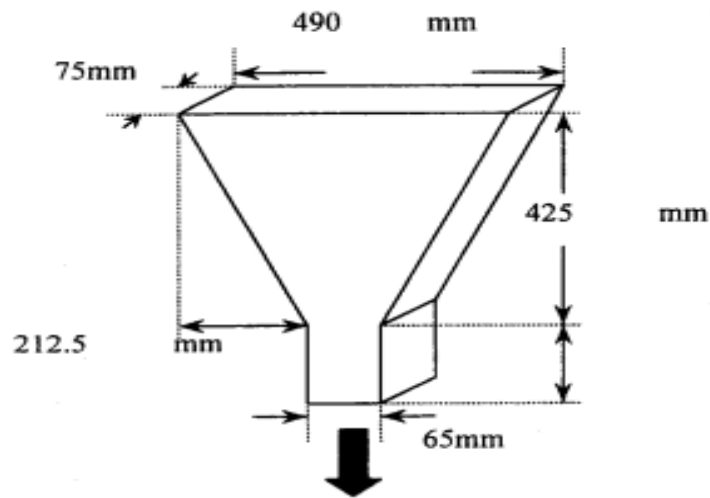


Figure 3.3: V Funnel [68].

3.3.1.3. L-Box Test

The L-Box test consists of an L shaped container divided into a vertical and horizontal section. A sliding door separates the vertical and horizontal sections. An obstacle of three bar can be positioned in the horizontal section just opposite of the sliding door. The vertical section of the container is filled with concrete to flow through the obstacle into the horizontal section. The height of concrete left in the vertical section h_1 and at the end of the horizontal section h_2 is measured. The ratio of h_2/h_1 is calculated [67].

Application steps of the test are given below;

- Place the L-Box apparatus on firm level ground. Use the spirit level to check that its base is in horizontal position and adjust it, if required.
- Dampen the inside of L-Box, removing any excess moisture. Close the column gate.

- Fill the column with concrete. Take care not to shake the apparatus and avoid any compaction or agitation of the concrete in it.
- Immediately strike off any surplus concrete from the top of the column using the straight edge and wait for one minute.
- Open the gate in one smooth movement. Ensure the apparatus is not jolted or shaken during the opening.
- Once the flow has stopped, measure the vertical distance between the surface of the concrete sample remaining inside and the top edge of column at three points equally spaced across the wider side of the column. Record the measurements as H_{1a} , H_{1b} , H_{1c} to the nearest millimeter.
- Measure the vertical distance between the surface of concrete sample at the far end of trough at three points equally spaced across the width of its top inside edge. Record the measurements as H_{2a} , H_{2b} , H_{2c} to the nearest millimeter.
- Check the concrete visually and record any indications of segregation or bleeding.
- It's optional to start timing when the separating door begins to be lifted and end the timing when the moving front of the concrete reaches either one of the marks along the length of the trough or its end. Record the times t_{L20} , t_{L40} , or t_L to the nearest 0,1 s.

The basic result of the L-Box test is the passing ratio $PR=H_2/H_1$, calculated the nearest 0,05. The PR is the ratio between the height of the concrete surface remaining within the vertical, column of the apparatus H_1 , obtained from,

$$H_1 = \frac{H_{1a} + H_{1b} + H_{1c}}{3} \quad (3.1)$$

And the height H_2 , of the concrete surface at the far end of trough, after its passage through the reinforcing bars. H_2 is obtained from,

$$H_2 = \frac{H_{2a} + H_{2b} + H_{2c}}{3} \quad (3.2)$$

The horizontal trough of the L-box may have two additional marks at 200 mm and 400 mm from the sliding door. These permit an assessment of the speed of flow of the fresh concrete. The time which elapses between the opening of the sliding door and the advancing ‘front’ of the concrete in the trough, reaching each of the marks, produces two additional result: times t_{L20} and t_{L40} (in seconds) [54].

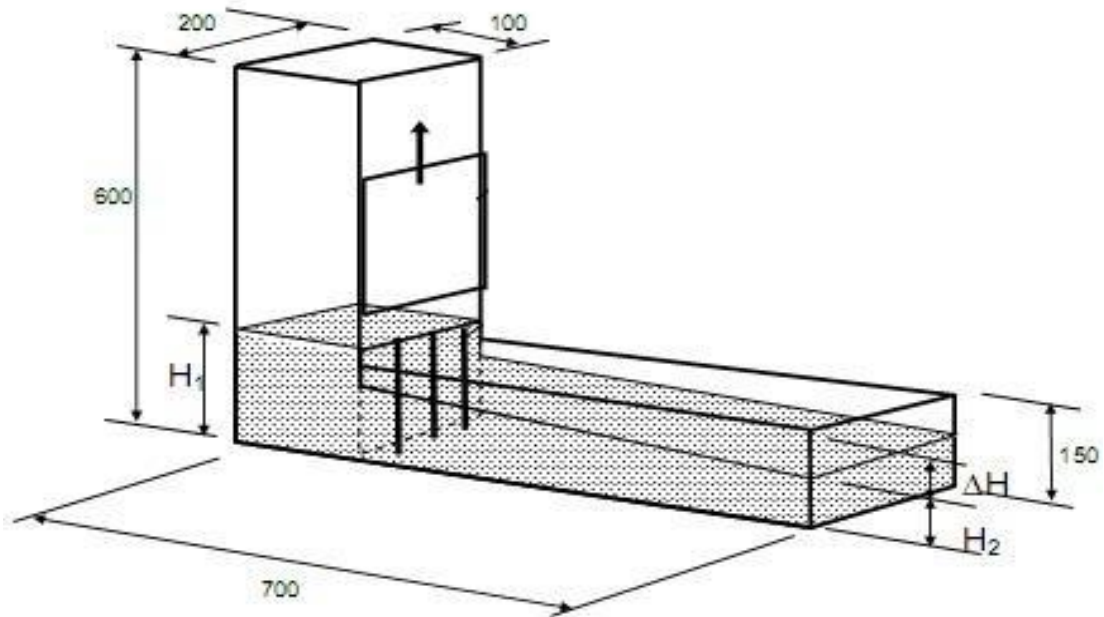


Figure 3.4: L Box

3.3.1.4. U-Box Test

The U-box test consists of a U-shaped container divided into two compartments. At the bottom of the dividing section is placed one of three obstacles through which the concrete must flow. The obstacles are classified as rank one, two or three. Rank one is the most restrictive and the rank three is the least restrictive. One side of the container is filled with concrete and a door is immediately raised allowing the concrete to flow through the obstacles. The rising height of the concrete in the initially empty side is measured [67].

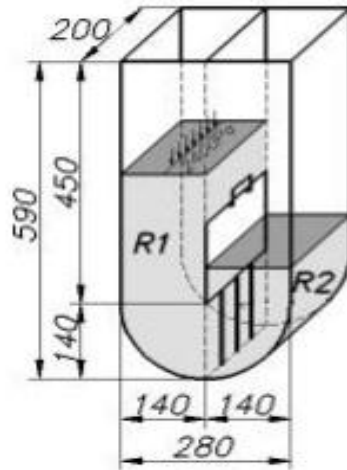


Figure 3.5: U Box [69].

3.3.2 Hardened Concrete Experiments

3.3.2.1 Ultrasonic Pulse Velocity Test (UPV)

The method consists of measuring the time of travel of an ultrasonic pulse passing through the concrete being tested. Comparatively higher velocity is obtained when concrete quality is good in terms of density, uniformity, homogeneity etc.

- **Preparing for use:** Before switching on the 'V' meter, the transducers should be connected to the sockets marked "TRAN" and 'REC'. The 'V' meter may be operated with either:
 - a) the internal battery,
 - b) an external battery or
 - c) the A.C line.
- **Set reference:** A reference bar is provided to check the instrument zero. The pulse time for the bar is engraved on it. Apply a smear of grease to the transducer faces before placing it on the opposite ends of the bar. Adjust the 'SET REF' control until the reference bar transit time is obtained on the instrument read-out.
- **Range selection:** For maximum accuracy, it is recommended that the 0.1 microsecond range be selected for path length up to 400 mm.

- **Pulse velocity:** Having determined the most suitable test points on the material to be tested, make careful measurement of the path length 'L'. Apply couplant to the surfaces of the transducers and press it hard onto the surface of the material. Do not move the transducers while a reading is being taken, as this can generate noise signals and errors in measurements. Continue holding the transducers onto the surface of the material until a consistent reading appears on the display, which is the time in microsecond for the ultrasonic pulse to travel the distance 'L'. The mean value of the display readings should be taken when the units digit hunts between two values.

$$\text{Pulse velocity} = (\text{Path length} / \text{Travel time}) \quad (3.3)$$

- **Separation of transducer leads:** It is advisable to prevent the two transducer leads from coming into close contact with each other when the transit time measurements are being taken. If this is not done, the receiver lead might pick-up unwanted signals from the transmitter lead and this would result in an incorrect display of the transit time [70].



Figure 3.6: Ultrasonic Pulse Velocity Device

3.3.2.2 Mass Loss Test

Weight changing by time tests were applied periodically to the 70x70x280 mm prismatic samples, consist of Reference concrete without filler, %20,30,40(by weight) Fly Ash concrete, % 24,36,48(By weight) Lime Stone Filler concrete, % 24,36,48(By weight) Sand Stone Filler concrete which were exposed to the sulfate solution.

Application steps of the test is given below,

- Dry weight of samples are measured before subjected to sulfate solution.
- The mass loss values were investigated by making a comparison between the first immersed weights (initial weight) of samples and following month's weights.
- When the samples are taken out from the sulfate solution, all of them are kept 24 hours in the air so that the samples could dry before the measurement.
- This process is continued every month periodically till the end of the test. Thus the changing by the time on the sample weight are determined.
- Finally data's are proportioned to initial weight, mass loss can be observed as a percentage.

3.3.2.3 Capillarity Test

The capillarity provides to observe the water penetration value of different mixes concrete samples and gives us a facility for comparing each of them.

Capillarity test is applied on the concrete samples usually when they are 40 days old after the water and air cure process. At first the dry weight of samples is measured. Then the samples are put in the low level water filled pot as only one surface of the samples are touched to water and the water penetration quantity of samples are measured in every 1th, 4th, 9th, 16th, 25th, 36th, 49th, 64th, 81th minutes with an electronic sensitive weighing device. Finally the capillarity coefficients are calculated by using the samples surface area, which exposed to water, water penetration level and time with this formula;

$$q = \sqrt{k \cdot t} \quad m = \left(\frac{q}{\sqrt{t}} \right) \quad (3.4)$$

k: Capillarity Coefficient (cm²/second)

q: Water amount which is absorbed at the unit area (g/cm²)

t: time (sec)

m: slope of line

3.3.2.4 Water Absorption Test

This test is applied to concrete samples in order to determine the amount of water absorption value by weight. Environment, cure conditions and also the mix design (material type and quantity) of specimens effect in the water absorption.

- The samples are dried in an oven under 65-75 ° C during 3 days.
- The samples are cooled under the room temperature during 24 hours.
- Dry weight of concrete are obtained (M_1).
- Dried samples are immersed completely to the 27 ± 2 ° C temperature clean water for 72 hours.
- At last the specimens are removed from the water and wipe out of the surface with a fabric and measured the ultimate weight (M_2).

The percentage of water absorption is determined with the formula given below:

$$W(\%) = \frac{M_2 - M_1}{M_1} \times 100 \quad (3.5)$$

3.3.2.5 Permeability Test

Permeability test is applied to concrete samples in order to reveal the water depth permeability of each mix under the pressure. At first the samples are saved at the water pool for wet curing process, then they are extracted out from the pool and during the 15 days they are kept in the air cure at the laboratory. After the cure process the samples are tested with permeability device 72 hours along subjected to 5 KB pressure. At the end of 72 hours the samples are taken out from the device and in order to understand how much depth water penetrate in the concrete, each sample is broken two pieces with press machine and measured the water penetration level as mm.

The main purpose why we are doing this test is summarized at the Şimşek and Akıncıtürk's study. According to their study, prevention of the reinforcement steel in the concrete is very important and thus load carrying capability of building doesn't damage with corrosion. Furthermore, reducing the water penetration depth increases

the concrete durability against to the potential crack effects, which can compose by the time inside of concrete [71].

3.3.2.6 Compressive Strength Test

Compressive strength of the samples was founded with using the ELE Autotest 3000 device and with 4KN/s loading velocity in Istanbul Technical Universities Building Material Laboratory. Compressive Strength test was applied to all samples at the 35th days after manufacturing. Grinding process was also applied to all samples before loading in order to achieve homogeneous distribution but not as much as conventional concrete because of SCC's smooth surface.

The samples are located to press at the vertical position. Then loading velocity is set on the press. When the test starts the press is begun to load vertically and the samples become to make deformations by the time. The load, which the sample is broken, saved. Breaking load over to sample's surface area gives the compressive strength value.

3.3.2.7 Modulus of Elasticity Test

The % 33 part of Strain-Displacement curve is assumed linear. This linear curve's slope gives the modulus of elasticity. Therefore, if the sample is loaded up to % 33 of predicted maximum load, Modulus of elasticity can be calculated.

The sample is located to press vertically. Loading velocity is set and the test is started. The displacement value is read from the press's screen and saved in every 20 KN up to predicted load (%33 of maximum load). The loading is completed at the predicted load. The recorded data over to sample's surface area gives strain value. Then strain and displacement values are settled to a Strain-Unit Deformation graphic and a curve is determined with using the points. Slope of this curve is calculated. Thus, it is reached to modulus of elasticity. The test is made at the Istanbul Technical Universities Building Material Laboratory with ELE Autotest 3000 device and 2 KN/s loading velocity.

3.3.2.8 Three Point Bending Test

The Bending strength and the toughness value of the sample can be obtained with this test. The prismatic samples are located on the test machine's braces with equally divided distance from the middle point of it. Then loading is applied from the top

side at the middle of sample. Before starting to loading an equipment, can be set on the machine in order to measure the displacement. Otherwise displacement can be measured directly from the machine's tamper. Then the loading velocity is set on and the test is begun. At first load increases by the time and when the sample is reached to maximum load carrying capacity, the load is begun to decrease. Test is stopped while the load is approached to near zero. The bending strength value is calculated with using the formula which is given below (3.6).

$$\sigma = \frac{M}{W} = \frac{P \times l}{\frac{b \times h^3}{6}} = \frac{6 \times P \times l}{b \times h^3} \quad (3.6)$$

σ :Bending Strength

l :Distance between braces

b :The width of the sample and,

h :The height of the sample .

Furthermore the toughness value of the sample is obtained from the area, which is under Load-Deformation curve exist. This area calculated and divided to sample's surface area. Besides to this value, the work, which is composed by the weight of sample, is calculated. The work of samples weight is equal to weight of sample multiply with total deformation value. Toughness is to total of both.

4. TEST RESULTS AND EVALUATIONS

4.1. Fresh Concrete Tests

4.1.1. Slump-Flow Test Results and Evaluations

Figure 4.1 shows flowing values of the mixtures and Table 4.1.a shows the limit values of Slump-Flow test for SCC according to EFNARC. As seen in this table, all the mixtures have a slump flow of more than 65 cm. It means all samples provide the first threshold which is known as over than 70 cm for Self Compacting Concrete. Reference mixture's, which is containing only Portland cement, slump-flow value is 73 cm. While Portland cement is replaced by fly ash, the flow goes to 70 cm for the replacement ratios of 20% and 30% but the flow is 73 cm for the fly ash content of 40%. Replacement of Portland cement with limestone filler increased the slump flow except for the replacement ratio of 24%. Besides using sandstone filler reduced the slump flow value of concrete. The smaller particle size of the sandstone filler may be the reason behind this reduction.

If the maximum flow values are evaluated as the mineral admixtures, it's obviously seen that F 40 ensures the greatest flow value for adding Fly Ash. Furthermore, when L 36 reach the highest flow value for adding Lime Stone Filler, S 24 obtains the biggest flow value for adding Sand Stone Filler instead of cement.

According to results the flow test values for all specimens vary between 70-74 cm band. Except for L 36, all of them are under the 75 cm limit which is known as the dangerous value for segregation. It can be said the 2nd threshold on the Slump-Flow test for SCC. By the way, there is no segregation was observed on L 36 at the end of the other fresh concrete tests.

Table 4.1a,b: Slump Flow and T_{500} time limit values according to EFNARC [73].

Class	Flow(cm)	Limit Values	
		Min.	Max
SF1	55-65	2	5
SF2	66-75	Segregation Risk	High Viscosity
SF3	76-85		

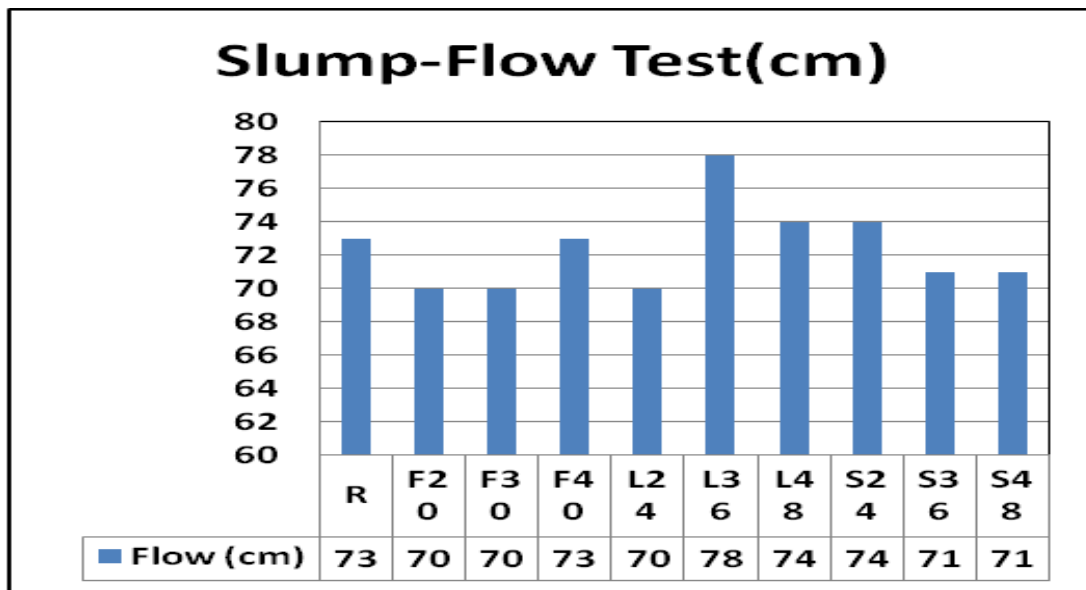


Figure 4.1: Slump-Flow tests results

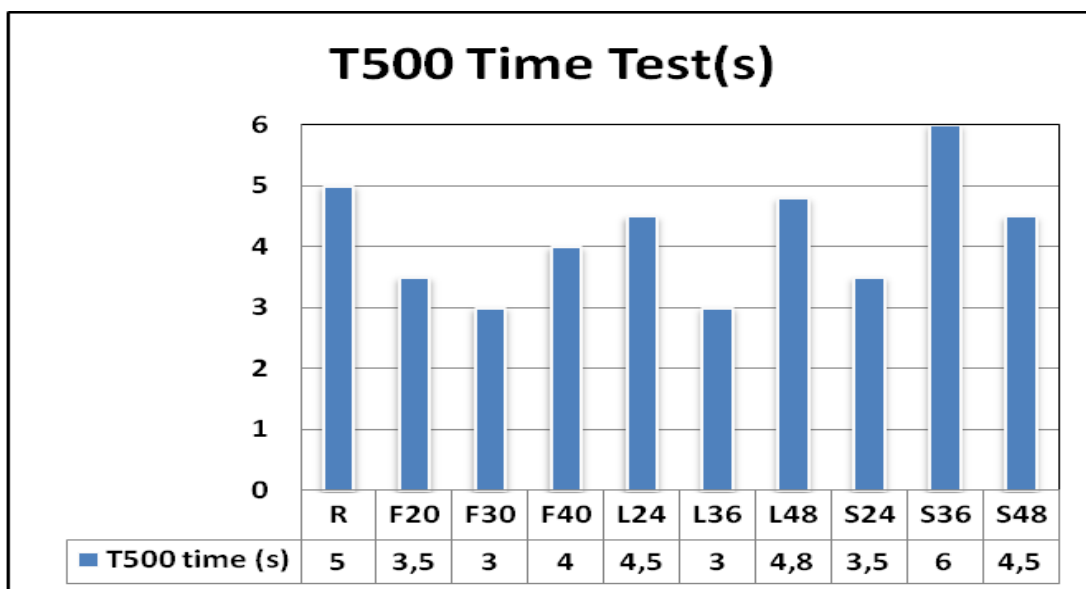


Figure 4.2: T₅₀₀ time tests results

4.1.2. T₅₀₀ Time Test Results and Evaluations

The times for concrete to spread to a diameter of 500 mm (T₅₀₀) are also shown in Figure 4.2. And Table 4.1.b shows the limit values of T₅₀₀ time test for SCC according to EFNARC. T₅₀₀ time test can be applied on the fresh concrete with slump-flow test. It represents the flowing time of SCC. Flowing speed can be tested with this test and it can give us some ideas in order to figure out and compare the viscosity of samples. However; it is impossible to find viscosity values directly with this test. The T₅₀₀ value is 5.0 seconds for the reference mixture. And it is accepted

the top limit for this test. As seen in the table T_{500} time values of all samples decline with putting into the mineral admixtures except for S 36. Although; there is no linear relation between increasing and decreasing ratio by adding mineral admixtures, it is clearly seen that minerals adding with low amounts contribute to increase the flowing speed. Except for L 36 and S 36, for adding minerals with low amounts provides fast flow times. Except for S36 all mixes are between 2-5 s values which is the highest and lowest limit for T_{500} test.

4.1.3. V Funnel Test Results and Evaluations

V-funnel test points out the flow-ability, filling and passing ability of concrete. In this test, when minimum time value is expected as 8 s, maximum time value is expected as 12 s for SCC. Table 4.2 a.b shows the limit values of V Funnel test for SCC according to EFNARC. According to this information as seen in the Figure 4.3 Fly Ash adding reduces to V funnel passing time up to F 40 and then its again increasing but still to 9,9 s for F 40. However even F 40 is lower than Reference concrete's flowing time. On the other hand, test results with adding Lime Stone filler are complicated and changed drastically. While the V funnel time decrease to 9,8 s for L 24, it shows 6,6 s for L 24 and again increase up to 12 s suddenly for L 48. Besides, with using Sand Stone filler increase the flowing time initially for S 24 and S 36 but then there is a reduction was observed on the flowing time up to 9,9 s for S 48. If the V Funnel times are compared with the T_{500} times, it is seen that both flowing time values are lower than Reference concrete for Lime Stone filler. Furthermore, when the S 36's time values increase over than Reference concrete for both test, they decrease and go near to Reference concrete For S 48 in both tests. According to V funnel Test results F 30 and L 36 seem in the segregation risk because of under 8 s time values. On the other hand, time values of S 36 and L 48 are so close to top limit for high viscosity risk. So before the last decision about these mixes other fresh concrete test results should be investigated carefully. Finally, it can be said that low amount of mineral addition, show better performance than Reference concrete.

Table 4.2a,b: V Funnel Test limit values according to EFNARC [73].

Class	Flow Time (s)	Limit Values	
		Min.	Max
VF1	≤ 8	6-8	12
VF2	9-25	Seggragation Risk	High Viscosity

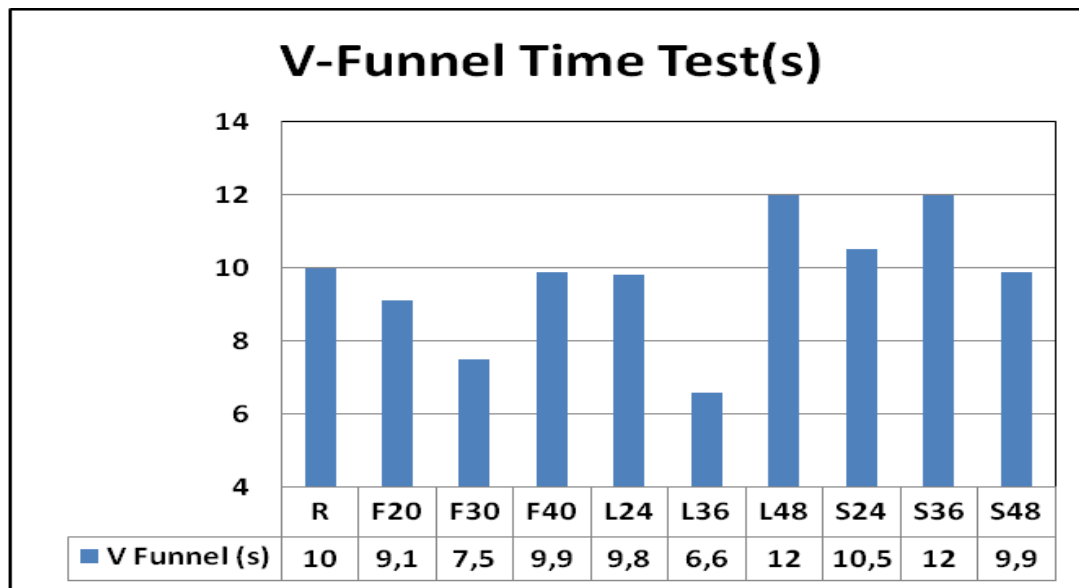


Figure 4.3: V Funnel test results

4.1.4. L Box Test Results and Evaluations

The L-box is one of the best ways in order to measure passing ability for SCC. The values which are given below at the Figure 4.4 and Table 4.3.a.b show the limit values of L Box test for SCC according to EFNARC. The H_2/H_1 value should not be under 0.8 for SCC. According to this rule, all mixes except for F 30 seem suitable for L Box test. As seen in Table 3.12, passing ability increases when the sandstone content increases. And it is seen from the Table 3.12 that adding Fly Ash doesn't change the passing ability value if it is compared with Reference concrete except for F 30. Additionally, Lime Stone Filler improves the passing ability. When L 24 and L 48 have better values than Reference concrete, L 36 gives the same value with Reference concrete. Generally, while the mixes, which include limestone or sandstone filler, show good performance than the reference mixture. On the other hand, there is no big influence with adding Fly Ash to concrete on the V Funnel values except for F 30.

Table 4.3a,b: L Box Test limit values according to EFNARC [73].

Limit Values		Class	Passing Rate(H_2/H_1)
Min.	Max	PA1	$\geq 0,80$ (2 bar)
0,8	1	PA2	$\geq 0,80$ 3 bar)

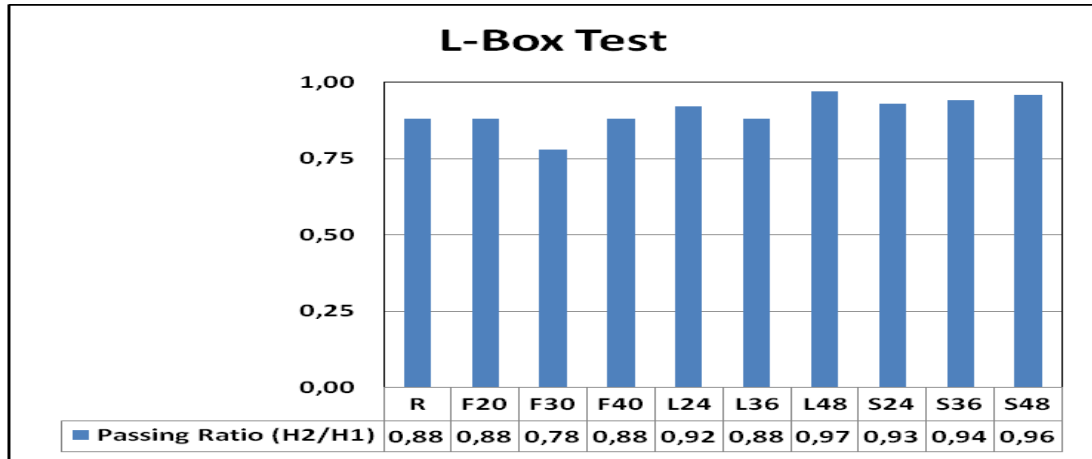


Figure 4.4: L Box test results

4.1.5. U Box Test Results and Evaluations

The U-box test is another way in order to measure the filling capacity and flowing ability of SCC. The U-Box test results are given below at the Figure 4.5. And Table 4.4 shows the limit values of U-Box test for SCC according to EFNARC. As seen from the Table when the U-Box filling height results pass the 30 cm, compaction problems might be observed. Except for S 48, all filling height values are closed each other and there is no significant compaction problems have seen for them. S 48 mix should be regarded related with compactability.

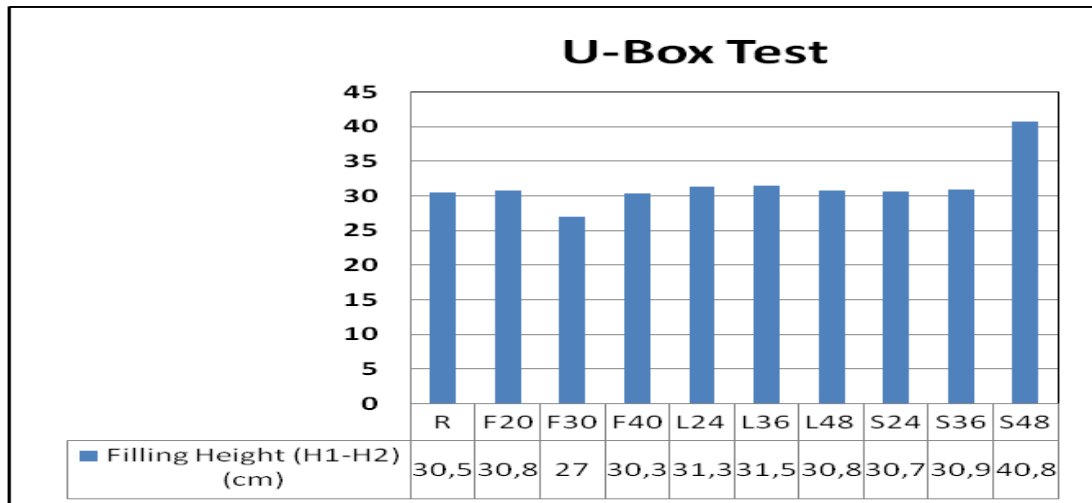


Figure 4.5: U Box test results

Table 4.4: UBox Test limit values according to EFNARC [73].

Class	U-Box
H1-H2 (cm)	>30

4.2 Hardened Concrete Tests

4.2.1. Compressive Strength Test Results and Evaluations

Compressive Strength test results are given below at both Table 4.5 and Figure 4.6. When the test results are investigated, it's obviously seen that, mineral addition to concrete reduce the compressive strength for all mixes. The most drastic reduction is observed at the Sand Stone filler mixes. When the reference concrete possess the 89,69 MPa compressive strength, it reduces to 65.56, 58.17 and 49.68 for S 24, S 36, S 48 respectively. The minimum reduction composed with Fly Ash using, when it was compared with the other fillers except for L 24. Fly Ash mixes perform 75.37, 73, 70.23 MPa compressive strength for F 20, F 30, F 40 respectively. Furthermore Lime Stone filler mixes give strange results. While L 24 reaches to 77 Mpa compressive strength, which is the highest value recorded between the mineral added mixes, L 36 and L 48's compressive strength go down to 69.43, 68.07 respectively.

As a result it can be said that, F 20 and L 24 mixes show good performance. The reduction, which was composed with mineral addition, was already expected. However; Sand Stone filler mix results are surprised. Even though, The Sand Stone filler, used in this study, was essentially finer than Lime Stone fillers, test result of Sand Stone filler is worse than Lime Stone filler. Finer particles should have filled the voids in concrete and reduced the porosity so Sand Stone Filler mixes should have given better performance. These unexpected results could be sourced from the mineralogical composition of these fillers. Besides, Fly Ash has not only filler effect but also pozzolonic effect and pozzolonic reaction is completed not in a short time. Therefore If the Fly Ash sample's compressive strength is measured at the later ages, it might be possible to obtain higher results.

And also it should be determined that the compressive strength values of all samples are still so high if it is compared with conventional concrete.

Table 4.5: Compressive Strength test results

Mix Code	Compressive Strength (Mpa)
R	89,69
F20	75,37
F30	73
F40	70,23
L24	77
L36	69,43
L48	68,07
S24	65,56
S36	58,17
S48	49,68

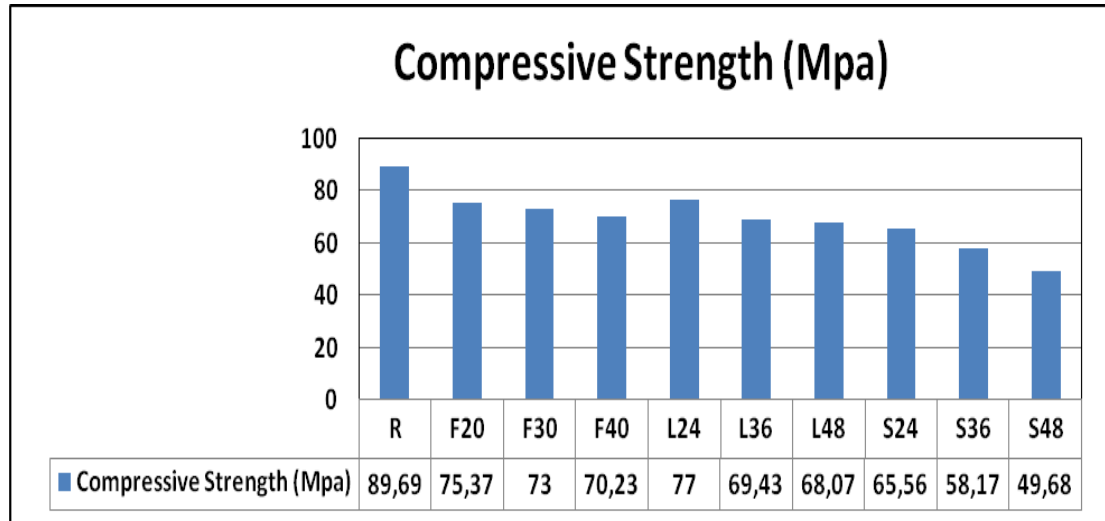


Figure 4.6: Compressive Strength test results

4.2.2. Modulus of Elasticity Test Results And Evaluations

Elasticity Modulus of the concretes, are given in Table 4.6. As shown in table, Modulus of elasticity values, are decreasing with the Fly Ash addition except for F 40 mix. It might be sourced from the age. As mentioned at the evaluation of Compressive Strength test result Fly ash has pozzolonic effect so modulus of elasticity values may change at the later ages. While Modulus of Elasticity values of samples with Fly Ash are 35700 and 34100 Mpa for F 20 and F 30 respectively ,it increased up to 38000 MPa for F 40 and passed the Reference concrete. Furthermore with Lime Stone Addition Modulus of Elasticity increase up to 40300 MPa for L 24 but it is going down for L 36 and L 48 and reaches to 36900, 38500 Mpa respectively. The lowest modulus of Elasticity values occurred with Sand Stone filler

addition. For instance S 24 mix Modulus of Elasticity value is 36800 Mpa and it reaches to 36700 and 32000 Mpa for S 36 and S 48 respectively. Actually it can be said that Modulus of Elasticity values for all mixes are closed each other. There are no big differences observed with Mineral Admixtures addition on the concrete.

Table 4.6: Modulus Of Elasticity test results

Mix Code	Modulus Of Elasticity (Mpa)
R	36900
F20	35700
F30	34100
F40	38000
L24	40300
L36	36900
L48	38500
S24	36800
S36	36700
S48	32000

4.2.3. Water Absorption Test Results and Evaluations

Water absorption test was applied to the 150x300 mm cylinders samples, 40 days later than they produced. During the first 28 days the samples were saved in the water pools, then, they were extracted in order to be exposed to air cure in the laboratory till the test time. After the dry weights of the samples were measured, were put in the water pool again 72 hours along. Finally, 72 hours later, the samples were taken out and dried the surfaces with a towel and then measured the water absorbed weight with the sensitive weighing device. Consequently, the results, are given below at the Table 4.7, determined both dry and water absorbed situation of each sample.

Water Absorption Test results are given below both as a table and as a graphic at Table 4.7 and Figure 4.7 respectively. As seen from both of them Mineral Admixture addition increase the water absorption except for F 20. While F 20's water absorption is 0,471 %, F 30 and F 40 give 0,845, 0,855 respectively. Lime Stone and Sand Stone filler addition influence the water absorption negatively than Fly Ash. L

24, L 36 and L 48 have % 0,929, 1,079, 0,983 water absorption values, respectively. Furthermore, Sand Stone filler has the worst values for water absorption.

As a consequence it could be said that water absorption amount of all samples are not so high when it is compared the conventional concrete with high W/C ratio. It is sourced from the low porosity properties of SCC. One of the main purpose of manufacturing SCC reduce the air content of concrete with chemical admixtures and low water/cement ratio so it reduces pore content of concrete's micro structure.

Table 4.7: Water Absorption test results

Mix Code	Dry Weight (gr)	Wet Weight (gr)	Water Absorption By Weight (%)
Reference	3623,4	3644,5	0,582
F 20	3500,4	3516,9	0,471
F 30	3444,3	3473,4	0,845
F 40	3438,2	3467,6	0,855
L 24	3593,4	3626,8	0,929
L 36	3560,1	3598,5	1,079
L 48	3560,5	3595,5	0,983
S 24	3552,8	3589,6	1,036
S 36	3524,2	3564,2	1,135
S 48	3473,9	3551,6	2,237

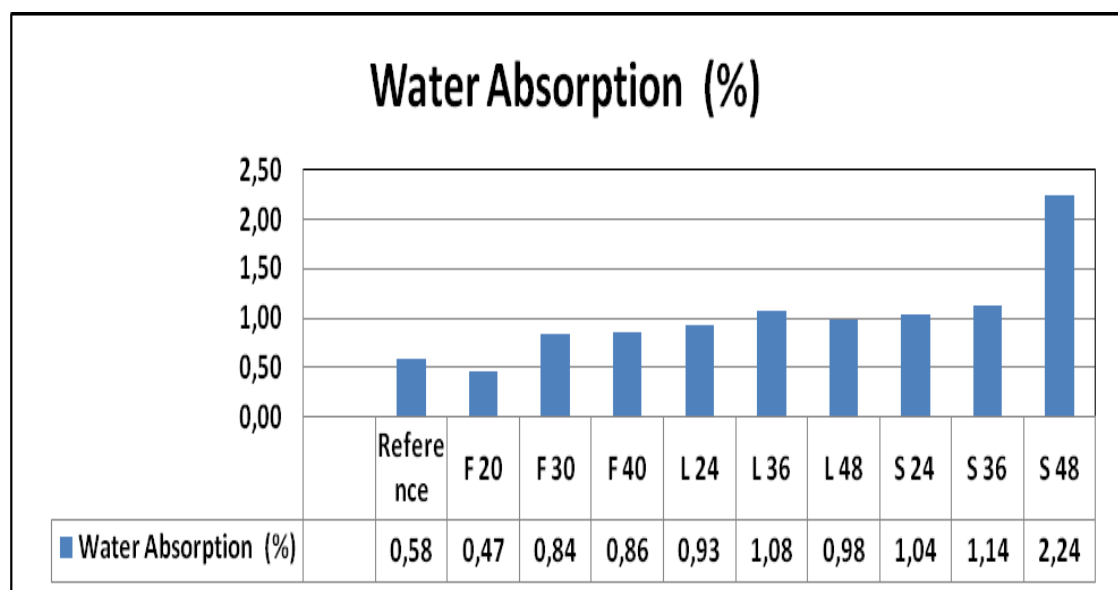


Figure 4.7: Water Absorption test results

4.2.4. Capillarity Test Results And Evaluations

Weight changing sourced from water absorption was measured in different time periods with this test. The main purpose of this test is, figure out of the microscopic pore structure of concrete. In a parallel with water absorption by weight test results, the capillary absorption of concrete, increase with the filler amount increase. As mentioned before, where the capillary test method explanation, Capillarity coefficient, increase with capillary water absorption. On the other hand Fly ash, perform better than fillers and reference concrete. As a result it can be said that Fillers are not so successful for filling the microscopic pores of concretes or in the other word the pores may increase with Filler addition to concrete. Fly ash is better about this matter. However the mineralogical properties of both Fly Ash and Fillers, which was used in this study, could affect the test results. Also, all results are still low compared to normal concretes having high water/cement ratios.

4.2.5. Permeability Test Results and Evaluations

Permeability test is made in order to reveal penetration level of mixes. Penetration is one of the most important threshold, which is expected, for reaching high durability on concrete. Permeability test results are shown below both Table 4.8 and Figure 4.8. As seen in the table water penetration values with pressure reduce with Fly Ash and Fillers amount increase except for F 30. However it couldn't be overlooked that the initial values, which composed with low amount Minerals addition, are higher than Reference concrete. For instance, When penetration level is 13.63 mm for reference concrete, it goes up to 15.65, 14.10, 31.80 mm with Mineral Admixture addition for F 20, L 24 and S 24 respectively. Furthermore, If all results evaluated together, it is clearly seen that, maximum penetration levels are made up with using Sand Stone filler. As a result, It could be said for impermeability test that, when usage of Sand Stone filler replacement increase the penetration level of concrete, Fly Ash and Lime Stone filler replacement doesn't make a significant influence.

Table 4.8: Permeability tests results.

Mix Code	Average Amount Of Impermeability (mm)
Reference	13,63
F 20	15,65
F 30	26,90
F 40	6,34
L 24	14,10
L 36	9,73
L 48	7,48
S 24	31,80
S 36	21,85
S 48	19,15

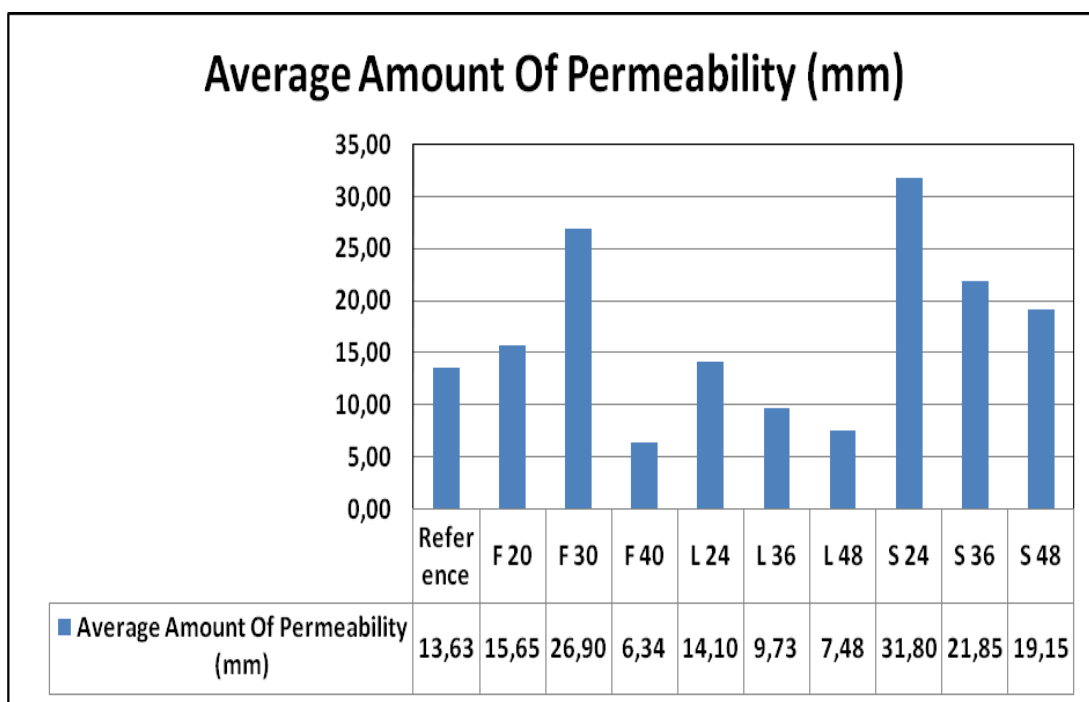


Figure 4.8: Permeability test results.



Figure 4.9: One sample which was applied on Impermeability test.

4.2.6. Sulfate Attack Test Results and Evaluations

4.2.6.1 Ultrasonic Pulse Velocity Test Results and Evaluations for SCC

Ultrasonic Pulse Velocity test was applied to all samples, which were in the Sulfate solution, once in every month during 9 months in order to figure out the durability changing of mixes against to Sulfate attack by the time. High Ultrasonic pulse velocity values represent good density and homogeneity. Test results are given below both a table and graphics. When the results investigated it has been seen that, almost all mixes act in a harmony each other by the time. However; as a general tendency Ultrasonic Pulse Velocity increased and reached a pick point then a drastic reduction observed but it was a not long time and Ultrasonic Pulse Velocity curve went up again. As seen in the Table 4.9 during first 4 months ultrasonic Pulse Velocity always increase and its understandable because of hydration reasons. When the samples waited in Sulfate solution hydration process could continue and samples could swell, So the Ultrasonic Pulse Velocity increase can depend on this process. After the 4th month a significant reduction was observed for all mixes, this reduction can be related with sulfate influence in the concretes microstructure. The most important reduction is observed F 40 and all Sand Stone Filler mixes. After the reduction process began it could be expected that the reduction period would continue slowly by the time. However, all specimens would tend to increase after fifth month and it was a strange result. It is impossible establish a direct relation between Water absorption tests and Ultrasonic Pulse Velocity test but it can be said that, Comparatively Sand Stone Filler replacement concretes compose the highest

pore structure. Therefore the biggest effect under sulfate attack may expect in these specimens. Furthermore there is not a significant surface abrasion observed on the as expected. As a result in addition to the strong mechanical properties, low Water-Cement ratio and more homogeneity, compared with conventional concrete, SCC also ensure more durable structure against to sulfate attack. If a stronger sulfate solution is prepared and the experiments are continued longer period more deterioration can be seen both surface and micro structure of SCC.

Table 4.9: Ultrasonic Pulse Velocity test results

Mix Code	1th Month	2th Month	3th Month	4th Month	5th Month	6th Month	7th Month	8th Month
Reference	4,21%	4,51%	5,32%	7,58%	5,76%	6,97%	9,84%	10,45%
F 20	2,90%	3,43%	4,21%	6,05%	5,00%	5,73%	7,88%	9,09%
F 30	3,38%	3,91%	4,39%	6,10%	5,49%	5,98%	7,81%	8,86%
F 40	2,64%	3,11%	4,32%	6,90%	3,95%	6,94%	9,49%	9,56%
L 24	4,65%	4,65%	5,20%	7,30%	6,12%	6,31%	9,40%	10,50%
L 36	4,31%	5,12%	5,72%	7,91%	5,05%	6,86%	10,09%	9,80%
L 48	4,69%	4,46%	5,52%	7,69%	6,06%	7,39%	9,86%	10,30%
S 24	4,32%	4,55%	5,83%	7,54%	4,91%	7,20%	9,26%	11,32%
S 36	4,15%	4,38%	4,50%	7,04%	4,05%	5,03%	9,59%	9,50%
S 48	3,35%	3,68%	4,61%	6,68%	3,68%	5,91%	8,76%	10,53%

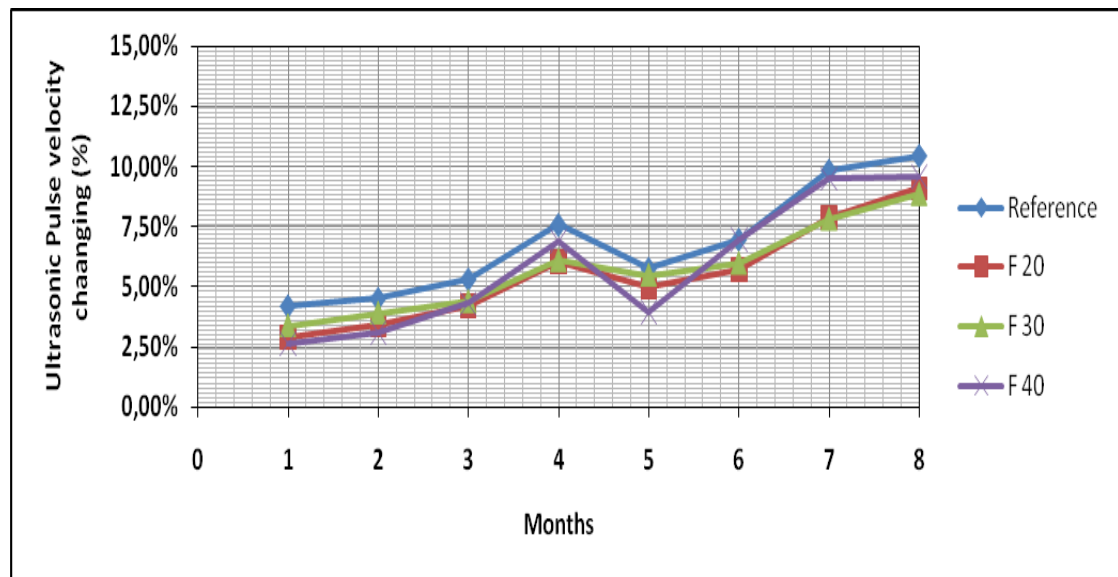


Figure 4.10: Ultrasonic Pulse Velocity changing between Reference and Fly Ash concretes under Sulfate Attack

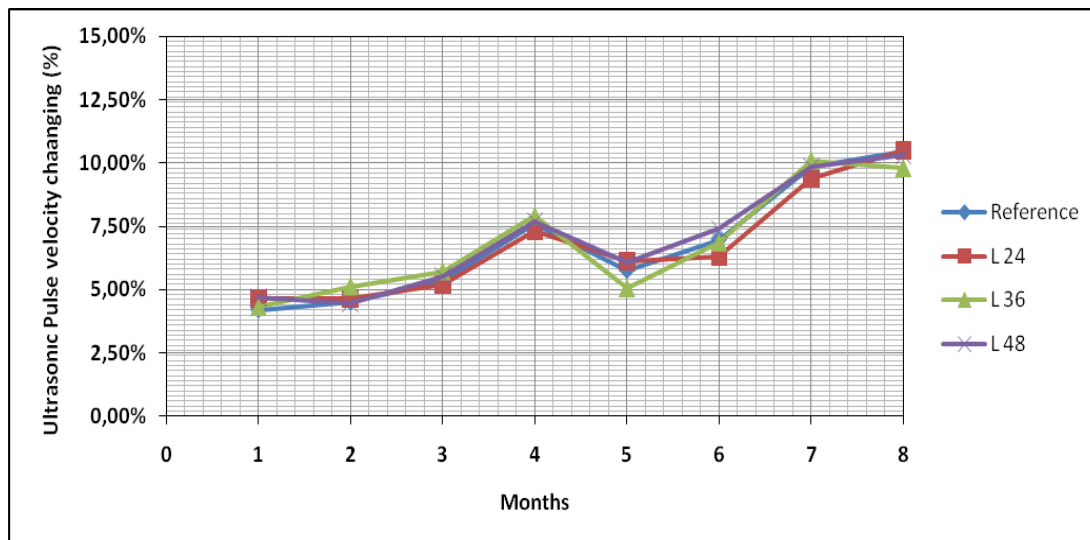


Figure 4.11: Ultrasonic Pulse Velocity changing between Reference and Lime Stone filler concretes under Sulfate Attack.

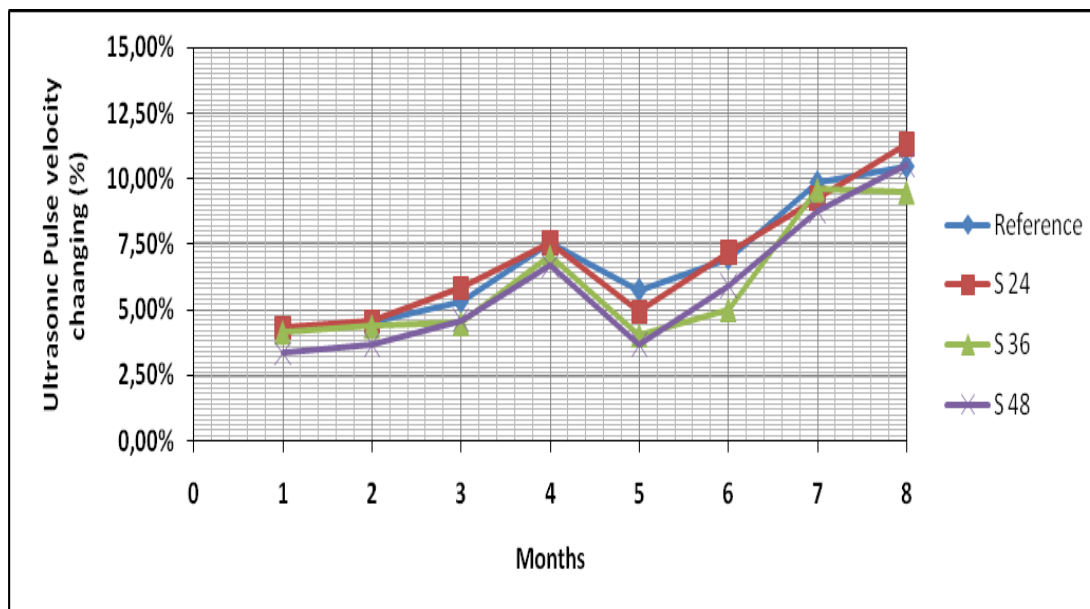


Figure 4.12: Ultrasonic Pulse Velocity changing between Reference and Sand Stone filler concretes under Sulfate Attack.

4.2.6.2 Mass Loss Test Results And Evaluations For SCC

Mass Loss values has read and recorded for all SCC samples, which has subjected to Mg Sulfate solution, one time in a month periodically during 9 months with a 0,1g sensibility weigh device. Before the weighing measurement all samples have taken out from the pool and dried 24 hours. Mass Loss changes, has calculated by percentage as the initial mass values. However, the first dry weights of samples, which are measured after one week air cure process, is not accepted as initial mass of specimens. Initial mass is considered as the first saved data which is measured at the

end of the Sulfate solution process. As shown in the both Tables and Graphics Weight of all samples increased during first 7 months due to the pores which are located in the microstructure of samples, swelling sulfate solution, Even though, this increasement became a reduction period, Sample weights couldn't achieve the initial values at the end of the test. As shown in the Table 4.10, the highest weight increase occurred at the Sand Stone Addition concretes. For instance S 36 has reached % 2.75 mass changes at the end of the 7th month. Also Lime Stone filler mixes show a bad performance if it is compared with Reference concrete. According to results it can be said that reference concrete shows the best results generally. Therefore, it can be said that, Fly Ash and Fillers addition concretes contain more pores in the concretes micro-structure. Maximum mass changes, was observed at the Sand Stone fillers concrete. Actually, it has seen that Mass Loss test results shows in a harmony with Water Absorption test results. As a conclusion, it is decided that 9 months is not enough in order to figure out the Mass Loss changes against to Sulfate Attack.

Table 4.10: Mass Changes for SCC against to Sulfate Attack by the time as %

Mix Code	Mass Changes amounts by months as Percentage								
	1th	2th	3th	4th	5th	6th	7th	8th	9th
Reference	0,75	0,93	1,12	1,30	1,52	1,65	1,83	1,73	1,65
F 20	1,00	1,29	1,51	1,76	1,98	2,23	2,43	2,24	2,20
F 30	0,68	0,86	1,04	1,26	1,44	1,67	1,75	1,68	1,44
F 40	1,18	1,49	1,60	1,83	2,14	2,24	2,40	2,11	1,95
L 24	0,98	1,25	1,47	1,70	2,00	2,24	2,30	2,25	1,98
L 36	0,77	1,00	1,23	1,56	1,85	2,08	2,20	2,10	1,79
L 48	0,83	1,19	1,47	1,76	2,03	2,21	2,33	2,13	2,05
S 24	1,05	1,32	1,49	1,79	2,10	2,36	2,55	2,21	1,70
S 36	1,20	1,58	1,88	2,20	2,42	2,61	2,75	2,27	1,71
S 48	1,06	1,43	1,78	2,06	2,34	2,52	2,58	2,20	1,58

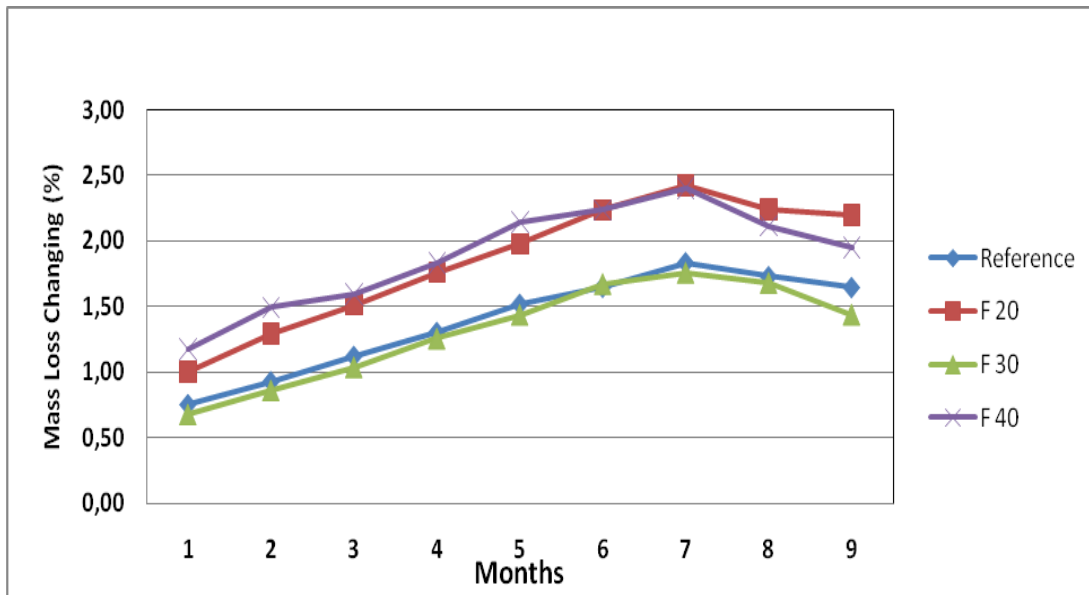


Figure 4.13: Mass Loss between Reference and Fly Ash SCC against to Sulfate Attack.

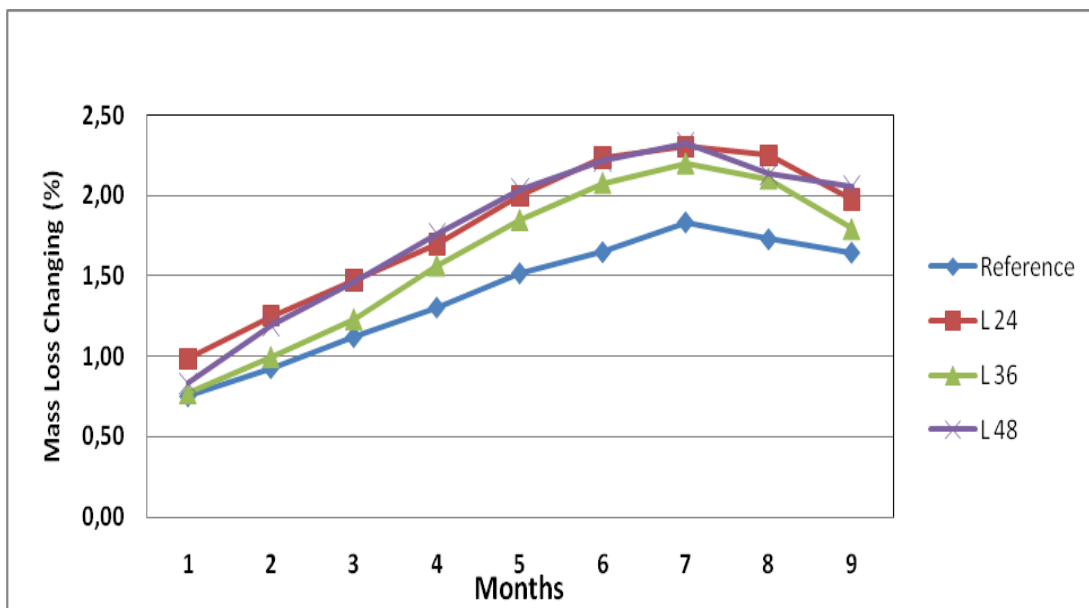


Figure 4.14: Mass Loss between Reference and Lime Stone filler SCC against to Sulfate Attack.

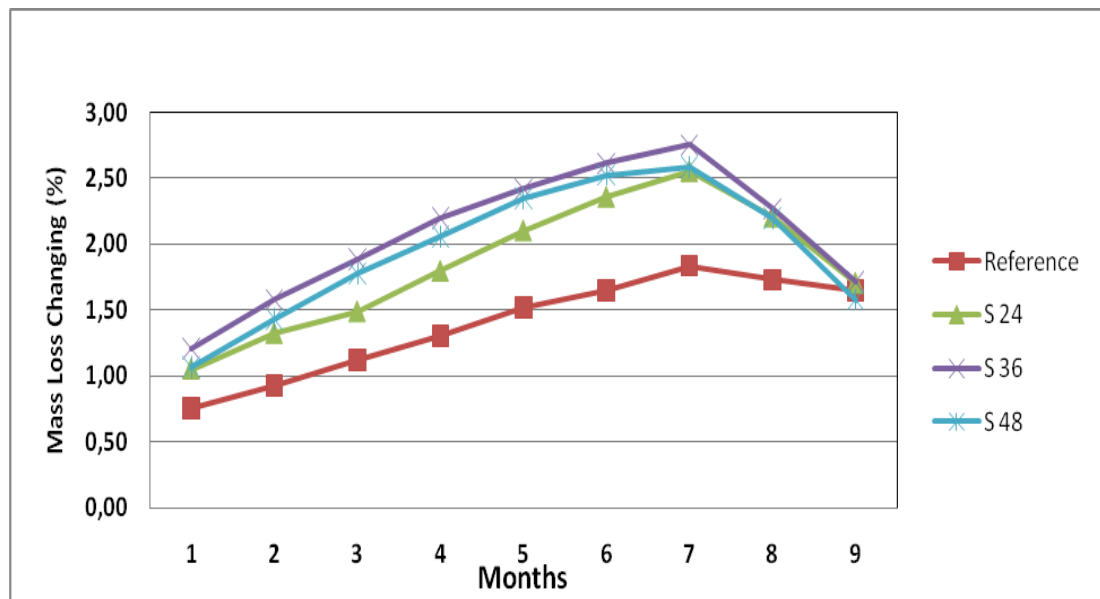


Figure 4.15: Mass Loss between Reference and Sand Stone filler SCC against to Sulfate Attack.

4.2.6.3 Flexural Strength and Energy Absorption Capability Test Results and Evaluations for SCC

Energy Absorption Capability is known as toughness and defined with the area which is made up under the load-displacement curve. As seen from the Figure 4.16. Toughness values are, generally tend to be reduction after the sulfate attack as expected. There is no significant change observed for Reference concrete. It can indicate Sulfate penetration and also destruction, which depends on sulfate ingress, couldn't achieve up to crucial levels for Reference concrete. Furthermore, the most drastic reduction occurred Fly Ash added SCC on the toughness values with the Sulfate impact. F 20 mix shows approximately % 30 reduction about the toughness before and after sulfate attack. In addition to Fly Ash SCC, Lime Stone SCC has also been influenced dramatically from the Sulfate attack. Reduction level reaches to % 27 for L 48 samples. However, Sand Stone Filler added concretes gave strange results at the end of the Sulfate test. Both there is an increase observed on the Toughness and maximum energy absorption is seen on Sand Stone Filler SCC.

As a conclusion it can be said that When Fly Ash usage in the mix, decrease the Toughness, Lime Stone Filler and Sand Stone Filler addition increase the Toughness especially at the high levels. It might be said that, the size differences between Portland Cement particles and Filler particles, which were utilized in this research, could lead an effect in the microstructure of concrete. In other words, larger filler particles in concrete may have behaved as aggregate so it might have led to

prevent crack propagation in concrete. Sand Stone filler needs more investigation in order to figure out real effect of it in concrete against to Sulfate Attack. Besides, there is direct relation can be established between the toughness and ductility in this case these results indicate Fly Ash decrease the ductility in concrete when compared with Lime Stone Fillers and Reference concrete.

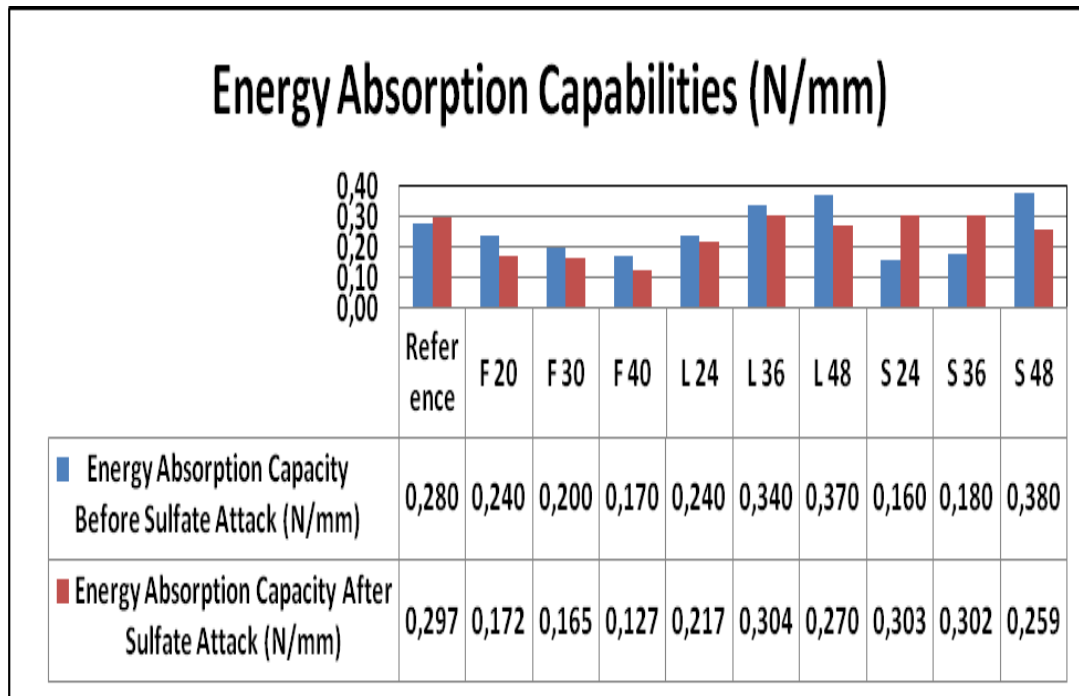


Figure 4.16: Toughness changing of SCC against to Sulfate Attack

Flexural Strength values of samples are given below at the Figure 4.17 both before and after Sulfate Attack. It has been obviously seen that Flexural Strength values of all mixes decrease after Sulfate attack. The most dramatic decrease compose at the F 30 concrete, % 49 reduction is observed on the Flexural Strength values of F 30 concrete before and after sulfate Attack. It can be said that generally Fly Ash Concrete show the worst performance after the sulfate attack among all the others.

On the other hand, when test results are investigated, it is clear that, not only Fly Ash but also Fillers usage decreased the Flexural Strength and Reference concrete reach the maximum value. According to these test results, it is hard to make an interpretation about the amount of Mineral admixtures effect on the Flexural Strength of mixes independent from Sulfate attack. For instance, when Flexural Strengths increase with Fly Ash and Lime Stone Filler Addition up to F 30 and L 36 respectively, both of them show a decrease period for F 40 and L 48. Besides, while

Flexural strength values are almost same for S 24 and S 36, there is a drastic increase observed for S 48.

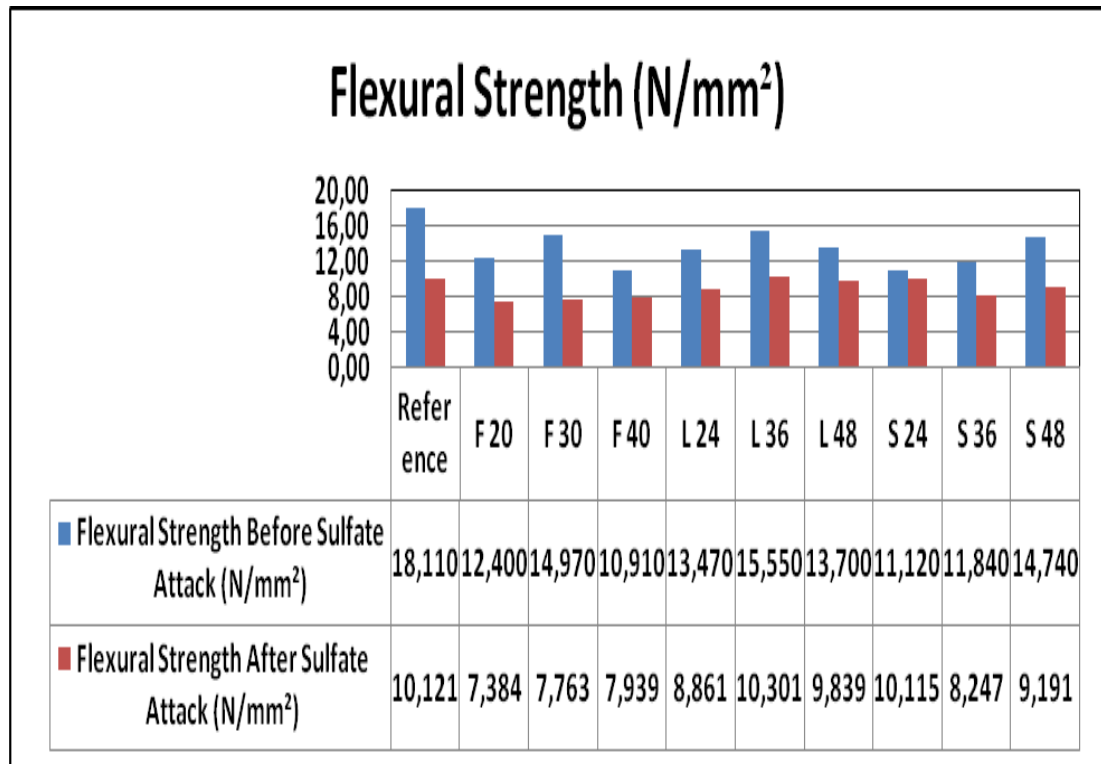


Figure 4.17: Flexural Strength changing of SCC against to Sulfate Attack.

5. CONCLUSIONS AND RECOMMANDATIONS

Based on the test results obtained the following conclusions can be drawn:

- Although; there is no linear relation between increase/decrease rate and Mineral materials content, it is seen that not only Fly Ash but also Fillers replacement especially into low amounts, improved the workability of SCC slightly.
- It can be said that two points are agreed upon by the world literature for evaluating workability properties of concrete. First of all the excessive viscosity problems which can prevent the self compacting abilities of concrete and the second one is high flowing speed which can lead to segregation between concrete components. Segregation was not observed at the end of the experiments. However, it should be regarded to segregation risk for L 36 and excessive viscosity risk for S 36.
- As a result of applied test, Compressive Strength decreased nearly linear by both Fly Ash and Fillers addition. Fly Ash replacement show better performance than Fillers for Compressive Strength. Especially, Sand Stone Filler addition led to % 25-45 Strength reduction.
- Even if, irregular changes, was acquired on the Modulus Of Elasticity values of SCC with Mineral materials addition, it can be said that Modulus Of Elasticity was not influenced significantly from the replacement.
- If the all permeability tests are evaluated together, when Fly Ash and Lime Stone filler performed well about permeability especially at the low levels replacement, Sand Stone Filler addition changed the results negatively. On the other hand all permeability values are still so low when it is compared with conventional concrete.
- Sulfate impact on the concrete was investigated with utilized Ultrasonic Pulse Velocity, Mass Loss and Three Point Bending tests, both SCC and SRC included conventional concrete which suffered to Sulfate before. There are no regular, big changes, were observed at UPV values with mineral material

addition to SCC.

- Mass Loss changing values are more distinctive than UPV test. Mineral Material addition caused a little bit negative effect on SCC. It is observed that the mineral addition rate increase led to a slight changing on the samples weight because of their more porous microstructure than Reference concrete. Furthermore, Lime Stone Filler and Fly Ash contained samples had closer results each other, and better than Sand Stone fillers added mixes.
- Low amount Mineral Material addition, have no significant effect on the Energy Absorption capabilities of SCC independently from Sulfate attack. Especially Fly Ash and Lime Stone Filler replacement test values appeared so close to Reference concrete at the small addition levels. Sand Stone filler caused some reduction. After sulfate attack almost all mix test values went down except for Reference concrete.
- Even if flexural strength of all SCC concrete decreased with Mineral addition independently from Sulfate attack, these reductions were not linear and regular. Also, Sulfate impact led to reduction on the Flexural Strength of all SCC samples as expected.
- According to results it can be said that SCC concretes were not influenced from the Sulfate Attack. Since there is not a large porous micro structure available at the SCC samples, they didn't swell so much solution inside as much as conventional concrete.
- No surface abrasion and destruction was observed on the SCC concretes during the test.
- It is decided that 9 months is not sufficient in order to figure out the behavior of SCC against to Sulfate attack.
- Fly Ash and Lime Stone Filler replacement with Cement, did not influence the mechanical and durability performance of SCC significantly. All SCC concretes were in the High Strength Concrete class except for S 48 samples. It should be regarded to Sand Stone Filler addition especially for High Compressive Strength demanded places.

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